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Synthesis of amidoximated polyacrylonitrile fibers and its application for sorption of aqueous uranyl ions under continuous flow

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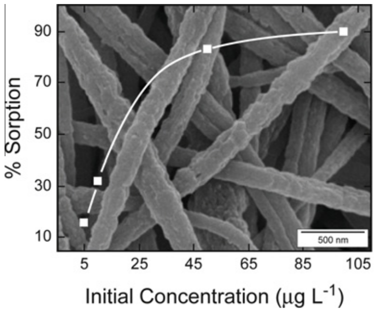
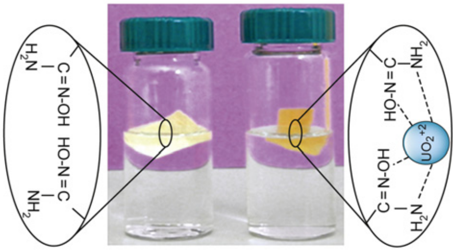
HIGHLIGHTS

- ▶ Submicron diameter PAN fibers were successfully prepared by electrospinning.
- ▶ PAN fiber mat was found to be promising in sorption of U(VI) ions by column method.
- ▶ The surface of PAN fibers were post-functionalized by amidoximation reaction.
- ▶ The surface modification remarkably enhanced U(VI) sorption capacity of PAN fibers.

GRAPHICAL ABSTRACT





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ABSTRACT

This study reports a feasible method for the removal of radioactive U(VI) ions from aqueous systems via column sorption under continuous flow. Electrospun polyacrylonitrile (PAN) fibers were used as sorbent materials in a homemade minicolumn. The nitrile groups on the fibers' surface were modified to amidoxime groups using hydroxylamine hydrochloride. Surface modification was observed to enhance the sorption capacity of PAN fibers toward uranium ions by more than 4-fold by virtue of the chelating ability of the amidoxime groups. The experiments investigated the effect of pH, initial concentration, and repetitive loading on the sorption properties of amidoximated PAN fibers. Based on the overall results, the surface-modified fibers seem to be a suitable potential sorbent material for applications in environmental cleanup, particularly for nuclear plants.

1. Introduction

Uranium is the heaviest naturally occurring radionuclide and has various harmful fouling effects in the environment. There are hundreds of uranium species, which account for 5% of all known minerals [1]. This element is present in most rocks, soil, surface water, and groundwater in the order of a few parts per million. It is also discharged into the environment from many anthropogenic activities such as mining, military applications, production and use of phosphate fertilizers, combustion from coal and other fuels, and nuclear power facilities. The increasing usage of nuclear reactors for large-scale energy production leads to radioactive contamination; hence, research concerning the separation of U(VI) ions from water has become a critical environmental issue in the last decade [2–4].

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There are two commonly used methods to remove U(VI) ions from solutions: (i) sequestration using organic compounds and (ii) fixation on surfaces of sorbent materials. The former involves the covalent interaction of uranyl ions with specific organic compounds until the ions are no longer radioactive [5]. However, use of this method requires reconsideration as radioactivity cannot be eliminated by chemical bonding. In the latter method, the ions are fixed onto the surface of a heterogeneous material through sorption. While the concentration of uranyl ions decreases in solution, it is enriched on the surface of the sorbent material.

The sorption of U(VI) ions can be achieved by various forms of natural and synthetic adsorbents, given in Table 1. Several works related to uranium sorption onto naturally occurring clay minerals and soil fractions have been performed. Hudson et al. [6] examined vermiculate and hydrobiotite, and Sylwester et al. [7] examined silica, alumina, and montmorillonite as sorbents. Both studies investigated the pH dependence of uranyl oxo-cation (UO_2^{2+}) sorption and determined the local structure around the sorbed uranium atom. Kowal-Fouchard et al. [8] illuminated the surface complexation of uranyl ions and montmorillonite sorption sites. Kilincarslan and Akyil [9] studied uranium sorption on clinoptilolite zeolite surfaces and determined optimum conditions such as pH, initial concentration, contact time, and temperature. The sorption behavior of uranium on sodium aluminosilicate solid phases was investigated by Addai-Mensah et al. [10] Greathouse and Cygan [11] concluded that siloxane groups of beidellite, montmorillonite, and pyrophyllite were responsible for uranyl sorption. Donat et al. [12] combined biomass and clay mineral to prepare an *Ulva* sp. sepiolite composite sorbent, and Khani [13] carried out optimization of uranium removal by a *Padina* sp. algal biosorbent.

To improve the sorption capacity of sorbents, many attempts have been made for chemical modification of sorbent surfaces using functional groups such as amidoxime [3,14,15], imidazole [16], and metal oxides [4,17,18], which possess chelating abilities toward U(VI) ions. As commonly used sorbents are in powder form, their utilization as a filter material is not convenient due to the difficulty in the isolation of the solid from the solution medium following the sorption stage. Therefore, additional treatments might be needed, such as the coating of these sorbents onto a supporting surface, to efficiently use them for uranium removal. Zou et al. [19] modified natural zeolite surfaces using manganese oxide and tested uranium(VI) sorption performance with a fixed bed ion-exchange column. The same authors reported the usage of manganese oxide-coated sand as a sorbent for the removal of uranyl ions in batch processing. Attention has recently been paid to amidoxime chelating adsorbent in removing heavy toxic metals and/or selective recovering of precious metals. Takeda et al. [14] proposed a fixed bed adsorption unit containing amidoxime-modified commercial polyethylene hollow fiber for the recovery of uranium from seawater. Pekel and Guven [3] studied uranyl ion uptake by amidoximated poly(acrylonitrile/N-vinylimidazole) complexing sorbents. It was reported that uranyl ion adsorption was achieved via the complexation abilities of the vinylimidazole and amidoxime groups. However, colloidal hydrogels as a filter medium are not favorable due to their lack of mechanical integrity accompanied by difficulty in the separation of the solid phase from aqueous media.

Table 1
Summary of sorption system suggested for uranium.

Sorbents	Size	Types of sorption	References
Streptomyces and chlorella cells	–	Column	[36]
Polyethylene hollow fiber	380 μm	Column	[14]
Montmorillonite	<2 μm	Batch	[7,8,11,37]
Vermiculite and hydrobiotite	<45 μm	Batch	[6]
Silica, alumina	0.48 μm	Batch	[7,10]
Amidoximated poly(acrylonitrile/N-vinylimidazole)	4, 5 mm in length	Batch	[3]
Clinoptilolite zeolite	<74 μm	Batch	[9]
Hydrogels based on PEG and methacrylic acid	–	Batch	[2]
Ulva sp.-Sepiolite	<125 μm	Batch	[12]
Manganese oxide coated zeolite	60–200 μm	Column	[18]
Manganese oxide coated sand	670–990 μm	Batch	[38]
Padina sp. algae biomass	1.0–1.25 mm	Batch	[13]
Titanium dioxide	4–240 nm	Batch	[17]
Iron oxide	<15 nm	Batch	[4]

Electrospun fibrous materials are emerging as suitable alternatives to conventional sorbents due to their structural advantages conveyed by the nanosized diameter of the constituent fibers [15,20–25]. A high surface area-to-volume ratio (which leads to high sorption capacity), porosity, and mechanical integrity are the benefits of electrospun fibers. The fibers also serve as substrates for functional groups upon surface modification [26,27]. They can thus be potentially used for sorption and desorption of metal ions. Based on this, it seems reasonable to investigate the sorption efficiency of amidoxime-modified electrospun fiber for the removal of radioactive and chemically toxic U(VI) ions from aqueous systems. The surface-modified electrospun fibers used in this work have large surface areas and porosity as well as mechanical integrity, which are desirable properties in filtration applications. This makes such fibers superior in terms of sorption capability as compared to many of the powdered sorbents and colloidal hydrogels reported in earlier works. The sorption study described herein was designed to survey the characteristics of amidoximated polyacrylonitrile (PAN) fibers and to test their properties as a sorbent for U(VI) ions from synthetic solutions via a column system. Column-type continuous-flow sorption has an advantage over batch-type sorption as the rate of sorption depends on the concentration of solute in the solution being treated. In column treatment, the filter material is continuously in contact with fresh solution. By virtue of column sorption, the concentration in the solution changes very slowly; however, in batch sorption, the concentration of the solute decreases much more rapidly and thereby reduces the effectiveness of the sorbent. Compared to batch sorption, column sorption is more convenient in industrial applications due to its simplicity, the fact that it does not require any additional processes such as filtration or centrifugation, and its ability to provide a higher residence time. Many applications of filtering processes involve the removal of undesirable species under continuous flow of the solution. For example, in agricultural irrigation pipes, the filtering material is placed on a cross-section of the pipes such that it is normal to the flux direction of solution, and as such the mechanical resistance to the continuous flow becomes the main requirement for filtering material. In this sense, electrospun fiber mat may be a promising candidate for such applications [28].

2. Experimental section

2.1. Materials

Acrylonitrile (AN) and benzoyl peroxide (BPO) were provided by Fluka Chemical Company. For the surface modification of PAN fibers, hydroxylamine hydrochloride ($H_3NO{\cdot}HCl$) and sodium hydroxide (NaOH) were supplied by Sigma–Aldrich and Riedel-de Haen Chemicals, respectively. N,N-dimethylformamide (DMF) (Sigma–Aldrich) was used as an electrospinning solvent and uranylacetate dihydrate ($UO_2(CH_3COO)_2{\cdot}2H_2O$; Merck) was used as a sorbate. Sodium bicarbonate ($NaHCO_3$; Fluka), ammonium citrate ($C_6H_{17}N_3O_7$; Sigma), and ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$; Riedel-de Haen) were used as desorbing eluents. All chemicals were of reagent grade and ultrapure water (18.2 MΩ) was used throughout the study.

2.2. Instrumentation and software

Electrospun fibers were analyzed by scanning electron microscope (SEM; Philips XL-30S FEG, Eindhoven, the Netherlands). ImageJ 1.43u software was used for the determination of fiber diameter from SEM micrographs. In each trial, 100 test fibers were measured and the average fiber diameter (AFD) and its standard deviation were determined. Energy dispersive X-ray (EDX) analysis was performed using an FEI XL30 W instrument equipped with an Apollo X Silicon Drift detector. Atomic distribution of the surface of the sorbents was obtained from randomly selected points.

The amidoximation reaction and uranyl sorption were investigated via Fourier transform infrared radiation (FT-IR) spectroscopy. FT-IR measurements of the samples before and after the amidoximation reaction as well as of uranyl sorbed-fibers were performed with a PerkinElmer Spectrum 100 FT-IR Spectrometer (Waltham, USA) with a PIKE MIRacle Single Reflection Horizontal ATR Accessory. The amount of uranium ions was determined using an inductively coupled plasma (ICP) spectrometer (Agilent 7500ce Series, Japan). The ICP-MS operation parameters are given in Table S1 of Appendix A. Standard solutions of 5.0, 10.0, 25.0, 50.0, 100.0, 200.0, 500.0, and 1000.0 $\mu g\,L^{-1}$ concentrations were prepared by appropriate dilution of 10.0 $mg\,L^{-1}$ U(VI) stock solution to the required volume. All samples and standard solutions were acidified through the addition of the proper amount of concentrated HNO_3 to produce 1.0% (v/v) acid in the final solution. The percentage of uranium sorption was calculated using Eq. (1), where C_i is the initial and C_f is the final concentration in the solution.

$$\%Sorption = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

The speciation analysis of uranium-containing ions at various pH values was performed using Visual MINTEQ software.

2.3. Polymerization of acrylonitrile

Polymerization of acrylonitrile was carried out at 60 °C using benzoyl peroxide as an initiator. AN (0.076 mol) and BPO (0.0076 mol) were mixed in a sealed glass tube after sonication for 15 min. Three cycles of a freeze–thaw process were applied prior to polymerization. The glass tube containing the AN and BPO was placed into a preheated bath at 60 °C; the polymerization was performed under an N_2 atmosphere and it was stopped after the desired time by quenching to room temperature. The resulting product was dissolved in DMF and purified in methanol under continuous mixing for 3 h, and then filtrated under vacuum. After filtration, the polyacrylonitrile were dried under vacuum for 6 h at 40 °C.

The viscosity average molecular weight of the synthesized polymer was determined by using a Petrotest capillary viscosimeter (Dahlewitz, Germany) placed in a water bath thermostatically controlled at 25 °C. The polymerization products were dissolved in DMF at concentrations ranging from 1.3 $g\,L^{-1}$ to 3.9 $g\,L^{-1}$. Calculations were made using the Mark–Houwink equation $[\eta] = KM_v^{\alpha}$, where K and α are the specific constants for a given polymer and vary for the used solvent system and temperature [29]. The K and α of PAN are equal to 0.21 $cm^3\,g^{-1}$ and 2.20, respectively. The polymer used in the experiment has viscosity molecular weight (M_v) in the range of 180 $kg\,mol^{-1}$.

To determine the number average molecular weight (M_n) of the polymer, a 400 MHz NMR system (Varian VnmrJ, Palo Alto, USA) was employed; M_n was calculated as 14 $kg\,mol^{-1}$. The ratio of protons on the end-groups to the protons on the polymer backbone was determined by integration of ^1H NMR signals.

2.4. Electrospinning of polyacrylonitrile

The electrospinning solution of the synthesized PAN was prepared by dissolving the polymer (4 wt%) in DMF. The PAN solution was placed in a 20 mL syringe fitted with a metallic needle of 0.2 mm in inner diameter. The syringe was fixed horizontally on the microinfusion pump (LION WZ-50C6), and the electrode of the high-voltage power supply (Gamma High Voltage Research, Ormond Beach, USA) was attached to the metal needle tip. The flow rate of the polymer solution was 2 $mL\,h^{-1}$, voltage of 15 kV was applied to the needle, and the distance between the needle and the collector was 5 cm. The electrospinning process was performed at room temperature and the resulting fiber mat was held in vacuum at 50 °C overnight to remove any residual solvent.

2.5. Surface treatment of PAN fibers

The hydrophilic character of the electrospun PAN fiber was increased by converting the nitrile groups of AN to amidoxime groups. For the amidoximation reaction, a recipe given in the literature was followed [30]. Hydroxylamine hydrochloride (0.375 g), sodium hydroxide (0.375 g), and 25.0 mg of PAN nanofiber mats were added to a 50 mL beaker and continuously stirred for 2 days at room temperature. After surface reaction, the nanofiber mats were washed several times with distilled water to remove the remaining salts and were dried in a vacuum oven at 60 °C.

2.6. Sorption studies

Aqueous U(VI) solutions were prepared by dissolving a proper amount of ($UO_2(CH_3COO)_2{\cdot}2H_2O$) in ultrapure water. Column studies were carried out in order to show the applicability of amidoximated PAN fiber sorbent in the continuous removal of uranyl from aqueous solution. A homemade microcolumn system involving Teflon tubing with an internal diameter of 1.5 mm and 50 mm of height was employed in the experiments. 30 mm of the tubing height was filled with amidoximated PAN fiber sorbents. Cylindrically shaped small sponge pieces were squeezed into both ends of the tube such that the amidoximated PAN fibers were sandwiched and the back-pressure of the continuous flow was prevented. The schematic representation of the experimental setup of the column study is illustrated in Fig. 1. The U(VI) solution flowed downward at a flow rate of 0.15 $mL\,min^{-1}$ with use of a peristaltic pump. The samples of effluent were collected regularly at 3 mL volume fractions at different initial concentrations and solution pH values.

The effect of pH on the extent of sorption was conducted after adjusting the initial pH levels of the solutions to 3.0, 4.0, and 8.0 using 0.01 M, 0.1 M, and 1.0 M of HNO_3 and NH_3 solutions. In each experiment, 45.0 mL of U(VI) solution was circulated.

The experiments investigating the effect of initial concentration were performed at 5.0, 10.0, 50.0, and 100.0 $\mu g\,g^{-1}$ concentrations. In each study, 3.0 mL of U(VI) solution (adjusted to pH 4.0) was circulated.

In order to study the effect of repetitive loading, a series of experiments were carried out. In each experiment, 3 mL aliquots of fresh U(VI) solutions having initial concentrations of 50.0 and 100.0 $\mu g\,g^{-1}$ were loaded 14 times. The experiments were further continued using 100.0 $\mu g\,g^{-1}$ solution and the sorbent was exposed to 80 successive doses of 3.0 mL of solution.

For desorption experiments, the uranyl ion-loaded sorbent was treated with 3.0 mL aliquots of 0.5 M $NaHCO_3$, 0.5 M $C_6H_{17}N_3O_7$, and 0.1 M EDTA. Consecutive sorption–desorption cycles were

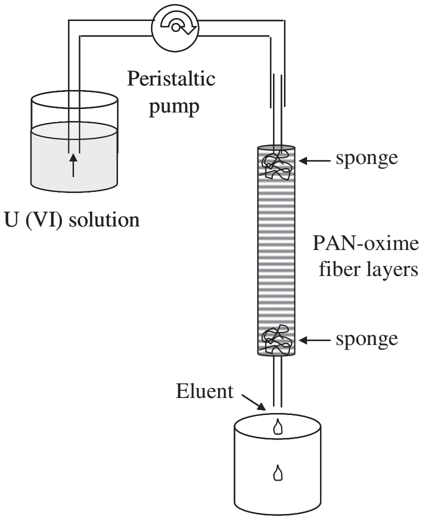


Fig. 1. Schematic representation of experimental setup of column experiment.

performed to study the reusability of the amidoximated PAN fiber sorbent. The eluted solutions were then analyzed for possible sorbed and released U(VI) ions.

3. Results and discussion

The main aim of this work was to design a sorbent material as well as an easily practicable column system for removal of contaminating uranium(VI) ions from aqueous solutions. We thus prepared submicron-diameter PAN fibers using the electrospinning method. The surface of the fibers was modified by amidoxime groups and the sorption ability of both the modified and unmodified fibers was studied.

3.1. Fabrication of PAN fibers

PAN was synthesized through free radical bulk polymerization at 60 °C using BPO as an initiator. Fig. S1 in Appendix A shows the NMR spectra of acrylonitrile and polyacrylonitrile. The number average and viscosity molecular weights are 14 and 180 kg mol^{-1}, respectively. PAN fibers were obtained through electrospinning of PAN/DMF solution at different concentrations. The concentration was fixed to 4 wt% in terms of solid content. A series of trials were carried out to obtain bead-free and uniform morphology at different potential differences and flow rates. The electrospinning process (the fiber fabrication) was optimized at a potential difference of 3 kV cm^{-1} and a flow rate of 2 mL h^{-1}.

3.2. Surface treatment of PAN fibers

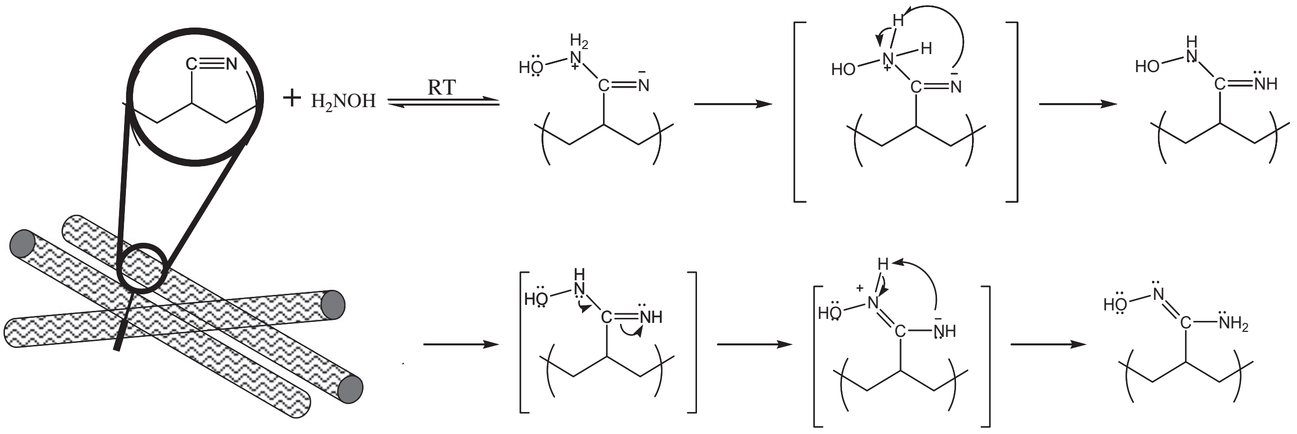
The surface modification of PAN fibers was performed by a wet chemical process. Scheme 1 shows the proposed reaction mechanism of hydroxylamine hydrochloride with the PAN nitrile group in a neutralized medium. The nitrile groups on the surface of PAN fibers react with H_2NOH at room temperature. The hydroxylamine undergoes nucleophilic addition to the fibers' surface and a subsequent arrangement to carboximidamide. Eventually, the surface of the fibers is functionalized for chelating uranyl cations. The conversion of the PAN nitrile group into an amidoxime group (C_n) was estimated using the following equation [31]:

$$C_n = \frac{W_1 - W_0}{W_0} \times \frac{M_0}{M_1} \times 100 \qquad (2)$$

Here, W_0 and W_1 are the weights of the PAN nanofiber mat before and after the amidoximation reaction, respectively. M_1 is the molecular weight of hydroxylamine (33 g mol^{-1}) and M_0 is the molecular weight of the acrylonitrile repeat unit (53 g mol^{-1}). The conversion of the PAN nitrile group into an amidoxime group was calculated as 30%. The resulting fibers were soft and light yellow, and this observation is compatible with previously reported results [15].

Fig. 2 shows the FT-IR spectra of PAN fiber and amidoximated PAN fiber, as well as the fiber after sorption of uranyl ions. A characteristic band of nitrile groups at 2260 cm^{-1} is present on the surface of all types of fibers. In the FT-IR spectrum of amidoximated PAN fibers, there are additional bands arising from the newly formed $H_2N{-}C{=}N{-}OH$ groups that support the successful surface modification. The reaction of hydroxylamine with nitrile groups leads to the formation of C═N groups characterized by the band at 1665 cm^{-1}. The broad band at 3000–3700 cm^{-1} can be attributed to H-bondings of NH_2 and O—H in the amidoxime structure (panel a). Upon the sorption of UO_2^{2+} ions, a shift was observed in the stretching band of C—N from 1218 cm^{-1} to 1248 cm^{-1} (panel b). The implication of this shift for the sorption mechanism is discussed in the last section.

Fig. 3 presents SEM micrographs and diameter distributions of PAN, amidoxime-modified PAN, and the modified fibers after uranyl sorption. Panel a of Fig. 3 shows PAN fibers prepared from 4 wt% PAN/DMF solution. The AFD was 122 ± 39 nm. The fibers appear to possess a homogeneous morphology with some surface roughness. Upon the amidoximation process, the AFD was slightly larger (127 ± 24 nm) than that of untreated PAN fibers (panel b). The sorption of uranyl ions by the amidoximated PAN fibers



Scheme 1. The conversion of nitrile groups to amidoxime groups in PAN fiber.

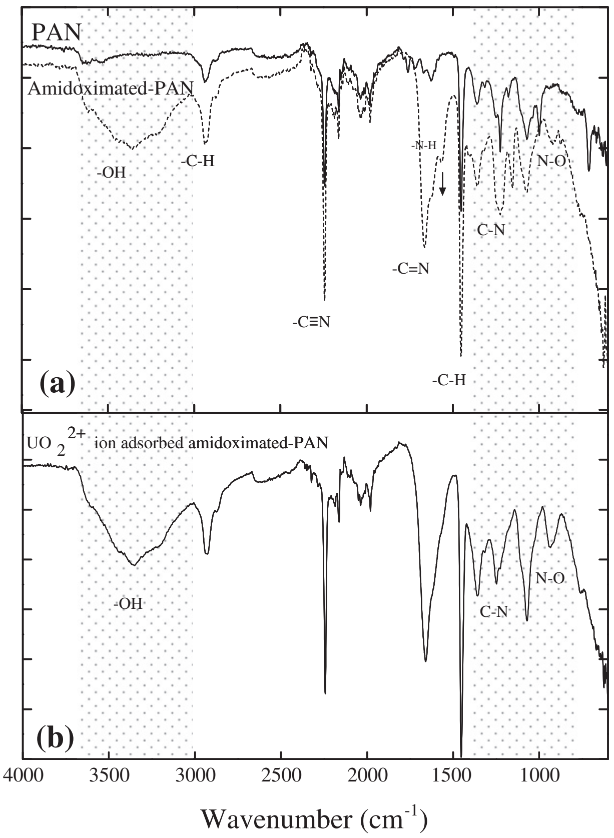


Fig. 2. FT-IR spectra of (a) PAN and amidoximated PAN fibers and (b) uranyl ion-adsorbed amidoximated PAN fibers.

seemed to render the fiber thicker and undulatory, as the AFD for the fibers increased to 132 ± 26 nm (panel c). No serious deterioration of the surface texture or roughness was observed after the sorption process, and the morphology and the integrity of the fibers were preserved. The elemental composition of amidoximated PAN fiber after uranyl ion sorption was elucidated using EDX analysis. Fig. 4 shows a typical EDX spectrum of uranyl ion-loaded fiber exposed to an initial concentration of 100 mg L^{-1}. A high U(VI) initial concentration was selected due to the detection limit of EDX. The quantification is given in Table 2. C, N, and O signals originated from the polyacrylonitrile and the presence of a uranium signal indicated that uranium was fixed on the surface of the amidoximated PAN fiber. The atomic percentage of *U* on the fiber surface was within the range of 0.50–1.09.

3.3. Sorption studies

The sorption capability of amidoxime-modified PAN fibers was compared with that of unmodified PAN fibers. The unmodified PAN fibers exhibited 19% sorption; on the other hand, amidoxime-modified PAN fibers showed nearly 4 times higher sorption capacity (81%). It is worth noting that the sponge that was used in the experiments has no contribution to uranyl sorption. The surface modification also transformed the hydrophobic nitrile groups into hydrophilic amidoxime groups, and the sorption of uranyl ions increased due to the chelating ability of the amidoxime groups [3,14,15].

3.3.1. Effect of pH

The initial pH value of the solution is a significant parameter in uranium(VI) sorption. Fig. 5 shows the speciation diagram of U(VI) as a function of pH (panel a) and the extent of sorption of U(VI) ions on amidoximated PAN fiber at different pH values (panel b). The percent U(VI) uptake increased as pH levels increased from 3.0 to 4.0. The amidoximated PAN fiber sorbent seemed to demonstrate maximum sorption at pH 4.0. At this pH, UO_2^{2+} ion is the main species (approximately 85% of the U(VI)) among other chemical forms. Under lower pH values, uranium is still present in the form of free UO_2^{2+} ions; however, competitive sorption with protons occurs and ion-exchange interactions are favored [6,7]. Protonation can occur on the imino group of amidoxime (p*K*a 5.95) [32], leading to a decrease in the chelating ability. For solutions adjusted at pH levels above 4.0, hydrated uranyl cations like $UO_2(OH)^+$, $[(UO_2)_3(OH)_5]^+$, $UO_2(OH)_2$, $[UO_2(OH)_3]^-$, and $[UO_2(OH)_4]^{2-}$ seem to be dominant according to the speciation analysis. In high pH media, carbonate might also contribute as ligands in solutions open to the atmosphere. The change in the chemical form in terms of charge and number of hydroxyl ligands associated with possible steric limitations might be expected to decrease the extent of the fixation of U(VI) at higher pH values. The major species present in solution at pH 8.0 is the neutral uranyl cation ($UO_2(OH)_2$), which is less liable to complexation than the positively charged U(VI) species and is expected to result in a lower extent of sorption.

3.3.2. Effect of initial concentration

The effect of initial concentration on the extent of removal of uranyl ions by amidoximated PAN fiber was investigated. Throughout these experiments, a fixed amount of sorbent (25.0 mg) was employed, and the initial concentration of the U(VI) solutions varied in the range of 5–100 μg L^{-1} at a fixed pH of 4.0. Fig. 6 displays uranyl ion sorption as a function of initial concentration. The amount of adsorbed uranyl ions increased with the increase of the initial uranyl ion concentration, and at an initial uranyl concentration of 100 μg L^{-1}, the sorption approached the saturation plateau. The observed behavior is probably due to the decrease in the hydration effects of water, the increase of the entropy effects of ions in solution, and, consequently, a greater mobility of the uranyl ions as concentration is increased. In addition, when more U(VI) ions are present in the solution, a higher fraction of available active sites takes part in the sorption process [33]. This could be attributed to the associated limitation in the number of water molecules available for hydration of the exposed hydrophilic groups at the fiber surface.

3.3.3. Repetitive usability

To test the repetitive usability of the amidoximated PAN fiber sorbent, 3 mL portions of fresh U(VI) solution at the initial concentrations of 100 μg L^{-1} and 50 μg L^{-1} were exposed to fiber samples for 14 successive trials. The results are presented in Fig. 7. The amidoximated PAN fiber sorbent seems to be effective in removal of aqueous U(VI) ions even after 14 consecutive uses. In the initial trials, more uranyl ions appear to be removed at a higher initial concentration, which is in line with the results above. Nonetheless, at the initial U(VI) concentration of 100 μg L^{-1}, the percent sorption seems to decrease gradually with more applications of the fiber. It is worth noting that the repetitive loading experiments continued for 80 trials before saturation of the sorbent was reached (see Fig. S2 in Appendix A). The results showed that more than 85% of the uranyl ions were sorbed after one use, and although sorption ability toward uranyl ions decreased steadily, 46% removal of uranyl ions could still be achieved even at the 80th trial of the same sorbent in the column. The most prominent consequence of this experiment is the high capacity of the sorbent under continuous flow.

The cumulative fixation of uranyl ions after dozens of trials is interesting. The first conclusion to be drawn from this behavior

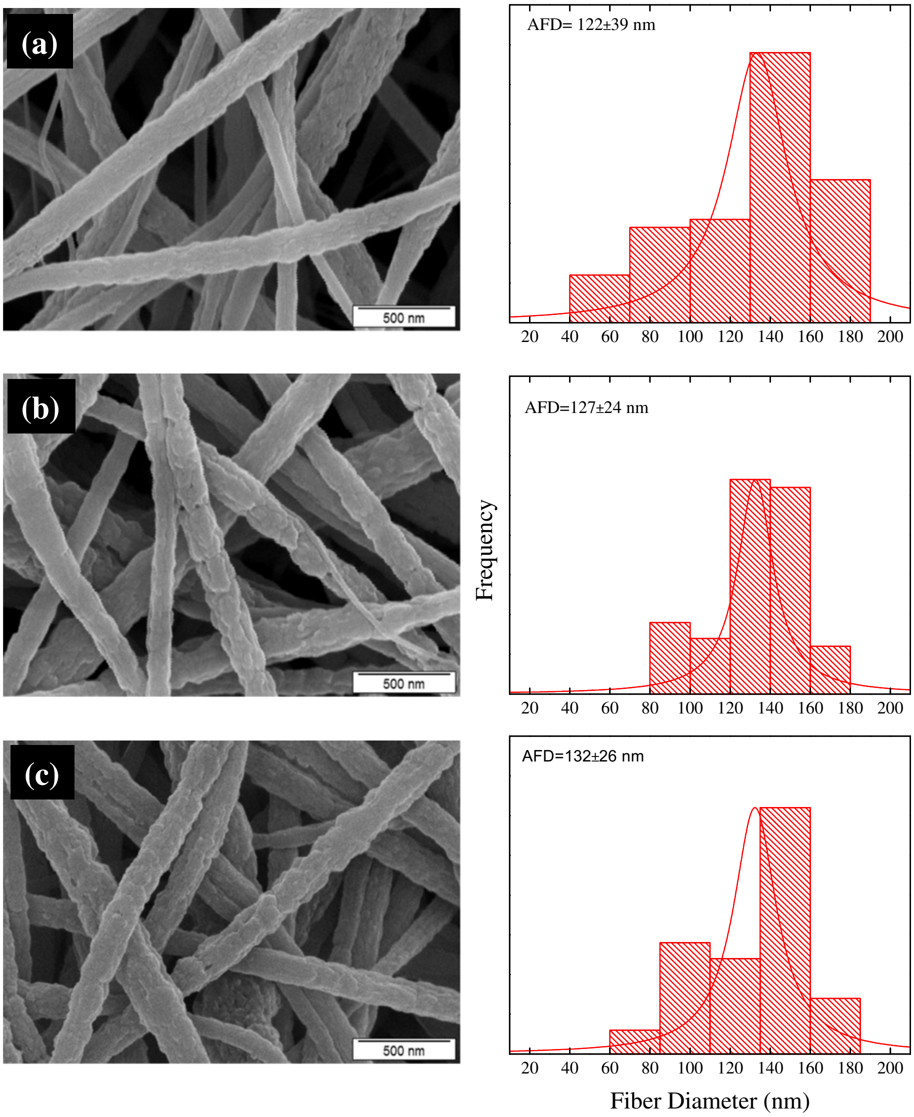


Fig. 3. Scanning electron micrographs and corresponding fiber diameter distributions of (a) PAN fibers, (b) amidoximated PAN fibers, and (c) amidoximated PAN fibers after uranyl ion sorption.

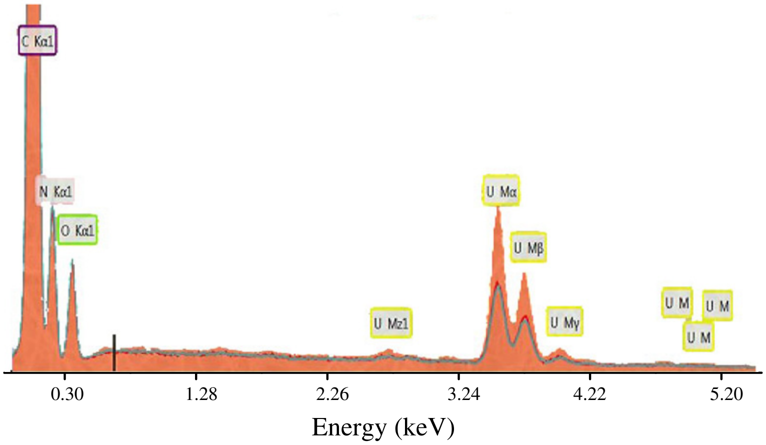


Fig. 4. EDX spectrum of amidoximated PAN fiber mat after uranyl ion sorption at pH 4.

is that the fibers possess a high density of sorption sites in comparison with the employed concentration of uranyl ions. The second conclusion relates to the apparent effectiveness of the hydration forces in solution. For ions with a high charge such as U(VI), the

Table 2
The weight percentages and atomic percentages (in brackets) of C, N, O, and U in amidoximated-PAN fiber after column sorption.

Element	C	N	O	U
Sampling area 1	58.69 (67.83)	26.19 (25.95)	6.60 (5.72)	8.52 (0.50)
Sampling area 2	59.62 (68.14)	26.21 (25.69)	6.70 (5.75)	7.48 (0.43)
Sampling area 3	55.62 (70.27)	20.39 (22.09)	6.87 (6.55)	17.06 (1.09)

chemical potential is largely affected by the hydration forces in solution, especially in dilute solutions. As long as the chemical potential of the adsorbate on the surface is less than its chemical potential in solution, sorption proceeds spontaneously. When the ionic concentration is high, the ions become more mobile (i.e. their chemical potential increases) due to ionic repulsions, and as a result they can reach the surface and compete for sorption sites more readily. This seems to be achieved when fresh solution is fed into the column.

3.3.4. Desorption tests

The uranyl ion-loaded amidoximated PAN fiber sorbents were subsequently treated with different desorbing eluents. $NaHCO_3$, EDTA, and ammonium citrate were employed as chelating agents for the release of uranyl ions and the regeneration of the sorbent. Fig. 8 shows the elution curves, which present almost similar behavior in each case. Most of the U(VI) ions were desorbed within the first 3.0 mL cycle, and the amounts of desorbed metal ions were almost unchanged. The desorption percentages of U(VI) were 80% for 0.5 M $NaHCO_3$, 45% for 0.5 M ammonium citrate, and 34% for 0.1 M EDTA. Therefore, $NaHCO_3$ was selected as the desorbing eluent due to its relatively higher desorption yield. Uranium forms negatively charged or neutral carbonate complexes, and the adsorbed uranyl could be eluted from the sorbent using $NaHCO_3$ through the addition of carbonate ions as ligands to uranyl complexes.

Fig. 9 displays the reusability of the fiber sorbent in five sorption/desorption cycles using 0.5 M $NaHCO_3$. After five cycles, the efficiency of sorption decreased from 86.0% to 59.5% while the recovery of U(VI) decreased from 80.0% to 55.0%. Therefore, $NaHCO_3$ can regenerate the sorbent effectively, thus facilitating the reuse of this new fibrous material.

3.3.5. Brief comments on sorption mechanism

As mentioned previously, the amidoximated PAN fiber sorbent demonstrated maximum sorption at pH 4.0. The speciation analysis discussed previously suggests that, at this pH, approximately 85% of the U(VI) exists in UO_2^{2+} chemical forms. From the sorbent side, as shown above based on FT-IR characterization, the surface of the functionalized fiber is dominated by hydroxyl, amine, and nitrile groups. In acidic media these groups would normally be expected to undergo protonation. Thus, at pH 4.0, the chemical forms of the sorbent surface and the sorbate ions do not support an electrostatic hypothesis of sorption. The fixation of the UO_2^{2+} ions might therefore be expected to proceed via formation of surface complexes that possess a coordinative nature, with the lone pairs on O and N atoms in the surface groups playing the main role in interaction with the uranyl species.

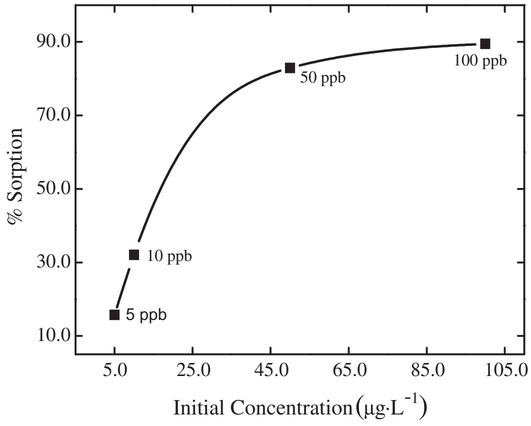


Fig. 6. Uranyl ion sorption at various initial concentrations. Reaction conditions: 3.0 mL sample volume, 0.15 mL min^{-1} flow rate, 25.0 mg sorbent, pH 4.0.

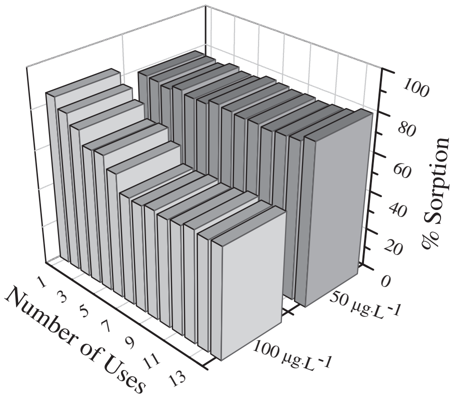


Fig. 7. Variation of percent sorption of uranyl ion with the number of repetitive usages of the same fiber sorbent at the initial U(VI) concentrations of 50 $\mu g\ L^{-1}$ and 100 $\mu g\ L^{-1}$. Reaction conditions: 3.0 mL sample volume, 0.15 $mL \cdot min^{-1}$ flow rate, 25.0 mg sorbent, pH 4.0.

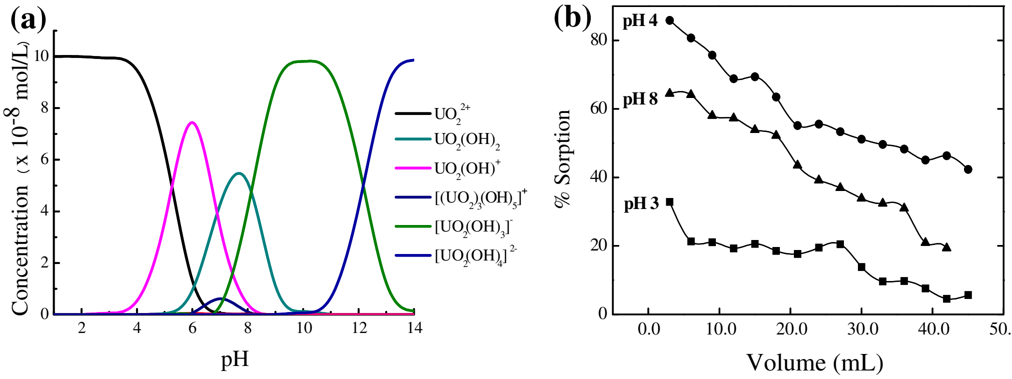


Fig. 5. (a) Speciation diagram of U(VI) and (b) microcolumn study of U(VI) at different pH values. Reaction conditions: initial U(VI) concentration of 100 $\mu g\ L^{-1}$, 0.15 mL min^{-1} flow rate, 25.0 mg sorbent.

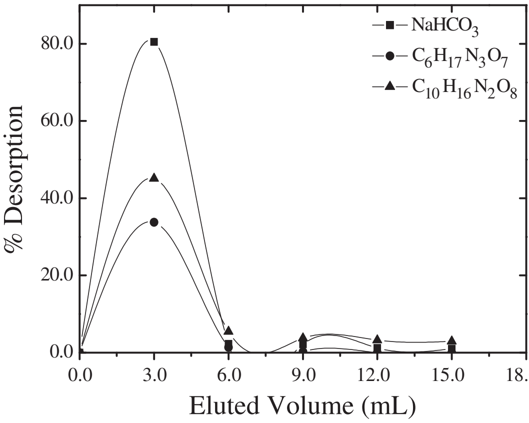


Fig. 8. Uranyl ion desorption as a function of eluted volume. Reaction conditions: initial U(VI) concentration of 100 μg L^{-1}, 0.15 mL·min^{-1} flow rate, 25.0 mg sorbent.

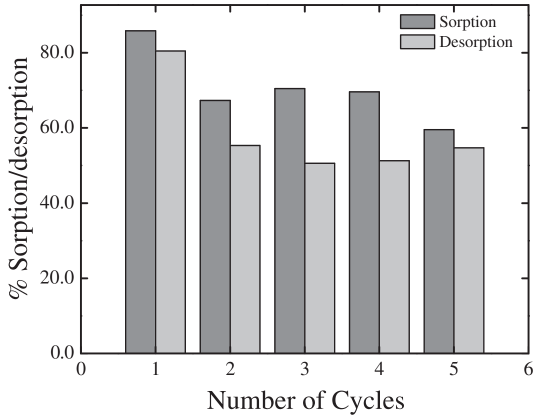
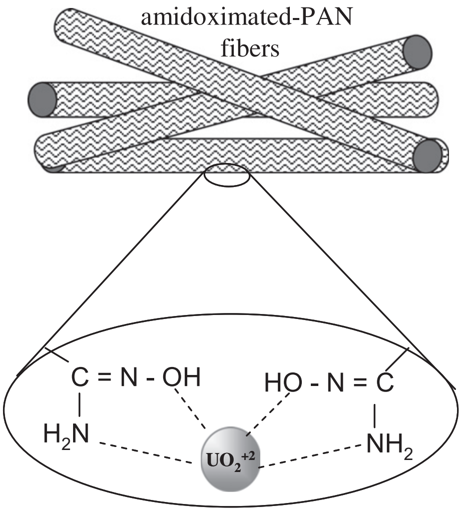


Fig. 9. Consecutive sorption/desorption cycles of amidoximated PAN fiber for 100 μg L^{-1} U(VI) solution using 0.5 M $NaHCO_3$ as the desorbing agent.

The interaction of UO_2^{2+} ions with amidoximated PAN fibers is reflected in a blue shift in the stretching band of C—N from 1218 cm^{-1} to 1248 cm^{-1}, as mentioned above in Section 3.2. This result is compatible with previous works. For example, Pekel and Guven [3] observed a similar type of shift at the C—N stretching band for amidoximated poly(acrylonitrile/*N*-vinylimidazole) complexing sorbent, which was taken as proof of the interaction of UO_2^{2+} ions with the vinylimidazole ring. It is proposed that the sorption of uranyl oxo-cations with amidoximated PAN fibers is achieved by virtue of the strong chelating ability of the amidoxime groups, which act as bidentate ligands. Based on the above discussion, a tentative binding mechanism is suggested in Scheme 2. This is in line with previously suggested chelation mechanisms. For example, Hirotsu et al. [34] reported that the sorption of uranium originated from ligand exchange between carbonate ions and amidoxime groups accompanied by deprotonation of the amidoxime groups. Similarly, Pekel et al. [35] proposed that the binding of the amidoxime group to UO_2^{2+} ions proceeded by replacement of protons by UO_2^{2+} ions.



Scheme 2. Speculative binding mechanism.

More spectroscopic and structural investigations are required to make more precise and detailed comments on the sorption mechanism.

4. Conclusions

This study demonstrated that amidoximated PAN fibers produced by electrospinning are an effective sorbent for the removal of U(VI) from aqueous media via column-type operations. In the fabrication process, PAN fibers were first produced. A wet chemical process was then applied for surface modification of PAN fibers. The nitrile groups on the PAN fibers were converted to amidoxime groups using hydroxylamine hydrochloride in a neutralized medium. The surface-functionalized PAN fiber network provided higher metal-binding ability. The extent of U(VI) sorption on the fibers was found to depend on the pH of the medium and the initial concentration of the salt. The optimum pH for U(VI) sorption by amidoximated PAN fibers was found to be 4.0, at which UO_2^{2+} ion is the main species. The adsorbed amount of U(VI) ions increased with an increase in initial U(VI) concentration. The ease and applicability of the process that we propose in filtration can offer a convenient method for the removal of U(VI) ions via a column system. Moreover, the amidoximated PAN fibrous filter material used in this study has high mechanical resistance, sorption ability, and efficient reusability, which are desired for filtration applications. Based on our preliminary results, this material is also capable of the uptake of various undesirable ions, such as Fe(III), Cu(II), and Cd(II), from aqueous solutions. A detailed study dealing with isotherms and sorption mechanisms is underway.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.09.114.

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