

Preparation of Amidoximated Polyester Fiber and Competitive Adsorption of Some Heavy Metal Ions from Aqueous Solution onto This Fiber

Ramazan Coşkun, Cengiz Soykan

Department of Chemistry, Faculty of Science and Arts, University of Bozok, Yozgat, Turkey

Received 6 February 2008; accepted 26 October 2008

DOI 10.1002/app.29668

Published online 11 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, a fibrous adsorbent containing amidoxime groups was prepared by graft copolymerization of acrylonitrile (AN) onto poly(ethylene terephthalate) (PET) fibers using benzoyl peroxide (Bz₂O₂) as initiator in aqueous solution, and subsequent chemical modification of cyano groups by reaction with hydroxylamine hydrochloride in methanol. The grafted and modified fibers were characterized by FTIR, TGA, SEM, and XRD analysis. The crystallinity increased, but thermal stability decreased with grafting and amidoximation. The removal of Cu(II), Ni(II), Co(II), Pb(II), and Cd(II) ions from aqueous solution onto chelating fibers were studied using batch adsorption method. These properties were investigated under competitive conditions. The effects of the pH, contact time, and initial ion concentration on the removal percentage of

ions were studied. The results show that the adsorption rate of metal ions followed the given order Co(II) > Pb(II) > Cd(II) > Ni(II) > Cu(II). The percentage removal of ions increased with initial ion concentration, shaking time, and pH of the medium. Total metal ion removal capacity was 49.75 mg/g fiber on amidoximated fiber. It was observed that amidoximated fibers can be regenerated by acid without losing their activity, and it is more selective for Pb(II) ions in the mixed solution of Pb-Cu-Ni-Co-Cd at pH 4. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1798–1807, 2009

Key words: graft copolymers; amidoxime; adsorption; chelating fiber; competitive removal; heavy metals; waste; crystallization

INTRODUCTION

In recent years, the removal of toxic and polluting heavy metal ions from industrial effluents, water supplies, and mine waters have received much attention. The presence of heavy metal ions in water systems causes multiple problems for agriculture and health. For instance, excessive intake of copper results in an accumulation in the liver, and it is also toxic to aquatic organisms even at very low concentrations.¹ Lead is a general metabolic poison and enzyme inhibitor.² It can cause mental retardation and further brain damage, especially in children. Cadmium is an irritant to the respiratory tract, and prolonged exposure to this pollutant can cause anosmia and a yellow stain that gradually appears on the neck of the teeth.³ Acute poisoning of nickel causes headache, dizziness, nausea and vomiting, chest pain, tightness of breath, rapid respiration, cyanosis, and extreme weakness.⁴ This underlines the need for developing methods for effective removal of heavy metal ions from wastewater at least below the regulatory level before mix-

ing with natural water sources. Various removal methods of heavy metals from wastewater have been developed, such as chemical precipitation, membrane filtration, ion exchange, liquid extraction, or electro-dialysis.^{5–8} However, these methods are not widely used because of their high cost and low feasibility for small-scale industries. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost.^{9–12} The literature survey reveals that a variety of solid adsorbents such as activated carbon, metal oxides, minerals, peanut skins, herbaceous peat, rice husk ash, wool, cotton, ion exchange, and chelating resins have been used for removal of heavy metal ions.^{13–20} Particularly, polymers that contain chelating amidoxime groups have been found effective in metal ion retention.^{21–24} In addition, the fibrous adsorbents containing amidoxime groups have been shown to exhibit superior adsorption characteristics, especially in view of the high adsorption rate,²⁵ high adsorption capacity,²⁶ and selectivity for ions.²⁷ The adsorption of heavy metal ions from aqueous solution to adsorbents is usually controlled by the properties of the surface functional groups of the adsorbents.^{28–30} The most common preparation methods for reactive fibers have included chemical conversion of the existing

Correspondence to: C. Soykan (soykan@erciyes.edu.tr).

reactive groups in the fibers^{31,32} and grafting of various vinyl monomers on the fiber by graft copolymerization.^{33–37} Most of the chelating fibers were reported by introduction of suitable functional groups on various types of fibrous polymers: poly(ethylene terephthalate),³⁸ polyvinyl alcohol,³⁹ polyacrylonitrile,⁴⁰ etc. Research on fibrous reactive agents has shown many advantages over their resin counterparts. The high specific surface areas of fibrous supports improve the accessibilities of functional groups resulting in higher reaction rate and conversion than the resin type agents.^{41,42}

The main purposes of this work are (1) to achieve graft copolymerization of AN onto PET fiber, using Bz₂O₂ initiator, (2) to introduce amidoxime groups onto the PET-g-AN via reaction with hydroxylamine hydrochloride, and (3) to investigate the effects of treatment time with the solution, initial pH, and initial ion concentration of ions on the competitive adsorption of Pb(II), Ni(II), Cu(II), Co(II), and Cd(II) ions from aqueous solutions.

EXPERIMENTAL

Material and reagents

The poly(ethylene terephthalate) (PET) fibers (133F34) were supplied from Sasa Co. (Adana, Turkey). The fiber samples were extracted with acetone in Soxhlet for 6 h and dried in air before grafting. Benzoyl peroxide (Bz₂O₂) was recrystallized twice from the methanol-chloroform mixture and dried in a desiccator. Acrylonitrile (AN; Merck) was used without further purification. Hydroxylamine hydrochloride (NH₂OH·HCl, Merck), sodium hydroxide (NaOH, Merck), methyl alcohol (CH₃OH, Merck), and the metal ion solutions were prepared by dissolving of Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O, and Pb(NO₃)₂ (Merck) with distilled water without pH adjustment. The pH values of the aqueous solution were adjusted with HCl (pH = 2–3) and buffer solutions of CH₃COOH–CH₃COONa (pH = 4–5) and KH₂PO₄–K₂HPO₄ (pH = 6).

Instrument and apparatus

A Fourier transform infrared (FTIR) spectrophotometer from Jasco FTIR 460 plus was used to analyze the chemical and/or physical interactions in the wavenumber range 400–4000 cm⁻¹. TGA studies were carried out with a Setaram labsys TG-DSC/DTA system. The thermograms were obtained under a nitrogen atmosphere at a uniform heating rate of 10°C/min from ambient temperature to 600°C. X-ray diffraction curves for the various investigated samples were measured using a Philips X-ray diffractometer system using nickel-filtered CuK α radiation. The concentra-

tions of the metal ions were measured with an Ati Unicam (Model 929) atomic absorption spectrophotometer. The microstructure of the fibers were examined by a scanning electron microscopy (SEM), Hitachi, Model:JSM-5600 imaging mode. The pH values of the buffer solutions were determined with a Ø50 pH meter (Beckman, Beckman Instrument).

Graft copolymerization

The graft copolymerizations were carried out in 100 cm³ Pyrex tubes. Fiber samples (0.10 ± 0.01 g) were placed into polymerization tube containing 0.40 g AN. Then, 2 cm³ of a Bz₂O₂ solution prepared in acetone (9.68 g/L) was added to it, and the mixture was made up to 20 cm³ with deionized water and placed into a water bath at 85°C ± 0.1°C for 4 h. The fiber samples taken from the polymerization mixture after grafting were immersed in N,N-dimethylformamide at 40°C for 1 h to remove unreacted monomers and homopolymers. Then, the fibers were rinsed with methanol at room temperature and dried. The graft yield (47%, maximum grafting) was calculated from the weight increase in grafted fibers as follows:

$$\text{Graft Yield (\%)} = [(w_g - w_o)/w_o] \times 100 \quad (1)$$

where w_o and w_g denote the weights of original and grafted PET fibers (g), respectively.

Functionalization with hydroxylamine hydrochloride of the fiber

A 1-L three-neck flasks equipped with a mechanical stirrer, reflux condenser, and thermometer served as reaction vessel. A solution of free hydroxylamine hydrochloride in methanol was prepared by method of Xia and Yan.⁴³ PET-g-AN copolymer and the methanol solution of hydroxylamine hydrochloride were added to the flasks afterward. The reaction mixture was heated at 80°C with stirring for 24 h. The modified fiber was taken from the flasks and washed with methanol and water, and the modified fiber was air-dried overnight.

Removal of metal ions

Competitive heavy metal removal from aqueous solution was investigated in batch experiments under competitive conditions. Dried samples (100 mg each) of the chelating fibers were added in 100 cm³ Erlenmeyer including volumes of 30 cm³ of each the metal ion solution (25 ppm) adjusted to desired pH. The mixture was stirred at 25°C. After filtration of the solution, the ion concentrations of the filtrates were analyzed with an atomic adsorption spectrophotometer. The removal percentage (%R) and metal ion removal capacity of the fiber were calculated as follows:

$$\%R = \frac{(C_1 - C_2) \times 100}{C_1} \quad (2)$$

$$Q = \frac{V(C_1 - C_2)}{W} \quad (3)$$

where Q is adsorption amount (mg/g), W is the weight of the chelating fibers (g), V is the volume of solution (L), and C_1 and C_2 are the concentrations (mg/L) of ion before and after adsorption, respectively.

Elution study of ions

Elution of metal ions was studied with HNO_3 in batch experiment. Metal ions loaded fibers were placed in elution medium and stirred at 25°C . The final metal ions concentration in the aqueous phase was determined with an AAS. The elution degree was calculated from the amount of metal ions adsorbed on the fibers and the final concentration of metal ions in the elution medium with the following equation:

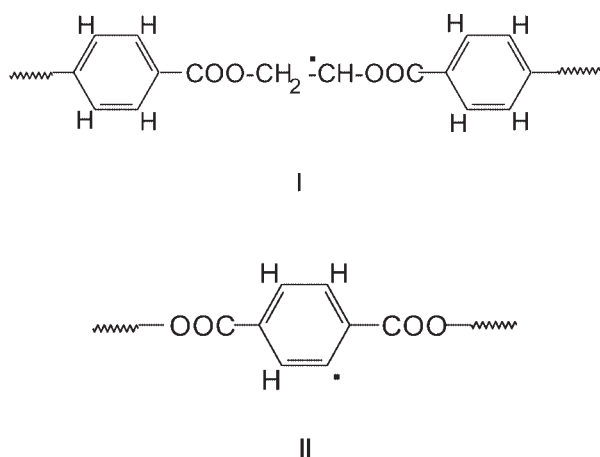
$$\text{Elution Degree} = \frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on the reactive fiber}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Preparation of amidoxime fibers based on PET fibers and characterization

Fibers containing amidoxime groups were prepared by graft copolymerization of acrylonitrile (AN) onto poly(ethylene terephthalate) (PET) fibers using benzoyl peroxide as initiator in aqueous solution.

The electron spin resonance (ESR) studies carried out on PET revealed that there formed two types of radicals, whose structures are given below:^{30,31}



These radical sites can be created either by the direct interaction of the initiator with the fibers or by the transfer reaction between the active homopoly

(CN) chains and PET fiber.^{32–34} Type II PET radicals are known to be predominant.³⁵ Graft copolymerization was carried out on these active radical of PET fibers to add AN monomer. Subsequently, chemical modification of cyano groups were converted by reaction with hydroxylamine hydrochloride in methanol, and the preparation scheme of the adsorbent were shown in scheme 1.

FTIR spectrum

The FTIR spectra of ungrafted, PET-g-AN, and amidoximated-PET fibers are given in Figure 1. The comparison of these spectra Figure 1(a,b) revealed that there appeared a absorption band at 2240 cm^{-1} coming from $\text{C}\equiv\text{N}$ stretching peak of AN. These results showed that AN units were introduced into the fiber structure. When Figure 1(b) was compared with Figure 1(c), a broad band in the $3650\text{--}3300\text{ cm}^{-1}$ (O—H of oxime group) and the $\text{C}=\text{N}$ of the oxime group at 1650 cm^{-1} were observed. The disappearance of the absorption at 2240 cm^{-1} indicated that the transformation of the nitrile group is complete.

SEM results

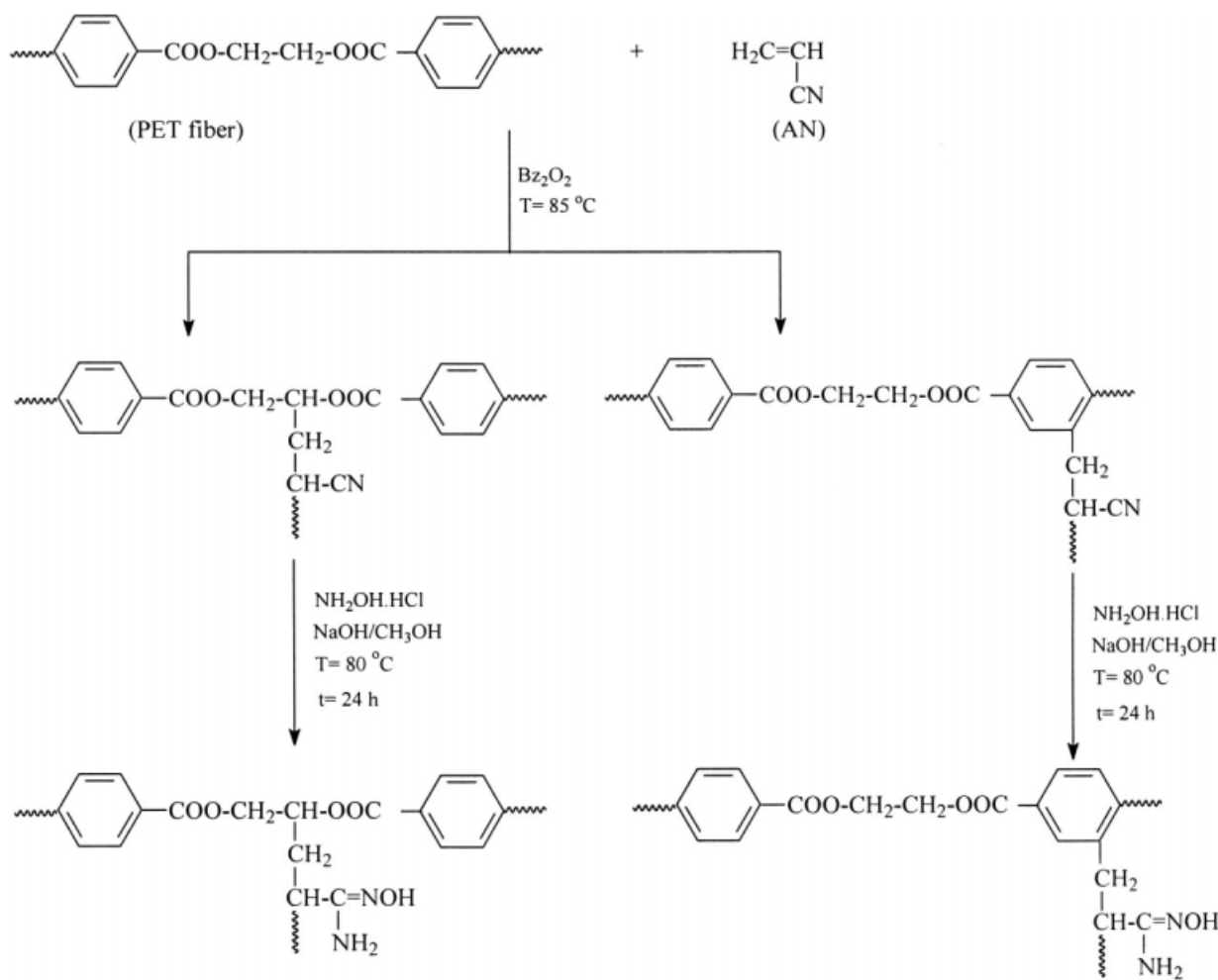
SEM image of ungrafted PET, PET-g-AN, and amidoximated-PET is shown in Figure 2. The surface of PET fibers before the grafting was relatively smooth and uniform. The morphology of the uniform surface of the ungrafted PET fiber was changed to form parallel layers to the fiber length with grafting [Fig. 2(a,b)]. After the amidoximation, the fiber surface was corroded and became rough, indicating that the modification reaction occurred on the surface of the PET fiber [Fig. 2(c)]. On the other hand, after the AN grafted on PET, the diameter of fiber increased. However, when this fiber was amidoximated, the diameter of PET decreased in respect to PET-g-AN. It may be attributed that the H-bonding occurred between N—OH groups. Thus, the molecule structure is stiffened.

TGA analysis

Thermograms of ungrafted PET, PET-g-AN, and amidoximated-PET are given in Figure 3. The onset temperatures of weight loss of the ungrafted PET is around 400°C , while PET-g-AN is 255°C and amidoximated-PET is 200°C . The thermograms clearly indicate that the residue of the polymers increases with an increase in AN content in the polymer, and the converse to amidoxime. The increasing thermal stability and residue at higher temperatures may probably be because of the presence of amidoxime group in the side chain, which form cross-links.

X-ray diffraction

Figure 4 shows the X-ray diffraction patterns of the pure PET fiber, PET-g-AN, and amidoximated-PET.



Scheme 1 Preparation of the adsorbent.

The pure PET is in noncrystalline state and has only a very broad peak around $2\theta = 15^\circ\text{C}$. Pure PET has a bulky and rigid backbone structure, whereas PET-g-AN and amidoximated-PET have a flexible backbone. When AN is introduced to PET molecule, the fiber shows a small amount of crystallinity (from very weak crystalline peak at 2θ). The amidoximated-PET is semicrystalline, the diffraction peak corresponding to $2\theta = 15^\circ\text{C}$ in agreement with the other polymers. The flexible amidoximated-PET is favorable for the close molecular packing and crystallization. From these results, it was found that the PET and AN were grafted together and after converted, amidoxime group and hydrogen bond affected each other in the crystallization.

Effects of pH

It is well known that the pH of the medium has a great effect on the adsorption amount of the chelating fibers that it influences its surface structure of sorbents, formation of metal ions. 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. The experimental results for the effects of pH on the competitive removal of

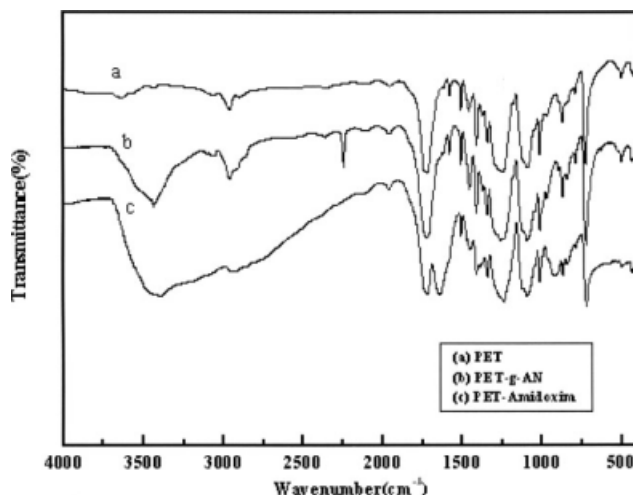
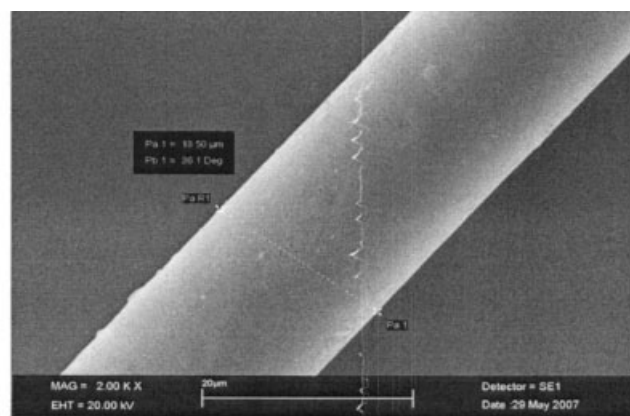
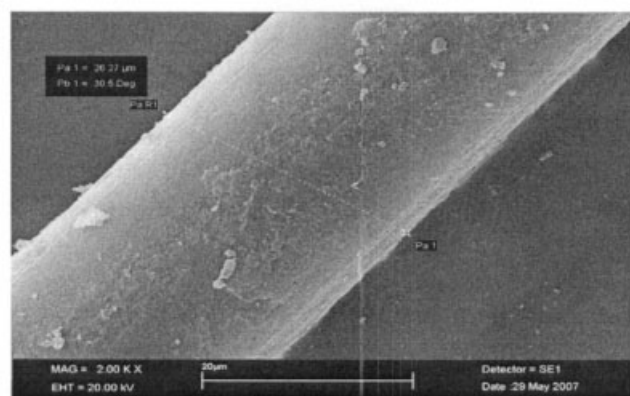


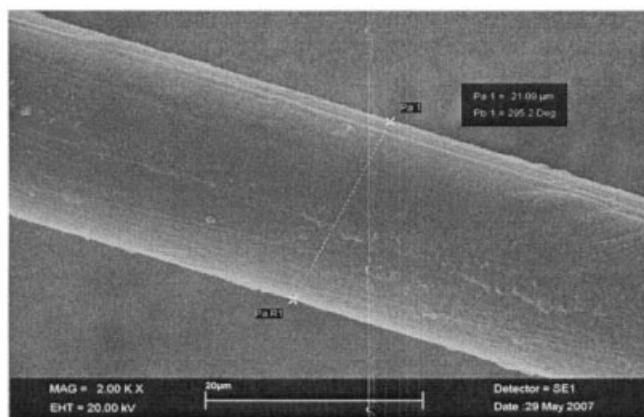
Figure 1 FTIR spectra of (a) ungrafted PET, (b) PET-g-AN, and (c) Amidoximated-PET.



(a)



(b)



(c)

Figure 2 SEM micrographs of (a) ungrafted PET, (b) PET-g-AN, and (c) Amidoximated-PET.

metal ions are shown in Figure 5. It can be seen that the removal of Cu(II), Co(II), Cd(II), and Ni(II) ions lowered in the amidoximated fiber at pH less than 4, but the removal of Pb(II) ion increased with increasing pH (within pH 2–4), a result which is indicative of the high preference of the fiber for Pb(II). Similar observation has been pointed out elsewhere.^{44,45} Moreover, it can be seen that the amidoximated fibers have shown more selectivity for Pb(II) at pH 4

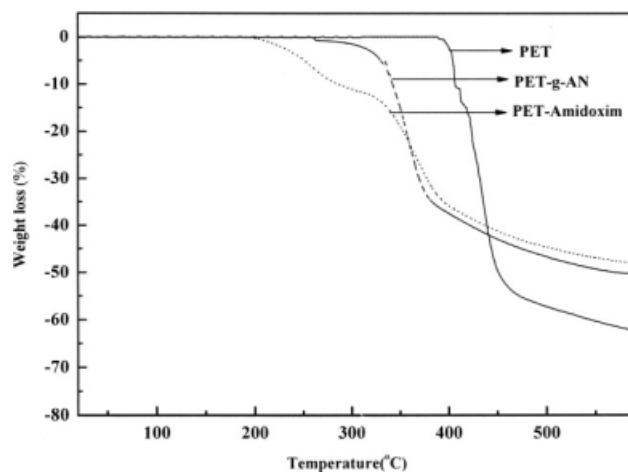


Figure 3 Thermograms of ungrafted, grafted, and amidoximated PET fibers.

than Cu(II), Ni(II), Cd(II), and Co(II) ions. The adsorbed amount of Pb(II) is much more than that of the others. This may be possible to selectively remove Pb(II) from a mixture containing the other metal ions by carefully adjusting the pH value and the other reaction conditions.

Effect of initial concentration on adsorption

The relationship between initial concentration of metal ions and the adsorption amount is shown in Figure 6. It is clear from the figure that the adsorption amount of metal ions increased with increasing initial ion concentration, and then reached a plateau value at higher concentration. This is attributed to the adsorption sites of the amidoximated fiber become saturated when the metal ion concentration is reached to 100 ppm.

Besides, as shown in Table I, the saturated adsorption capacity of the amidoximated fiber is 0.3229, 0.1858, 0.0936, 0.1424, and 0.1171 mg/mol for Pb(II),

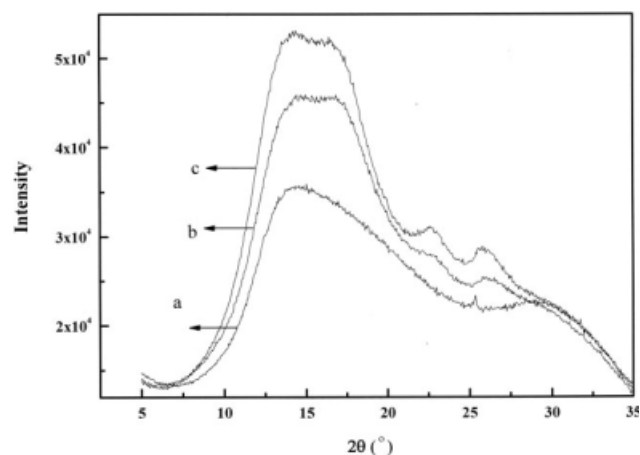


Figure 4 X-ray diffraction of (a) ungrafted PET, (b) PET-g-AN, and (c) Amidoximated-PET.

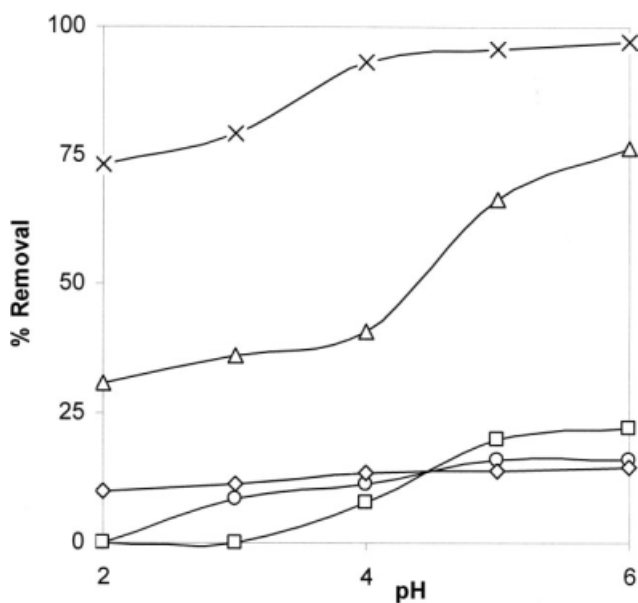


Figure 5 Effect of pH on the removal of metal ions onto amidoximated PET fibers [(x) Pb(II); (Δ) Ni(II); (○) Cu(II); (◇) Cd(II); (□) Co(II)]. $t = 4$ h; $C_i = 25$ ppm].

Ni(II), Cu(II), Co(II), and Cd(II), respectively. Total metal ion removal capacity of the amidoximated fiber is 0.8688 mmol/g fiber. The adsorption on chelation of the metal ions onto amidoximated fiber can be explained with coordination between the electron-donating nature of O- and N-containing groups in the fiber and electron-accepting nature of metal ions as shown in Scheme 2. Lower Cu(II), Co(II), and Cd(II) removal capacity may be attributed to the active adsorption sites on amidoximated fibers, which are mostly occupied by Pb(II) and Ni(II) ions because of their affinity being higher than that of the Cu(II), Co(II), and Cd(II). If metals are competing for the same active sites on an adsorbent, those metals with a stronger affinity can replace others with a weaker affinity.⁴⁶

The adsorption capacity data were fitted to two well known adsorption isotherm models of Langmuir (Fig. 7) and Freundlich type (Fig. 8). The experimental data were also exploited for D-R (Dubinin_Radushkevich) (Fig. 9) isotherm model. All metal ions were found to fit Langmuir type adsorption isotherm

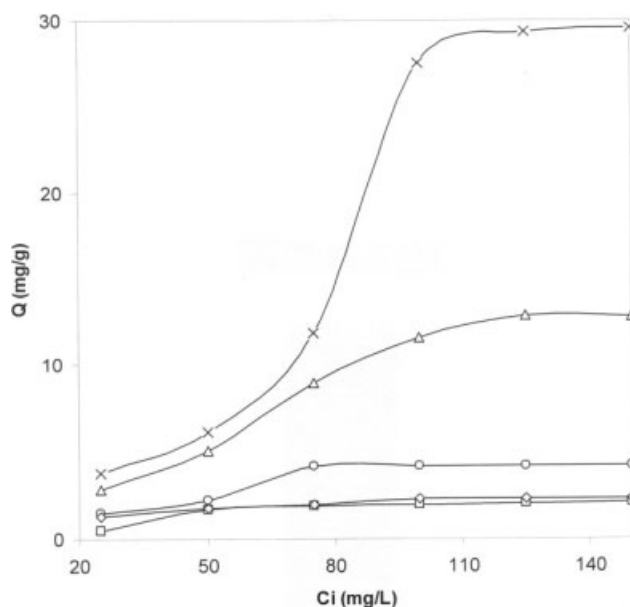


Figure 6 Effect of initial concentration of metal ions on the adsorption amount [(x) Pb(II); (Δ) Ni(II); (○) Cu(II); (◇) Cd(II); (□) Co(II), pH = 4; $t = 4$ h].

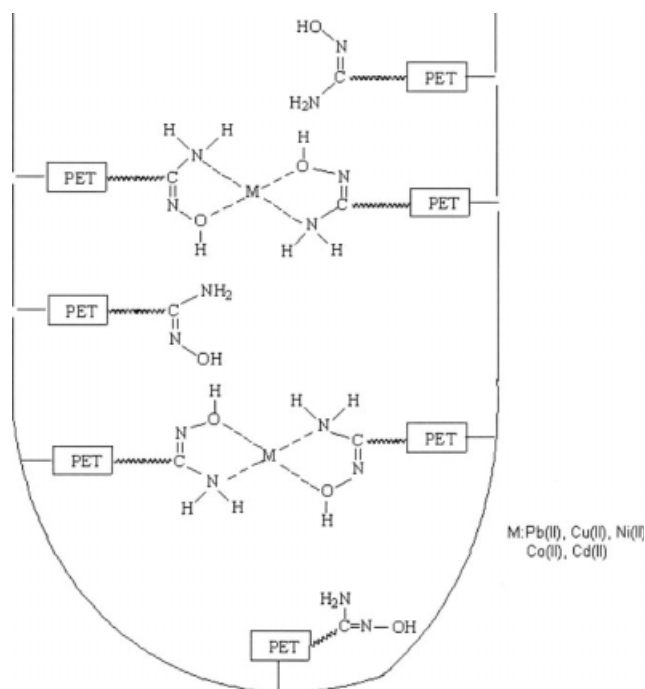
model better. The constants related to these isotherms have been given in Table I.

If we have a closer look at the inorganic chemistry of the metal ions, Co^{2+} and Ni^{2+} behave like hard acids, and according to HSAB (Hard-Soft Acid Base) theory, they are expected to give stronger complexes with O-bearing amidoxime (hard base) functional groups. Cu^{2+} with intermediate character gives weaker complexation when compared with the Co^{2+} and Ni^{2+} . The other metal ions Cd^{2+} and Pb^{2+} are soft acids and are not expected to encounter such complexation reactions with the functional groups on the fiber.

When we consider energy-related constants (b and E) obtained from Langmuir and D-R isotherms in Table I, we can conclude that Co^{2+} , Ni^{2+} metal ions encountered stronger interactions with amidoxime groups. Although the b and E values for other metals can be assumed to be in the same order of magnitude, those values are very high for Co^{2+} (E value) and Ni^{2+} (b value). These results are in accordance with the theoretical expectation given above for Co^{2+} and Ni^{2+} .

TABLE I
First-Order and Second-Order Rate Constants

Metal	First-order rate constants				Second-order rate constants			Intraparticle diff. rate constants	
	$q_e(\text{exp.})$ (mg g^{-1})	k_{ad} (min^{-1})	$q_e(\text{theor.})$ (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_e(\text{theor.})$ (mg g^{-1})	R^2	k_{id} ($\text{g } \mu\text{g}^{-1} \text{min}^{-1/2}$)	R^2
Pb	7.126	1.587	12.885	0.98	0.854	7.231	0.9998	4.416	0.9701
Ni	5.775	0.854	2.203	0.9924	0.119	6.506	0.9946	0.769	0.923
Cu	2.175	0.259	2.292	0.9905	0.034	3.834	0.998	0.622	0.8798
Co	1.029	0.972	2.953	0.9944	0.986	1.122	0.9977	0.477	0.9893
Cd	1.725	0.314	1.862	0.9949	0.147	2.194	0.9969	0.520	0.846



Scheme 2 Schematic representation of the proposed structure of metal ions (M) complex of amidoximated fiber.

The presence of functional groups on a resin may not always explain the adsorption capacities of a resin. For a chelating exchanger, it is not only important to have some functional groups in the structure, but accessibility of those functional groups is also important. There should not be sterical hindrances, which sometimes play great role in the accessibility of the functional groups. Therefore, in our study, we

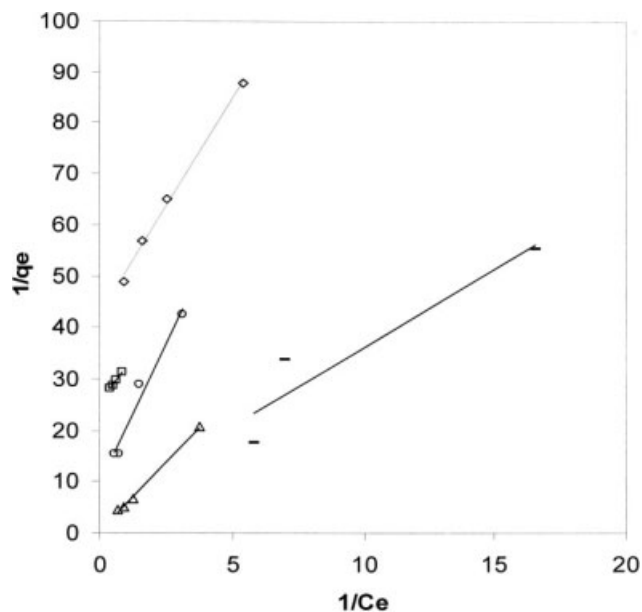


Figure 7 Langmuir isotherm curves of metal ions [(–) Pb(II); (Δ) Ni(II); (○) Cu(II); (◇) Cd(II); (◻) Co(II)].

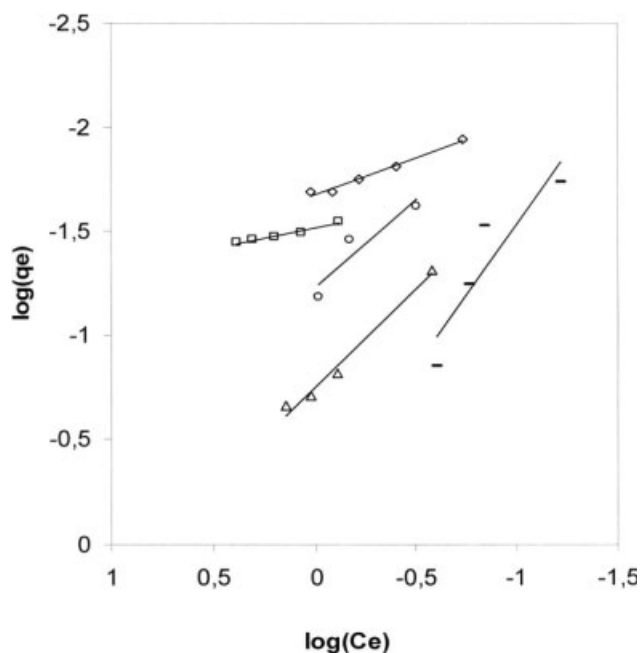


Figure 8 Freundlich isotherm curves of metal ions [(–) Pb(II); (Δ) Ni(II); (○) Cu(II); (◇) Cd(II); (◻) Co(II)].

consider that sterical hindrances play important role in the desorption capacities of the metal ions.

The adsorption capacities of the metal ions studied were found to be in the order of $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$. If we consider the hydrated ionic radii of the metals, we can write $\text{Co}^{2+} = \text{Ni}^{2+} = \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. When we compared the capacities obtained from Langmuir isotherms, we conclude that capacities are clearly related to the hydrated ionic radii of the metal ions. The smaller metal ions have the greater adsorption capacities, which may be attributed to the fact that the smaller particles could

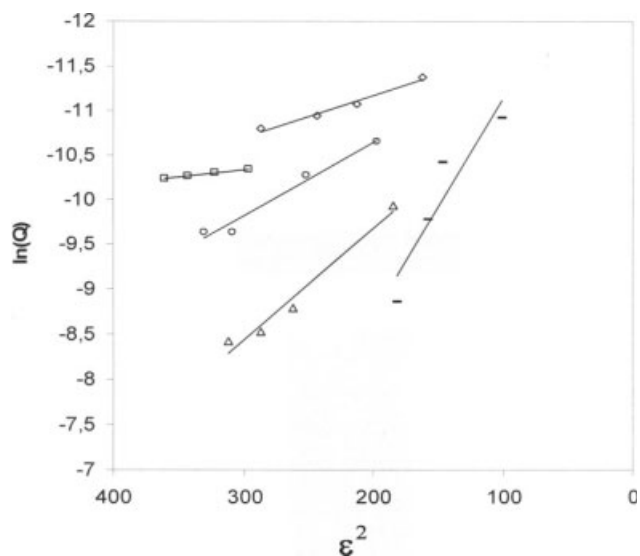


Figure 9 D-R isotherm curves of metal ions [(–) Pb(II); (Δ) Ni(II); (○) Cu(II); (◇) Cd(II); (◻) Co(II)].

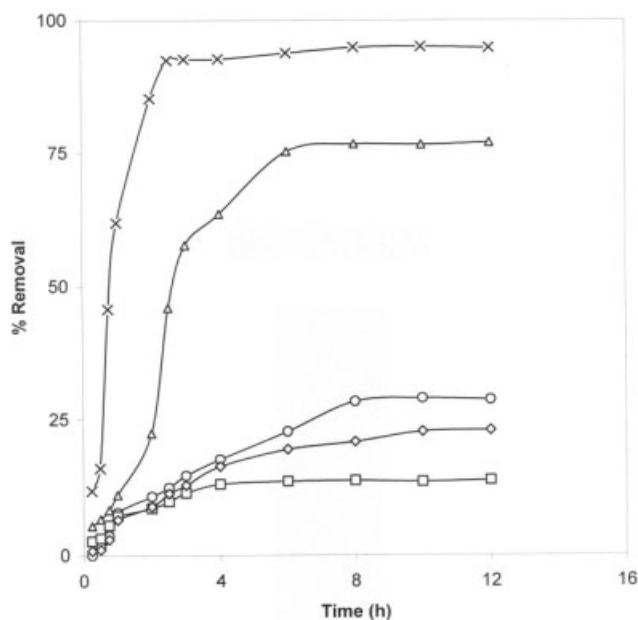


Figure 10 Competitive adsorption rate of metal ions onto amidoximated PET fibers [(x) Pb(II); (Δ) Ni(II); (○) Cu(II); (◇) Cd(II); (□) Co(II). pH = 5; C_i = 25 ppm].

reach easily to the active adsorption sites. According to this assumption, it could normally be expected to have adsorption capacities in the order of $Co^{2+} < Ni^{2+} < Cu^{2+} < Cd^{2+} < Pb^{2+}$. We believed that there are some sterical hindrances, and therefore, ionic radii of the metal ions are playing important role in determining the adsorption capacities of the meal ions. Another thing is that capacities of Co^{2+} and Ni^{2+} are greater than Cu^{2+} . This difference can be attributed to the greater complexation abilities of the Co^{2+} and Ni^{2+} ions with the amidoxime functional groups when compared with Cu^{2+} ions. Therefore, capacities obtained from Langmuir isotherms are logical and in good accordance with the theoretical expectations.

Adsorption rate of metal ions

Using a constant ion concentration (25 ppm) and reactive fibers (0.1 g/30 cm³), the concentrations of the ions in solution were determined at regular times. The experimental results obtained are shown in Fig-

ure 10. It shows that the adsorption rate of Pb(II) and Ni(II) ions is much higher than that of Cu(II), Co(II), and Cd(II) ions. According to the results from Table II and considering the k_2 values calculated from pseudo-second order kinetics, the removal order for amidoximated fiber is $Co(II) > Pb(II) > Cd(II) > Ni(II) > Cu(II)$. The initial rate of chelated metal ions and the maximum uptake value are very dependent on the type of metal ion, its coordination and stability constant, and the steric effect of these graft polymer complexes. As a consequence, it is likely that the movement of hydrated Cu(II), Cd(II), Ni(II), and Co(II) in fiber structures is stereo-chemically hindered. However, the ionic size of the investigated metal ions has a great influence not only on the maximum uptake but also on the initial rate. This can be reasonably explained by a consideration of the diffusion of these metals through the porous ionic hydrogels, which is mainly dependent on their polarity, electronic configuration, ionic radii, and so forth and also is dependent on the nature of the interaction with the functional groups of the fibers.

Kinetic data were evaluated by applying pseudo-first order (Lagergren equation), pseudo-second order, and intraparticle diffusion models. Figure 11 shows the second-order kinetic model, and we have only given this figure in the kinetics of the adsorption section. The constants related to the first and second order kinetic models are given in the Table II together with experimental and theoretical q_e values. Intraparticle diffusion model constants were also given in the same table. Constants related to the intraparticle diffusion model were calculated by considering the linear parts of the q_e versus $t^{1/2}$ plots. As it can be seen from Table II, both kinetic models (first and second order) gave good correlation with the data. Infact, experimental and theoretical values q_e values are expected to be close to each other and must be comparable. This was maintained only for the second-order kinetic model.

In intraparticle diffusion model, there were some interesting results. As it can be seen from Table II, Pb^{2+} and Co^{2+} seemed to more likely fit to the model. For Pb^{2+} , q_e versus $t^{1/2}$ plot linearity is achieved some times later after the beginning of the time course of

TABLE II
Langmuir, Freundlich, and D-R Isotherm Constants

Metal	Langmuir isotherm parameters			Freundlich isotherm parameters			D-R isotherm parameters			
	Q^0 (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2	K_F (mmol g ⁻¹)	n	R^2	Q_m (mmol g ⁻¹)	k mol ² kJ ⁻²	E kJ mol ⁻¹	R^2
Pb	0.3299	0.528	0.8886	0.674	0.735	0.8409	16.644	-0.0125	6.32	0.8246
Ni	0.1858	57.26	0.9958	0.178	1.059	0.9815	3.7373	-0.0107	6.84	0.9881
Cu	0.0936	1.125	0.9653	0.059	1.176	0.8852	0.4107	-0.0075	8.16	0.9701
Co	0.1434	0.276	0.9965	0.030	5.187	0.967	0.0538	-0.0019	16.22	0.9995
Cd	0.1171	0.203	0.9952	0.021	2.84	0.9853	0.0583	-0.0037	11.62	0.9967

the adsorption. But for Co^{2+} , linearity starts from the very beginning. These results concluded that intraparticle diffusion process is more effective and is a rate determining step in Co^{2+} adsorption process. This may also stem from some sterical hindrances and relatively bigger hydrated radius of the Co^{2+} ion. Although Co^{2+} has the greatest affinity to the amidoxime ligand, its adsorption capacity was not high as expected. This may arise from some sterical hindrances and intraparticle diffusion characteristics of the adsorption process for Co^{2+} . Intraparticle diffusion was also observed to some extent in Pb^{2+} adsorption process. Although Pb^{2+} is a soft acid and is not expected to make complex with amidoxime, it has the highest adsorption capacity among the metal ions. We thought that intraparticle diffusion behavior seemed to support the adsorption capacity of the metal. With its smallest hydrated radius and most

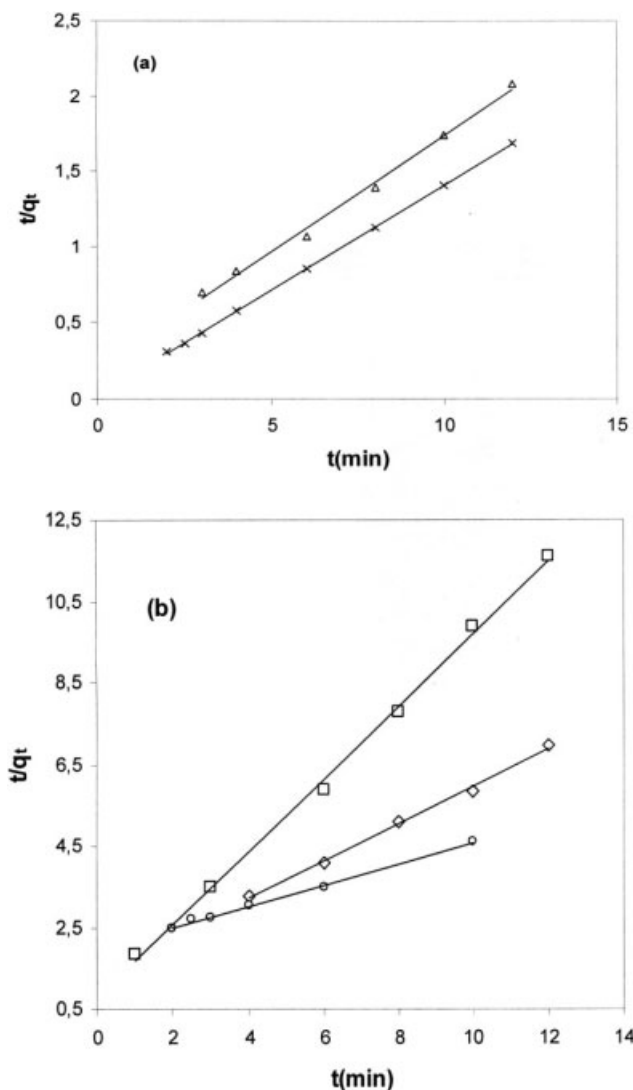


Figure 11 Second-order rate plot for the competitive adsorption (a) [(x) Pb(II); (Δ) Ni(II)] (b) [(○) Cu(II); (◇) Cd(II); (□) Co(II)]. pH = 5; $C_i = 25$ ppm].

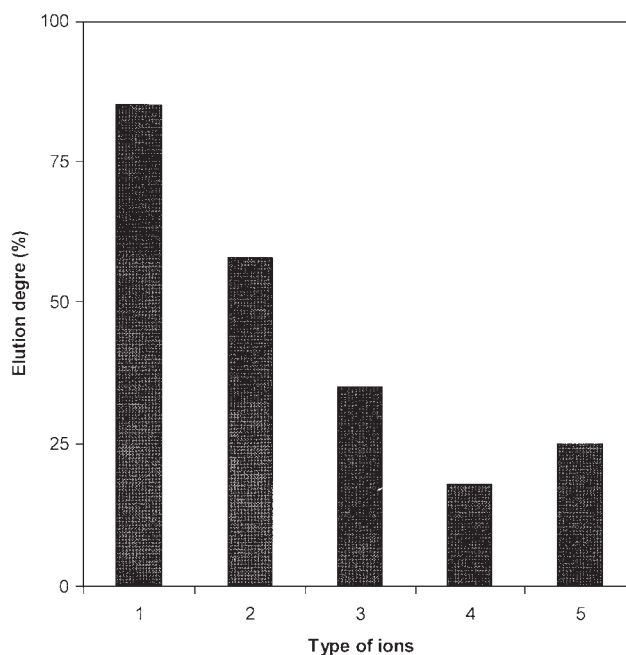


Figure 12 Elution degree of metal ions [1 : Pb; 2 : Ni; 3 : Cu; 4 : Co; 5 : Cd].

polarizable character, Pb^{2+} could be expected to show good adsorption characteristic because, E values from D-R isotherms concluded that physical forces were more effective in the adsorption processes of the metal ions.

Elution study

An important characteristic of an adsorbent is the possibility for its regeneration for further use. This is why the elution of the metal loaded fibers was studied. The elution was performed with 1M HNO_3 , and the elution degrees of metal ions are presented in Figure 12. As shown in Figure 12, the elution degree of Pb (II) is higher than the other metal ions. This may be attributed to weaker coordination bonds between Pb (II) ions and adsorbents' functional groups.

CONCLUSIONS

In this study, a fibrous adsorbent containing amidoxime groups was prepared by graft copolymerization of acrylonitrile (AN) onto poly(ethylene terephthalate) (PET) fibers using benzoyl peroxide (Bz_2O_2) as initiator in aqueous solution, and subsequent chemical modification of cyano groups by reaction with hydroxylamine hydrochloride in methanol, and its adsorption behaviors for Co(II), Pb(II), Ni(II), Cu(II), and Cd(II) metal ions were investigated. The following conclusions were obtained:

1. The amidoximated fibers showed lower thermal stability than the PET-g-AN and pure PET.

2. Adsorption rates for Pb(II) onto amidoximated fiber is very rapid than Ni(II), Cu(II) Co(II), and Cd(II).
3. It was observed that the amidoximated fibers were more selective for Pb(II) in the mixed solution of Pb-Ni-Cu-Co-Cd.
4. It was found that the amidoximated fibers could be used as an active adsorbent for Pb(II) in the mixed solution of Pb-Ni-Cu-Co-Cd without losing their activity.

References

1. Gupta, V. K. *Ind Eng Chem Res* 1998, 37, 192.
2. Stokinger, H. E. In *Patty's Industrial Hygiene and Toxicology, the Metals*; Clayton, G. D.; Clayton, F. E., Eds.; Wiley: New York, 1981; Vol. 24, Chapter 29, p 1493.
3. Hashem, A.; Elhammali, M. M. *Polym-Plast Technol Eng* 2006, 45, 707.
4. Parker, P. *Encyclopedia of Environmental Sciences*, 2nd ed.; McGraw Hill: New York, 1980.
5. Karthikeyan, K. G.; Elliott, H. A.; Chorover, J. J. *Colloid Interface Sci* 1999, 209, 209.
6. Tritt, R. E.; Weber, J. H. *Water Res* 1979, 13, 1171.
7. Hubicki, Z.; Jakowicz, A. *Desalination* 2003, 155, 121.
8. Sarfarazi, F.; Ghoroghchian, J.; *Microchem J* 1994, 50, 33.
9. McKay, G.; El-Geundi, M.; Nassar, M. M. *Water Res* 1987, 22, 1527.
10. Nassar, M. M.; Magdy, Y. H. *Chem Eng J* 1997, 66, 223.
11. Robinson, T.; Chandran, B.; Nigam, P. *Environ Int* 2002, 28, 29.
12. Kadirvelu, K.; Kavipriya, M.; Kathika, C.; Radhika, M.; Vennilamani, N.; Pattabhi, S. *Bioresour Technol* 2003, 87, 129.
13. Randall, J. M.; Reuter, W.; Waiss, A. C. *J Appl Polym Sci* 1975, 9, 1563.
14. Friedman, M.; Harisen, C. S.; Ward, V. H.; Lundgsen, H. P. *J Appl Polym Sci* 1973, 9, 377.
15. Friedman, M.; Masri, M. S. *J Appl Polym Sci* 1974, 18, 2367.
16. Roberts, E. J.; Rowland, S. P. *Environ Sci Technol* 1973, 7, 552.
17. Gündoğan, R.; Acemioğlu, B.; Alma, M. H. *J Colloid Interface Sci* 2004, 269, 303.
18. Feng, Q.; Lin, Q.; Gong, F.; Sugita, S.; Shoya, M. *J Colloid Interface Sci* 2004, 278, 1.
19. Pagano, M.; Petruzzelli, D.; Tiravanti, G.; Passino, R. *Solvent Extr Ion Exch* 2000, 18, 387.
20. Saha, B. B.; Iglesias, M.; Cumming, I. W.; Streat, M. *Solvent Extr Ion Exch* 2000, 18, 133.
21. Egawa, H.; Nakayama, M.; Nonaka, T.; Sugihara, E. *J Appl Polym Sci* 1987, 33, 1993.
22. Rifi, E. H.; Leroy, M. J. F.; Brunette, J. P.; Becker, C. *Solvent Extr Ion Exch* 1994, 12, 1103.
23. Pekel, N.; Şahiner, N.; Güven, O. *J Appl Polym Sci* 2001, 81, 2324.
24. Kondo, K.; Matsumoto, M.; Okamoto, K. *J Chem Eng Jpn* 1999, 32, 217.
25. Morooka, S.; Kusakabe, K.; Kago, T.; Inada, M.; Egawa, E. *J Chem Eng Jpn* 1990, 23, 18.
26. Weiping, L.; Yun, L.; Hanmin, Z. *React Polym* 1992, 17, 255.
27. Weiping, L.; Ruowen, F.; Yun, L.; Hanmin, Z. *React Polym* 1994, 22, 1.
28. Lezzi, A.; Cobianco, S. *J Appl Polym Sci* 1994, 54, 889.
29. Saraydin, D.; Karadağ, E.; Güven, O. *Sep Sci Technol* 1995, 30, 3287.
30. Kojima, T.; Sowa, T.; Kodama, S.; Sato, M.; Shigetomi, Y. *Anal Chim Acta* 1992, 59, 264.
31. Lin, W. P.; Lu, Y.; Zeng, H. M. *React Polym* 1992, 17, 255.
32. Malinowskii, E. K.; Ososkov, V. K.; Zeverev, M. P.; Barash, A. N. *J Appl Chem USSR* 1990, 63, 1342.
33. Lin, W. P.; Fu, R. W.; Lu, Y.; Zeng, H. M. *J Appl Polym Sci* 1994, 22, 1.
34. Lu, Y.; Wu, C.; Lin, W. P.; Tang, L. Y.; Zeng, H. M. *J Appl Polym Sci* 1994, 53, 1461.
35. Lu, Y.; Zhang, Z.; Zeng, H. *J Appl Polym Sci* 1994, 47, 45.
36. Saldatov, U. S.; Shunkevich, A. A.; Sergeev, G. I. *React Polym* 1988, 7, 159.
37. Lu, Y.; Zhang, Z.; Zeng, H. *J Appl Polym Sci* 1994, 53, 405.
38. Yiğitoğlu, M.; Ersöz, M.; Coşkun, R.; Şanlı, O.; Ünal, H. I. *J Appl Polym Sci* 1998, 68, 1935.
39. Rao, L.; Xu, J.; Zhan, R. *J Appl Polym Sci* 1994, 53, 325.
40. Liu, R.; Zhang, B.; Tang, H. *Fresenius J Anal Chem* 1998, 362, 258.
41. Sugasaka, K.; Katoh, S. *Sep Sci Technol* 1981, 16, 971.
42. Vernon, F.; Shah, T. *React Polym* 1983, 1, 301.
43. Xia, Y.; Yan, J. *Chem Reagent* 1982, 4, 133.
44. Feng, D.; Aldirch, C.; Tan, H. *Hydrometallurgy* 2000, 56, 359.
45. Maria, L. C. S.; Amorim, M. C. V.; Aguiar, M. R. M. P.; Guimaraes, P. I. C.; Costa, M. A. S.; Aguiar, A. P.; Rezende, P. R.; Carvalho, M. S.; Barbosa, F. G.; Andrade, J. M.; Ribeiro, R. C. C. *React Funct Polym* 2001, 49, 133.
46. Kang, S. Y.; Lee, J. U.; Moon, S. H.; Kim, K. W. *Chemosphere* 2004, 56, 141.