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## FABRICATION OF CHELATING DIETHYLENETRIAMINATED PAN MICRO- AND NANO-FIBERS FOR HEAVY METAL REMOVAL

*In this study, commercial acrylic fibers were modified with diethylenetriamine to prepare metal chelating fibers. The effects of process parameters on the efficiency of the reaction were investigated. FTIR spectroscopy and TGA analysis were used to confirm the chemical changes made to the fibers during the reaction. The ability of the modified fibers for removal of Pb(II), Cu(II) and Ce(IV) ions from aqueous media was determined. The modified fibers showed a slight decrease in mechanical properties compared to raw ones. Furthermore, the acrylic microfiber polymeric solutions were electrospun to nanofibers and the ability of modified nanofibers for the adsorption of the metal ions was studied.*

*Keywords:* acrylic fiber; chelating; ion exchange; modification; adsorption.

Nowadays, due to increasing environmental concerns and economic factors, great attention has been paid to the removal and recovery of heavy metal ions from industrial wastewater. Several methods for reducing the metallic content of effluents have been described. Chemical precipitation, adsorption into activated carbon, mineral oxides, resins and biosorbents, ion exchange, chelating fiber, electro dialysis, reverse osmosis membrane filtration, solvent extraction and common adsorption are the main approaches [1-2]. Chelating resins and polymers are widely used for wastewater treatment and selective concentration, removal and recovery of metal ions from a wide variety of sources [1,3-4].

Fabrication of chelating fibrous materials by introducing functional groups to the chemical structure of commercial fibers is a new approach for producing novel high efficiency metal adsorbents [5-10]. Their sorption mechanism is supposed to work through chelation instead of simple ion exchange and consequently, they should be highly selective. Chelating

fibers possess high specific surface which is at least five times larger than that of the porous beads. The functional groups on the fibers are more accessible for metal ions, which is the reason they present better kinetic characteristics [7].

There are many types of fibers or modified fibers, including activated carbon fiber, cotton fiber, glass fiber, and synthetic fibers (polyester, polypropylene, polyethylene terephthalate, polystyrene), that have been used to adsorb metal ions or to enrich trace amount of metals from aqueous solutions [6].

Polyacrylonitrile fiber is the most used fiber for this purpose because of its low cost, ease of modification and good stability in aqueous media at prolonged times. Amidoximation of acrylic fiber has been studied widely. The amidoximated fiber showed high adsorption capability for Au(III) [11], Pd(II) [12] and Fe(III) [13] ions. Zhang *et al.* [14] showed that hydrazine modified polyacrylonitrile fibers have the ability to remove Cu(II), Cd(II), Zn(II), Co(II), Pb(II), Cr(III), Ni(II) and Hg(II) ions from water. Furthermore, acrylic fibers modified by phenylhydrazine have shown the ability for adsorbing trace Ga, In, Bi, V and Ti ions from solution [5].

In another study [15], a polyacrylaminothiourea chelating fiber has been synthesized for removal of Au(III), Pt(IV), Pd(IV) and Ir(IV) ions from solution.

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Deng *et al.* [6] showed that acrylic fiber hydrolyzed by sodium hydroxide can adsorb copper ions from aqueous media. In one of our previous studies [16], we showed that polyacrylonitrile fibers hydrolyzed by sodium hydroxide and functionalized by thiourea can efficiently remove Cr(III), Pb(II) and Hg(II) ions from industrial effluents.

Recently, several studies have focused on the synthesis of metal chelating fibers using amination treatments on acrylic fiber. In this regard, different compounds, including ethylenediamine [3], diethylenetriamine [17–18], hydroxylamine hydrochloride [8], tetramethylene diamine [10] and ethanolamine [1] have been used.

In this study, we used diethylenetriamine (DETA) to prepare chelating fibers from commercial acrylic fibers. The aim of the study was to prepare more crosslinks (to avoid high strength losses made by previous methods) and more functional sites on the fiber to achieve more metal ion chelation. The chemical modifications made to the fiber as well as the mechanical changes and ion adsorption capacities of the modified fibers for some metals were evaluated.

## EXPERIMENTAL

### Materials

Commercial acrylic fibers (PAN) with 3.3 dtex, consisting of 93.5 wt.% acrylonitrile (AN) monomer and 6.5 wt.% methylacrylate (MA) comonomer were purchased from Polyacryl Co., Isfahan, Iran. The fibers were cut into 7 cm staple length, washed with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) followed by distilled water, and finally air-dried. All chemicals used in this study were analytical grade reagents purchased from Merck.

### Chemical modification of PAN with DETA

To prepare Modified PAN fiber (MPAN), each 1 g of PAN fiber was added to a solution containing 20 mL of DETA and 40 mL distilled water (L:S = 60:1) and heated under reflux at different temperatures and times. Then the solution was cooled to room temperature, and the filtered MPAN was washed with acetone followed by distilled water and air dried.

The efficiency of modification reaction,  $E$  (mmol/g), was estimated using the following equation:

$$E = (W_1 - W_0) / W_0 M_1 \quad (1)$$

where  $W_1$  and  $W_0$  are the weights of the PAN fiber after and before the reaction and  $M_1$  is the molecular weight of DETA (103.17 g/mol).

### Characterization of the samples

The FT-IR spectrums of the samples were recorded on a Bruker (Equinox 55) spectrometer with single reflection ATR system. TAQ 50 derivatograph (Shimadzu, Japan) was used for thermo gravimetric analysis (TGA). The samples were heated from 25 to 800 °C at the rate of 10 °C/min under argon.

The mechanical properties of the samples (tenacity, elongation, modulus and work of rupture) were determined using vibromat and fafograph from Tex-techno. Elongation rate of 20 mm/min and sample length of 20 mm were selected for all samples.

Scanning electron microscopy (SEM) was used to examine the external surface of the fibers before and after modification and after the adsorption of metal ions. The micrographs were taken using a Philips XL30 scanning electron microscope.

### Adsorption studies

The adsorption capacity of the modified fibers for  $\text{Ce}^{4+}$  (cerium sulfate,  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ),  $\text{Pb}^{2+}$  (lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ ) and  $\text{Cu}^{2+}$  (copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) ions were investigated using a batch method. Experiments were carried out in an Erlenmeyer flask at the pH 5 (using acetic acid) at 25 °C under stirring up for 2 h. The initial metal ion concentration was 20 ppm. The amount of adsorbed metal was determined by the difference between the initial metal ion concentration and the final one after equilibrium. The concentration of the ions in the liquid samples was determined using a Philips flame atomic absorption (FAA) spectrometer model PU9100.

The efficiency of metal ion adsorption was estimated by sorption yield ( $R$  / %) and quantity of ions adsorbed (retention capacity) by modified fibers ( $Q$  in mg/g) which were calculated using Eqs. (2) and (3):

$$R = (c_0 - c_t) / c_0 \times 100 \quad (2)$$

$$Q = (c_0 - c_t) / G \times V \quad (3)$$

where  $c_0$  is the initial metal ion concentration (mg/L),  $c_t$  is the ion concentration after the adsorption period,  $V$  is the volume of solution (L) and  $G$  is the dry mass of the MPAN fiber sample (g).

### Electrospinning of PAN

PAN was electrospun using the method explained in our previous work [19]. The base PAN solution was prepared at 14 wt.% from the PAN polymeric fibers in DMF. The as-prepared solution was then electrospun under a fixed electric field of 20 kV, onto an aluminum (Al) sheet with a collection distance of 20 cm from the nozzle as the collector. Prior to use, the electrospun fibers were collected and placed in vacuum at room temperature (25 °C) to remove as

much solvent from them as possible. The diameter of electrospun nanofibers was 356 nm.

## RESULTS AND DISCUSSION

### FTIR Analysis

The FT-IR Spectra of raw acrylic fibers (PAN) and the modified fibers (MPAN) are shown in Figure 1, indicating that the CN groups at  $2244\text{ cm}^{-1}$  in the modified fibers are diminished. The FTIR spectrum of the raw fibers (Figure 1a) shows the peaks at  $1000\text{--}1300\text{ cm}^{-1}$  (C-O stretching),  $1371\text{ cm}^{-1}$  (CH bending),  $1449\text{ cm}^{-1}$  ( $\text{CH}_2$  bending),  $1732\text{ cm}^{-1}$  (C=O stretching),  $2244\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching) and  $2936\text{ cm}^{-1}$  (CH stretching in CH,  $\text{CH}_2$  and  $\text{CH}_3$  groups) which are the confirmation of the original fibers as a copolymer of acrylonitrile (AN) and methylacrylate (MA).

Figure 1b shows the FT-IR spectrum of modified fiber (MPAN, 8 h,  $92^\circ\text{C}$ ). The presence of the high

intensity peaks at  $3351$  and  $1637\text{ cm}^{-1}$  correspond to the stretching vibration of NH and bending vibration of NH and C=O groups, respectively. The appearance of this peaks and reduced intensity of the peak at  $2243\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching) compared with the same peak of PAN, confirms the conversion of  $\text{C}\equiv\text{N}$  groups to amide  $\text{NH-C=O}$  groups due to reaction of DETA with the polymeric chains of PAN fibers.

The location of chemical reaction and the proposed mechanism for it are shown in Figures 2 and 3, respectively. As shown in Figure 2, the PAN chains are crosslinked with DETA. This phenomenon was confirmed by insolubility of MPAN in dimethyl formamide (DMF) even at boiling. Only MPAN samples with low reaction time and temperature were soluble in boiling DMF which shows that the efficiency of the cross linking increased with increase in time and temperature of the reaction.

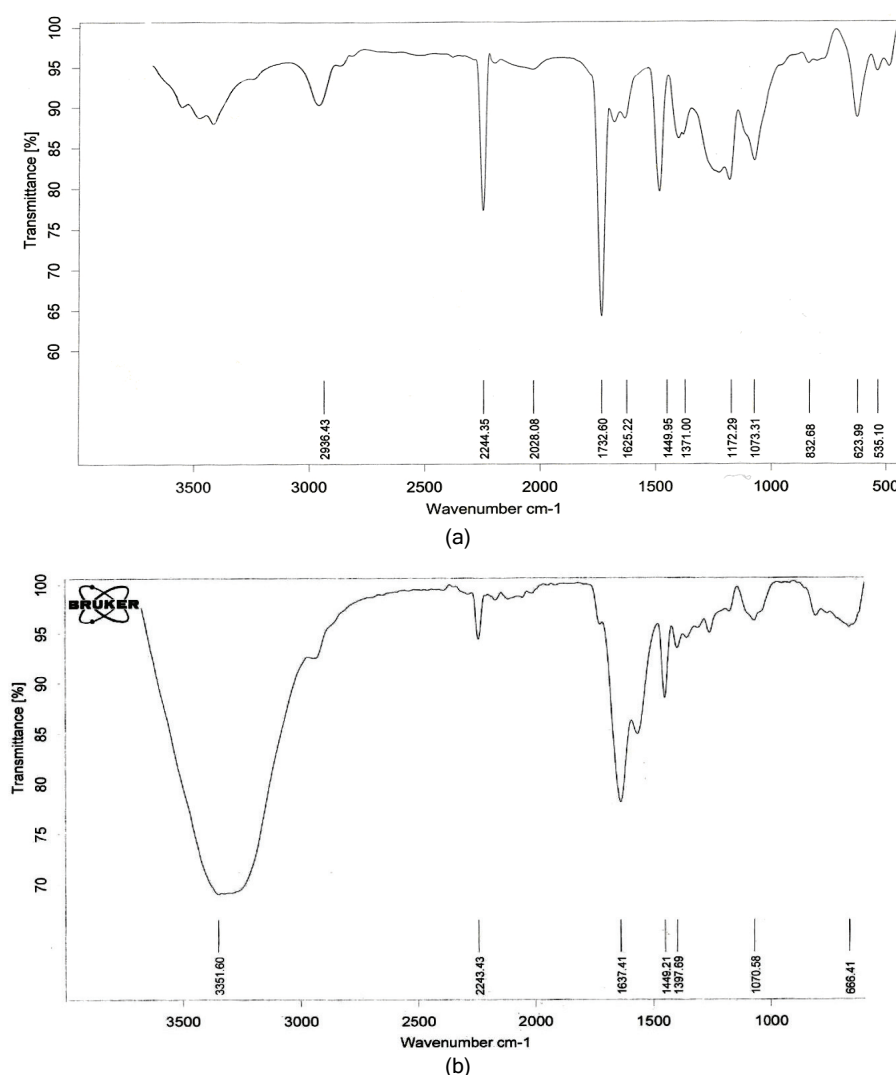


Figure 1. FT-IR spectra of raw acrylic fibers (PAN) (a) and of modified fibers (MPAN) under optimum condition (b).

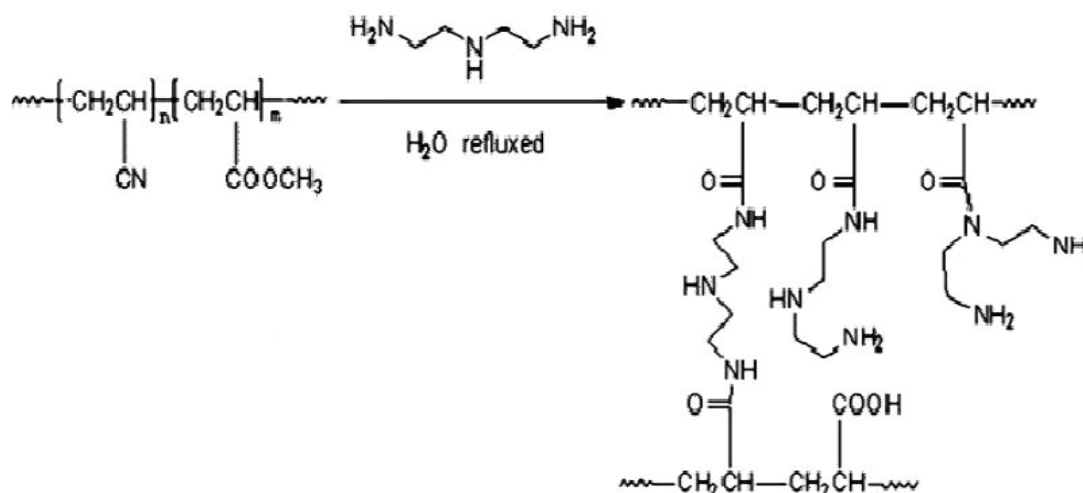


Figure 2. The chemical reaction between DETA and PAN.

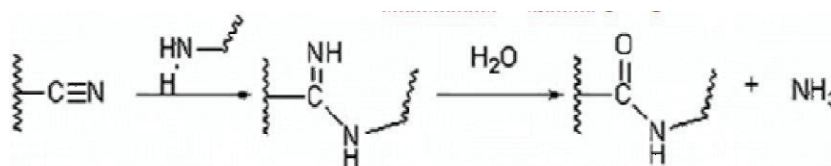


Figure 3. The mechanism of chemical reaction between DETA and PAN.

### Effect of reaction conditions

Figure 4a shows the effect of DETA concentration on the content of the functional groups in the modified fiber (E). It is obvious that there is an optimum concentration for DETA at 3.2 M that above it the increase in the amount of E is negligible. To investigate the effects of temperature and time, the concentration of DETA was kept constant at 3.2 M. As it can be seen from Figures 4b and 4c, by increasing the temperature and treatment time, the content of functional groups was increased. The optimum condition for grafting was the use of 3.2 M DETA aqueous solution at 92 °C for 8 h treatment time (L:S = 60:1).

### Thermal behavior of raw and modified fibers

Figures 5a and 5b show the thermo analytical TG curves of raw (PAN) and modified fibers (MPAN). PAN decomposes in the temperature range of 312 to 464 °C and decomposition temperatures of MPAN (maximum rate of mass loss) were at 58, 247 and 362 °C. The thermo gravimetric data indicates that the initial thermal stability of MPAN is lower than that of PAN due to conversion of nitrile groups into amine and amide groups.

### Mechanical properties

Figure 6 and Table 1 show the small difference in mechanical properties between PAN and MPAN.

The small decrease in modulus and max stress of MPAN compared to PAN is due to chemical changes of PAN structure through modification. The increase in work of rupture and extension at max load after modification is due to cross linking occurred between polyacrylonitrile chains.

### Ion adsorption capacity

Table 2 shows the sorption yield (*R*) and quantity of ions adsorbed by modified fibers (*Q*). As it can be seen the sorption yield of MPAN is obviously greater than PAN especially for Pb<sup>2+</sup>. The adsorption of these ions to MPAN is due to complex formation between the ions and the newly created functional sites on MPAN. The ability of complex formation is proportional to charge (*q*)/radius of ion, which is greater for Pb<sup>2+</sup> (2/84), compared to Cu<sup>2+</sup> (2/96) and Ce<sup>4+</sup> (4/111) [20].

### Ion adsorption by nanofibers

The modification reaction was done on nanofibers prepared from raw PAN at optimum conditions mentioned earlier (MNPN). The sorption yield (*R*) of MNPN (Table 2) was 96, 81 and 89% for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cr<sup>4+</sup>, respectively. The increased amount of ion adsorption for MNPN was due to reduced diameter and increased accessible functional sites of the modified nanofibers (MNPN) compared to microfiber MPAN [19-20].

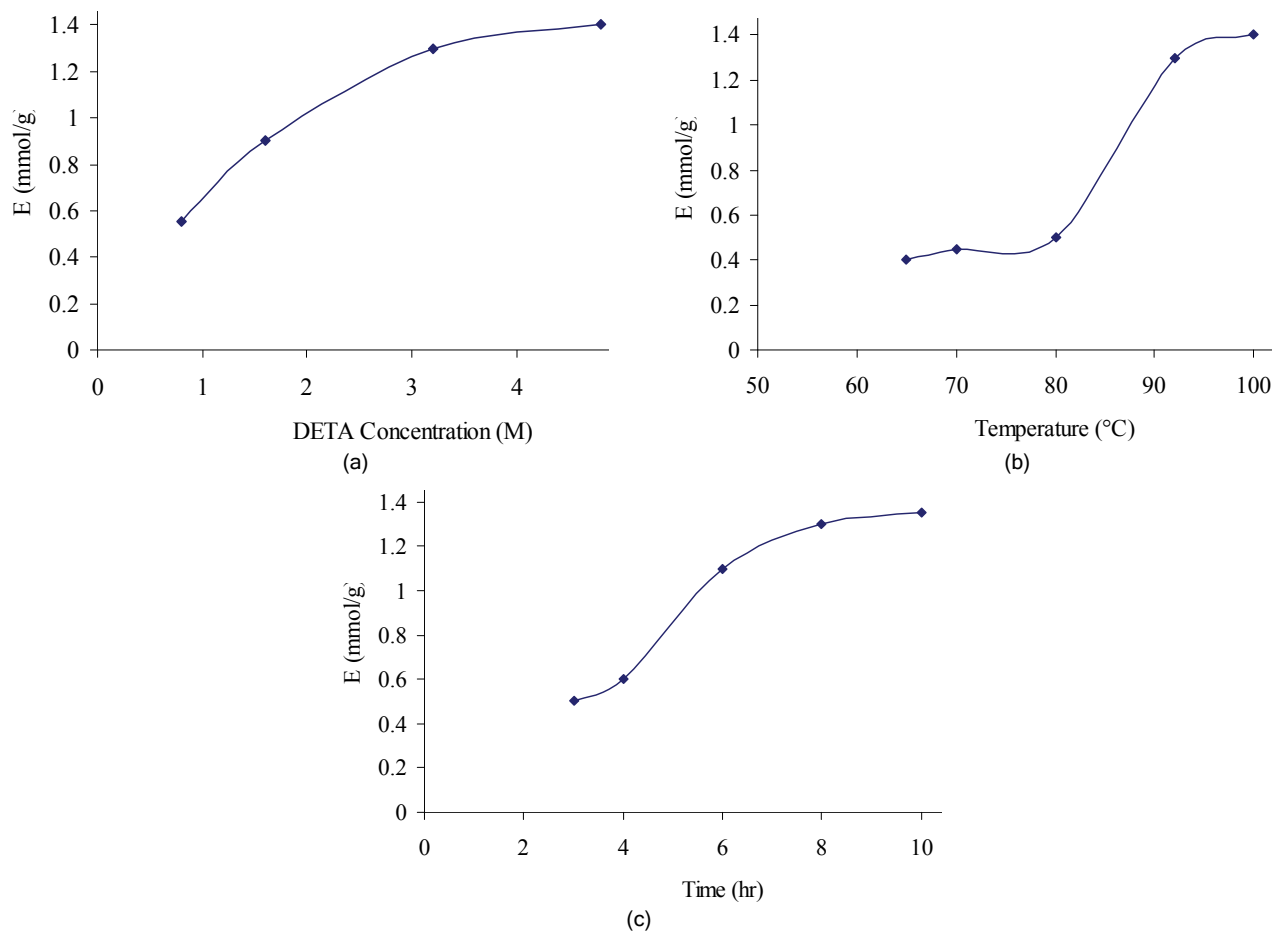


Figure 4. The effect of a) DETA concentration (temp. = 70  $^{\circ}\text{C}$ , time = 3 h, L:S = 60:1), b) temperature (time = 3 h, L:S = 60:1, concentration = 4.8 M) and c) treatment time (L:S = 60:1, concentration = 4.8 M, temp. = 70  $^{\circ}\text{C}$ ) on the content of the functional groups in the modified fiber.

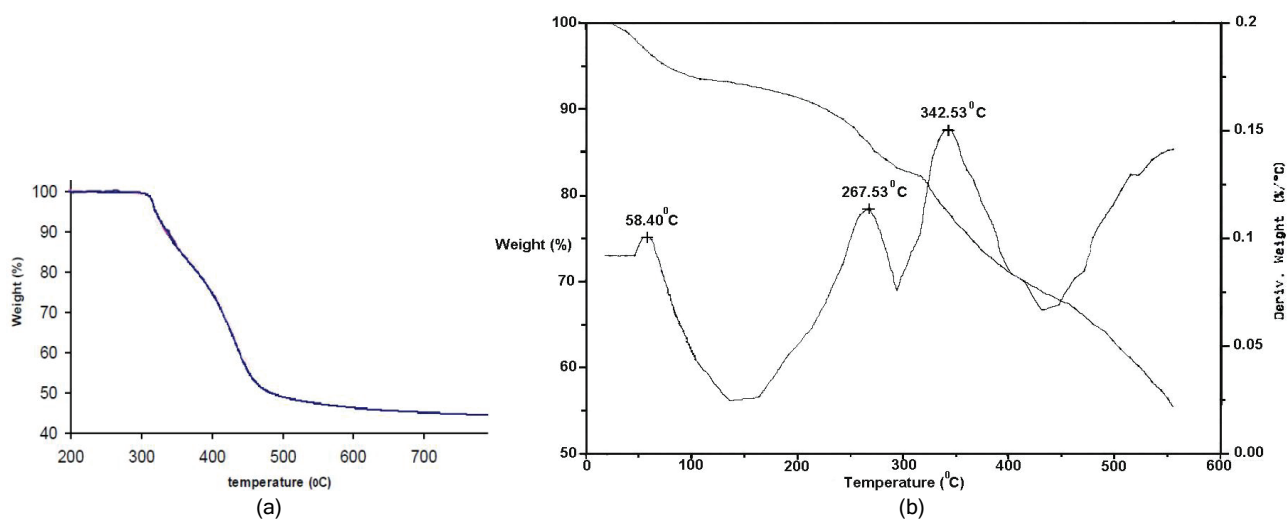


Figure 5. The thermo analytical TG curves of PAN (a) and modified fibers (b).

### Effect of pH on ion adsorption

Figure 7 (a, b and c) shows the effect of solution pH values on the adsorption of copper, lead and cerium ions on PAN, MPAN and MNPAN fibers respectively.

vely. PAN fibers adsorbed very little amounts of all ions at varying pH values. All ions display a general trend of increased adsorption on the modified fibers with the increase of solution pH values. At pH values

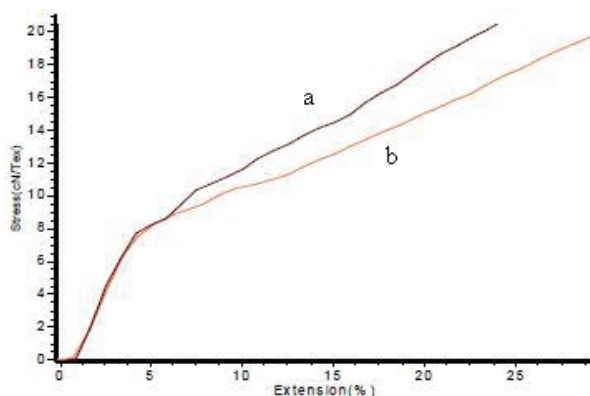


Figure 6. Stress strain curves of raw PAN (a) and modified MPAN fibers (b).

below 3 very little adsorption of all ions took place. For pH from 3 to 5, the adsorption amount of ions on the modified fibers increased with the increase of the pH but appeared to reach a plateau above pH = 5 and no further noticeable increase was observed at pH values more than 5.

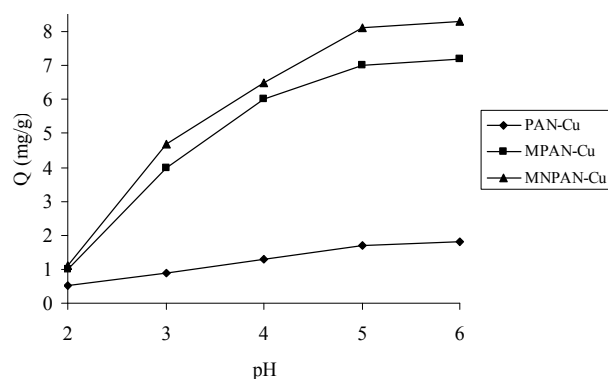
Table 1. Mechanical Characteristics of raw and modified fiber at optimum conditions

Sample	Work of rupture gf/den	Modulus cN/Tex	Max. stress cN/Tex	Extension at max. load, %
PAN	3.179	309.1	21	25.31
MPAN	3.741	270	19.01	29.8

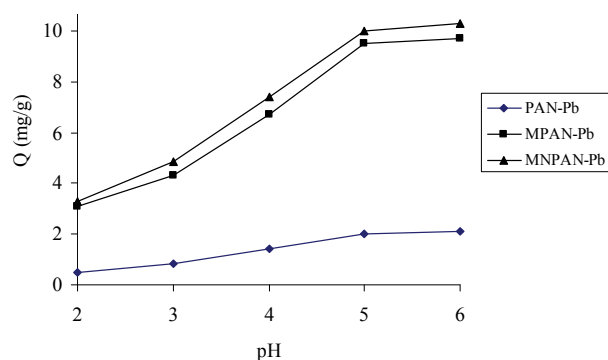
Table 2. Metal ion adsorption of PAN, MPAN and MNPAN (initial ion concentration, 20 ppm, pH 5 at 25 °C)

Sample	Ion adsorption (R / %)		
	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Ce <sup>4+</sup>
PAN	20	20	26
MPAN	95	70	85
MNPAN	96	81	89
Q / mg g <sup>-1</sup> (for MPAN)	9.5	7	8.5

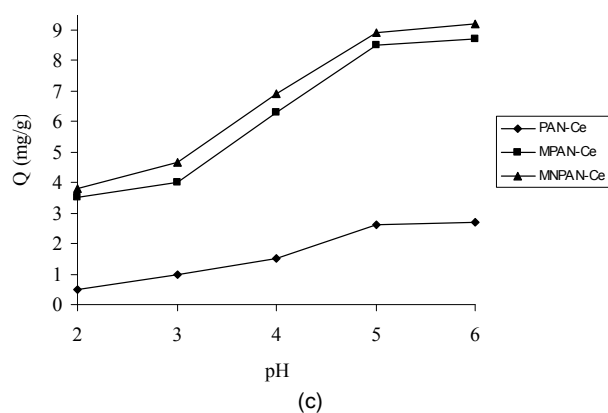
Since modified acrylic fibers gain positive charge at pH values under 8 [17], it seems that when pH was below 3-4, the strong electrical repulsion prevented the metal ions from contacting the surfaces of the fibers, resulting in little adsorption of metal ions on the fibers. With the increase of solution pH values, the electrical repulsion force became weaker and the metal ions may be transported to the surface of the fibers and become attached on the surface due to the action of other factors such as the van der Waals force, the formation of chemical or non-chemical bonds, and particularly the formation of metal complexes through chelating or ion exchanges [17].



(a)



(b)



(c)

Figure 7. The effect of solution pH values on the adsorption of copper (a), lead (b) and cerium (c) ions on PAN, MPAN and MNPAN fibers (at 25 °C for 2 h).



### SEM investigations

The SEM images of raw PAN, MPAN and MNPAN after adsorption of metal ions besides PAN nanofibers before and after modification (MNPAN) are shown in Figure 8. It is obvious from the images 8a and 8b that the reaction of PAN with DETA has made no visible changes in the outer layers of the fibers. So it can be concluded that the main changes are occurred only in the chemical structure of the fibers. The adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cr^{4+}$  is evident from Figures 8c, 8d and 8e. Figure 8g shows that the nanofibers were adhered together during chemical modification.

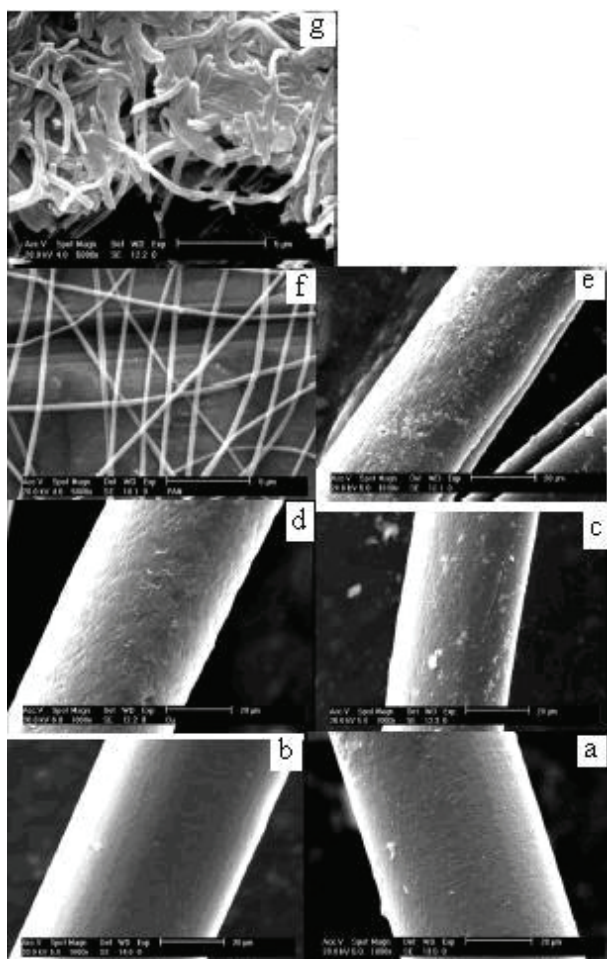


Figure 8. The SEM images of raw PAN (a), MPAN (b), MPAN after adsorption of metal ions (Pb (c), Cu (d) and Ce (e)) and PAN nanofibers before (f) and after (g) modification (MNPAN).

### CONCLUSION

In this study, a new chelating fiber was synthesized from polyacrylonitrile fiber. The optimum condition for the reaction was the use of a 3.2 M solution of DETA at L:S = 60:1 for 8 h at 92 °C. The grafting of

DETA and crosslinking of polymeric chains of PAN were done simultaneously. The so prepared MPAN fiber showed a good ability to adsorb  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cr^{4+}$  from aqueous media. For  $Pb^{2+}$ , this ability is greater than for others. The FT-IR spectroscopy, TG analysis and SEM investigations confirmed the expected changes. The mechanical characteristics of the fibers were decrease slightly after modification (excepting the work of rupture and extension at max load).

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NAUČNI RAD

## IZRADA HELATNIH DIETILENTRIAMINSKIH PAN MIKRO I NANO VLAKANA ZA UKLANJANJE TEŠKIH METALA

*U ovom radu, komercijalna akril vlakna su modifikovana pomoću dietilentriamina sa ciljem dobijanja metal helatnih vlakana. Ispitivan je uticaj parametara samog procesa na efikasnost reakcije. Hemijske promene nastale na vlaknu za vreme reakcije su praćene FTIR spektroskopijom i TGA analizom. Određena je i sposobnost modifikovanih vlakana da helatizacijom uklone jone Pb(II), Cu(II) i Ce(III) iz vodenog rastvora. Modifikovana vlakna pokazuju neznatno smanjenje mehaničkih osobina u odnosu na sirova vlakna. Osim toga, ispitivana je i sposobnost adsorpcije jona metala od strane nanovlakana nastalih elektropredanjem mikrovlakana.*

*Ključne reči: akrilna vlakna, helatizacija, jonska izmene, modifikacija, adsorpcija.*