

# Preparation of Hydrazine-Modified Polyacrylonitrile Nanofibers for the Extraction of Metal Ions from Aqueous Media

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**ABSTRACT:** Polyacrylonitrile (PAN) nanofibers (prepared by an electrospinning technique) were chemically modified with hydrazine. The Fourier transform infrared spectrum of the hydrazine-modified polyacrylonitrile (HM-PAN) showed that the intensity of the nitrile peak ( $2250\text{ cm}^{-1}$ ) of the PAN nanofibers decreased significantly after treatment with hydrazine. New peaks at about  $3400\text{--}3100\text{ cm}^{-1}$  (N—H stretching vibration) also appeared, which showed that the hydrazine was chemically attached to the PAN nanofibers. HM-PAN had a smooth surface (as confirmed by a scanning electron

microscopy) and was a suitable material for the adsorption of metal ions from aqueous solutions. The adsorption capacity of HM-PAN increased as the adsorption time increased and became constant at 114 and 217 mg/g for Cu(II) and Pb(II) ions, respectively, after 24 h. In addition, more than 90% of the adsorbed Cu(II) and Pb(II) ions were recovered in a 1M HNO<sub>3</sub> solution after 1 h. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 869–873, 2011

**Key words:** FT-IR; Electrospun nanofibers; morphology

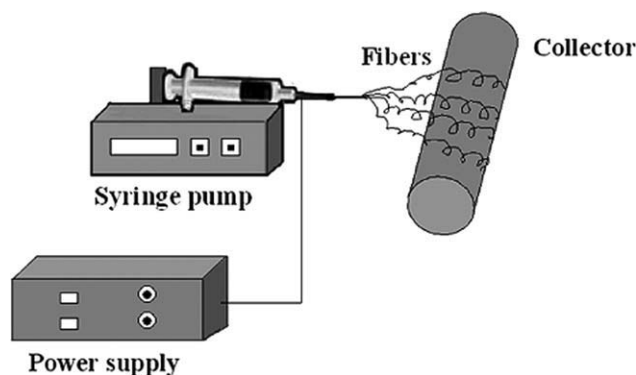
## INTRODUCTION

The separation of micrometer to submicrometer contaminants has been paid great attention in air filtering, water purification, and effluent treatment. During the filtration process, these contaminants tend to clog or foul membrane elements and considerably decrease the efficiency and output of the treatment. Various types of filters, such as packed sand beds and woven and nonwoven fibrous meshes, are available for separation into two distinct phases. The choice of filter is usually governed by its properties, performance, and durability. The materials (e.g., beads and fibers) of filters that have extremely large surface areas are very effective for the separation/adsorption of contaminants. The surface area increases with decreasing fiber diameter. When the smaller diameter fibers are used as a filter media, they not only appreciably adsorb pollutants because of their larger surface area but are also effective for the retention of small-size particles.<sup>1</sup> Recently,

researchers have paid great attention to nanofibers for the preparation of filters, which can be made with an electrospinning technique. In electrospinning, a polymer solution (or melt) is stretched and then elongates into fibers after a sufficient voltage is applied; it is then collected as an interconnected nonwoven fiber membrane. The electrospun nanofiber membrane has a wide range of applications, such as in drug-delivery systems,<sup>2</sup> scaffolds in tissue engineering,<sup>3</sup> nanofibrous membranes for fine filtration,<sup>4</sup> clothing protection,<sup>5</sup> sensors,<sup>6</sup> and wound dressings.<sup>7,8</sup> These applications are made possible because of the nanofibers' unique characteristics, such as a large surface area per unit mass, high porosity, high gas permeability, and small interfibrous pore size.

The removal of heavy-metal ions from water and industrial effluents is important in terms of the protection of public health and the environment because of their accumulating characteristics in nature and living tissues throughout the food chain as nonbiodegradable pollutants.<sup>9</sup> These effluents come from various industrial sources, such as the textile, storage battery, dyestuff, pharmaceutical, metallurgical, chemical, and glass industries as well as electroplating, metal finishing, and many other areas, and cause heavy-metal pollution in the environment. It has been reported that arsenic, chromium, mercury,

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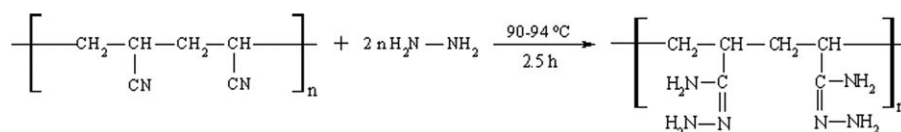


**Figure 1** Schematic representation of the electrospinning apparatus.

cadmium, lead, and copper are commonly found in industrial pollutants. These metals cause various ailments, such as dehydration, stomachache, nausea, dizziness, lack of coordination in muscles, nervous system damage in young children, lung irritation, eye irritation, skin rashes, vomiting, abdominal pain, lung insufficiency, and liver damage.<sup>10–12</sup>

Traditional methods (ion exchange, solvent extraction, chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, electro dialysis, and adsorption)<sup>13–17</sup> have been commonly applied to the removal of the heavy-metal ions present in industrial wastewaters. The adsorption technique is widely used for the removal of the heavy-metal ions from aqueous solutions. The separation of metals can also be achieved with macromolecular compounds containing functional groups, such as amino, carboxyl, hydrazine, phosphoric, imidazoline, thio-amido, and amidoxime groups, all of which have complexing abilities toward metal ions.<sup>18–21</sup> The utilization of nanofibers as filter materials is desirable because of their high specific surface area; this leads to a high adsorption rate and a high capacity compared to other types of materials, such as resins, foams, and conventional fibers.<sup>22–24</sup>

In this study, we prepared polyacrylonitrile (PAN) nanofibers and then chemically modified the nitrile groups via hydrazine treatment. Cu(II) and Pb(II) were adsorbed onto the HM-PAN nanofibers from an aqueous solution. The morphologies of the PAN nanofibers before and after chemical modification were also investigated.



**Scheme 1** Reaction of hydrazine with PAN nitrile groups.

## EXPERIMENTAL

### Materials

Hydrazine, dimethylformamide, lead nitrate, and copper(II) chloride dehydrated were purchased from Ducksan Chemicals (S. Korea). PAN [copolymer of acrylonitrile (91.4%) and methacrylate (8.6%)] was supplied by Taekwang Co (S. Korea). The average molecular weight of PAN was in the range 100,000–200,000.

### Electrospinning of PAN

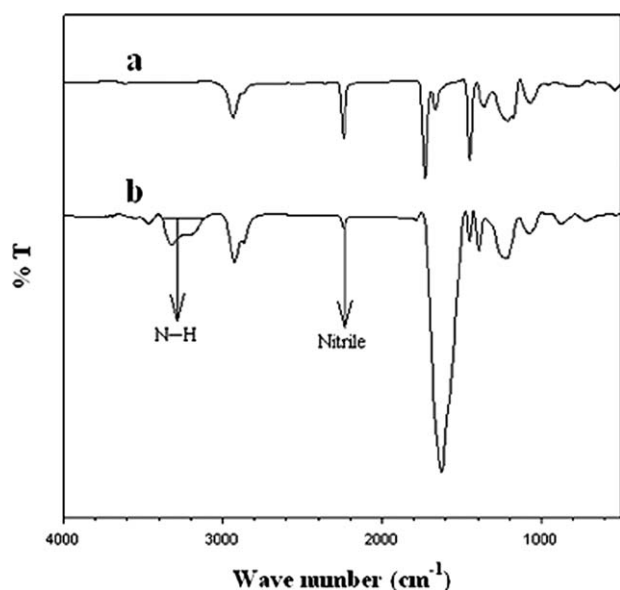
The solutions of PAN were prepared by the individual dissolution of 10 and 15 wt % samples in dimethylformamide.<sup>25</sup> The schematic representation of the electrospinning apparatus is shown in Figure 1. The prepared polymer solutions were added to a 10-mL glass syringe with a needle tip 0.5 mm in diameter. The flow rate (1 mL/h) of the polymer solutions was fixed by a syringe pump. An electrospinning voltage of 20 kV was applied to the needle, and the distance between the needle tip and the collector was 15 cm. PAN was electrospun at 50°C to evaporate the solvent quickly. At a critical voltage, a jet of the polymer solution came out from the needle tip and was collected on the collector. When the solvent evaporated, a nonwoven PAN mat was formed.

### Functionalization of the PAN nanofibers

Scheme 1 shows the reaction of hydrazine with the nitrile group of PAN. Hydrazine (100 mL) and the PAN nanofiber mat (0.2 g; the edges of the mat were fixed with a Teflon frame to prevent shrinkage of the nanofibers during the reaction) were mixed in a reaction vessel and then heated at 90–94°C for 2.5 h. After conversion, the nanofiber mat was washed several times with distilled water and then by 200 mL of ethanol and was then dried in an oven at 60°C.<sup>26</sup> The increase in weight was 5.2%.

### Adsorption of Cu(II) and Pb(II) onto the HM-PAN nanofiber mat

Dried samples of the HM-PAN nanofiber mat (0.2 g) were stirred in 30 mL of a metal-ion solution (400 ppm) for different time durations at room temperature. The concentration of the metal ions in the solutions was determined by inductively coupled plasma (ICP).



**Figure 2** FTIR spectra of the (a) PAN and (b) HM-PAN nanofibers.

#### Desorption of Cu(II) and Pb(II) from the HM-PAN nanofiber mat

The metal-loaded HM-PAN samples were added to a 1M HNO<sub>3</sub> solution, and the solutions were stirred during sampling. The sample solutions were collected after 2, 5, 15, 30, and 60 min, and then, the concentrations of metal ions were determined by ICP.

#### Instrumentation

Fourier transform infrared (FTIR) spectra were recorded with a Jasco FT/IR 620 spectrometer (UK). The spectra were derived from 50 coadded interferograms, which were obtained at a resolution of 1 cm<sup>-1</sup>. The micrographs of the gold-coated electrospun PAN and HM-PAN nanofibers were analyzed with a Hitachi S-570 field emission scanning electron microscope Japan. The metal-ion determination was carried out by a spectro flam ICP argon-plasma emission spectrometer (Modle Themo Jarrell Ash Co., IRIS/AP). The ICP was calibrated with 0.1, 1, and 10 ppm copper solutions; these were prepared by the dilution of a standard solution (1000 ppm copper) with 2–3% HNO<sub>3</sub>. The concentration of metal ions was determined at room temperature.

## RESULTS AND DISCUSSION

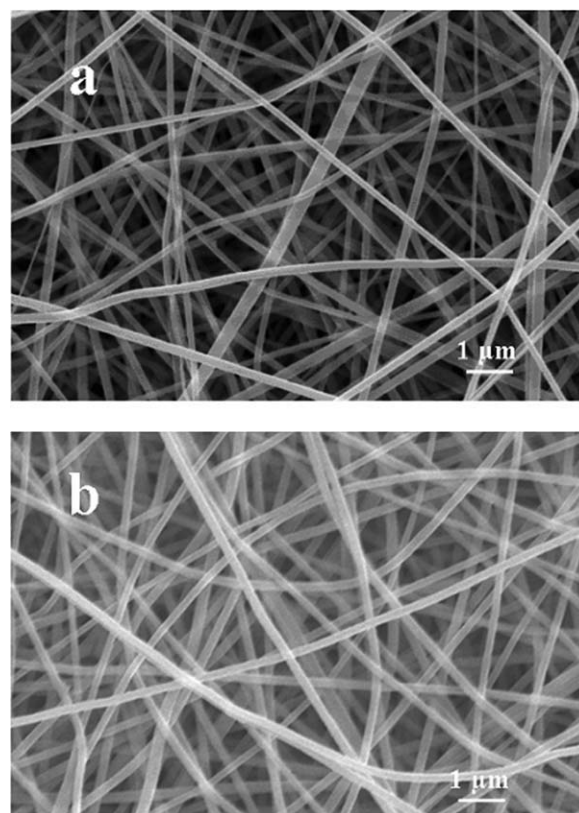
#### FTIR study

Figure 2 shows the FTIR spectra of the PAN and HM-PAN nanofiber mats. The FTIR spectrum of PAN [Fig. 1(a)] exhibited characteristic bands due to the stretching vibration of nitrile (2250 cm<sup>-1</sup>), carbonyl (ca. 1730 cm<sup>-1</sup>), and ether (1250 and

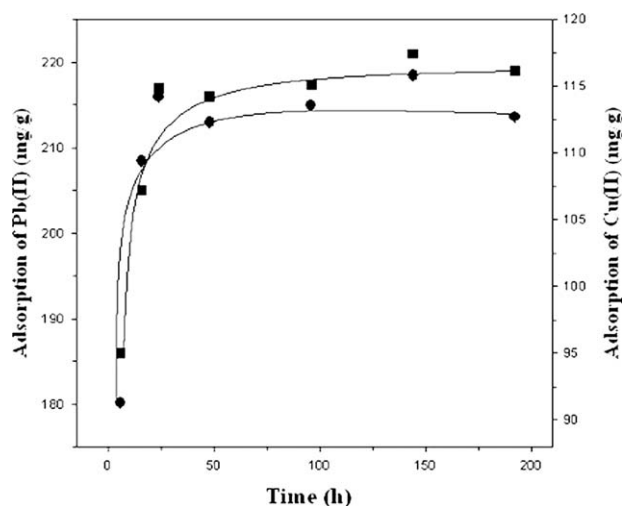
1150–1060 cm<sup>-1</sup>) groups. The carbonyl and ether bands came from the methylacrylate comonomer. The FTIR spectrum of HM-PAN [Fig. 2(b)] showed new peaks at about 3100–3400 cm<sup>-1</sup>, which were due to the N–H stretching vibration of the secondary amino group. The broad band in the region of about 1700–1630 cm<sup>-1</sup> was probably due to the coupling of carbonyl and C=N groups, whereas the weak band at about 1570–1560 cm<sup>-1</sup> contributed to the overlapping of the C–N stretching vibration with the N–H bending vibration. The intensity of the nitrile peak (2250 cm<sup>-1</sup>) of the PAN nanofibers decreased significantly after treatment with hydrazine [Fig. 2(b)]; this showed that the hydrazine was chemically attached to the PAN nanofibers.<sup>25,27</sup>

#### Morphology of PAN and HM-PAN

Figure 3 shows the field emission scanning electron microscopy (FESEM) images of the PAN and HM-PAN nanofiber mats. The beads were formed during the electrospinning of a 10 wt % PAN solution and disappeared as the concentration increased from 10 to 15 wt %, as shown in Figure 3(a). The diameter of the nanofibers increased when the concentration of the PAN solution increased.<sup>28</sup> The average diameters



**Figure 3** FESEM images of the (a) PAN and (b) HM-PAN nanofiber mats, which were electrospun from a 15 wt % solution.



**Figure 4** Adsorption of (■) Pb(II) and (●) Cu(II) on the HM-PAN nanofiber mat in a 400-ppm solution as a function of time.

of the PAN nanofibers were about  $300 \pm 50$  nm. The FESEM image of the HM-PAN [Fig. 3(b)] was very similar to that of the PAN nanofibers [Fig. 3(b)]; this indicated that the surface of the HM-PAN nanofiber mat was not seriously cracked or degraded during the chemical reaction between the PAN nanofibers and hydrazine.

#### Adsorption of metal ions onto the HM-PAN

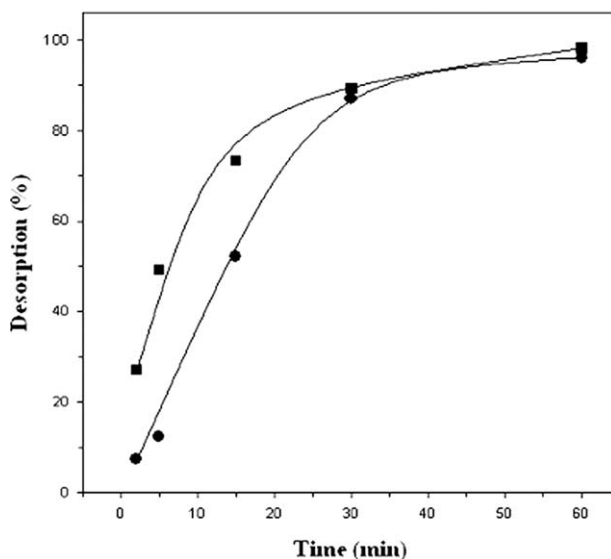
The metal adsorption ability of chelating fibers greatly depends on the type and contents of the functional groups present on the adsorbent. Adsorbents with N-donor atoms can strongly bind with metals. Figure 4 shows the adsorptions of Cu(II) and Pb(II) on the HM-PAN nanofiber mats. The amount of adsorption of both metal ions increased as the adsorption time increased. The HM-PAN adsorbed Cu(II) at levels of about 91 and 109 mg/g and Pb(II) at levels of about 186 and 209 mg/g in 6 and 16 h, respectively. The increase in the adsorption of metal ions with increasing time might have been due to the availability of more time for the adsorption of both metal ions onto HM-PAN; this became constant after 24 h. The adsorption capacities (at 24 h) of Cu(II) and Pb(II) onto the HM-PAN nanofibers were 114 and 217 mg/g, respectively. Also, the HM-PAN nanofiber mats adsorbed more Pb(II) than Cu(II); this might have been due to the different number of chelating groups bound to the metals. A greater adsorption of Pb(II) compared to Cu(II) was also reported by Alakhras et al.<sup>29</sup> in a study on the adsorption of metal ions on amidoxime-modified PAN. They suggested that Pb(II) preferred a 1 : 1 chelate complex with amidoxime, whereas two oxime groups preferred to make metal complexes with Cu(II).<sup>29</sup>

#### Desorption of the metal ions from metal-loaded HM-PAN

The desorption of Cu(II) and Pb(II) from the already metal-loaded nanofibers was also tested. The extraction of Cu(II) and Pb(II) was studied with a 1M HNO<sub>3</sub> solution at room temperature. Figure 5 shows the desorption of Cu(II) and Pb(II) from the HM-PAN nanofiber mat. Both Cu(II) and Pb(II) were desorbed by 52 and 73%, respectively, within 15 min. The desorption of both metal ions increased as the desorption time increased. The amount of extracted metal ions was over 90% after 1 h. This result strongly suggests that the HM-PAN nanofiber mat had a great potential for the recovery of metal ions from aqueous/industrial effluents.

#### CONCLUSIONS

We concluded from this study that the hydrazine treatment did not seriously crack and/or degrade the PAN nanofibers, and the HM-PAN nanofiber mat showed an almost similar morphology to that of the pure PAN nanofibers. The adsorption capacity of HM-PAN increased as the adsorption time increased and then leveled off after 24 h. The desorption capacity of both Cu(II) and Pb(II) from the HM-PAN nanofiber mat in a 1M HNO<sub>3</sub> solution increased as the desorption time increased. More than 90% of the absorbed metal ions were extracted within 1 h; this indicated the potential use of HM-PAN nanofibers as filters for the recycling of metals from wastewater.



**Figure 5** Desorption of (■) Pb(II) and (●) Cu(II) on the HM-PAN nanofiber mat in a 400-ppm solution as a function of time.

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