



Preparation of aminated-polyacrylonitrile nanofiber membranes for the adsorption of metal ions: Comparison with microfibers

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ABSTRACT

Polyacrylonitrile nanofibers (PAN-nFs) were produced using the electrospinning method. Subsequently, the electrospun fibers were modified by diethylenetriamine to produce aminated polyacrylonitrile (APAN) nanofibers. Finally, the adsorbability of copper ions on the surface of the nanofibers was examined in an aqueous solution. Attenuated total internal reflection (ATR) analysis confirmed the surface amination of the produced PAN-nFs. The grafting yield was calculated by the gravimetric method. The optimum condition was determined to yield the maximum grafting of amine groups to PAN with no losses in sample flexibility. Atomic absorption spectroscopy (AAS) was used to measure the copper ion concentration in the solution. Results indicate that the adsorption process in nanofibers is three times faster in comparison with microfibers. Moreover, the pH effect was studied based on the adsorption behavior of copper ions on the APAN nanofibers. In addition, thermodynamic parameters were calculated, revealing that the process was endothermic and demonstrating that randomness increased at the solid–solution interface during the process. The obtained enthalpy value indicates that the chelation of copper ions among the aminated polyacrylonitrile can be regarded as a chemical adsorption process. The adsorption data fit well with the Langmuir isotherm. The saturation adsorption capacity obtained from the Langmuir model for Cu(II) ions was 116.522 mg/g which is five times more than the reported value for APAN microfibers [S. Deng, R. Bai, J.P. Chen, Aminated polyacrylonitrile fibers for lead and copper removal, *Langmuir*, 19 (2003)5058–5064]. Analysis using atomic force microscopy (AFM) showed that the surface roughness increased upon adsorption of the metal ion. Scanning electron microscopy (SEM) examination demonstrated that there were no cracks or sign of degradation on the surface after amination.

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1. Introduction

In recent years, industrial development and the advent of new technologies have resulted in a significant increase in the amount of heavy metal ions in wastewater. As a result, many environmental threats are now causing human health concerns. These harmful materials, such as metal ions, should be removed from the environment. Thus, the removal of heavy metals has become a primary goal for obtaining clean water resources and non-threatening wastewater. Many methods have been introduced for the removal of heavy metals such as solvent extraction, membrane separation, electrochemical operation, adsorption, ion exchange, etc. [1–4]. Chelation, adsorption, and ion exchange are the most common and widely studied methods for the removal of metal ions from solutions. Activated carbon, oxide minerals, polymer materials, resins, and biosorbents have been applied as adsorbents to remove metal ions. They have also been utilized in the enrichment recovery of

precious metals from aqueous solutions [2,4–10]. The adsorption efficiency of these materials depends on the functional groups on the adsorbent surface [5]. Carboxyl, tetrazine, sulfonic, amino, and phosphoric groups have been studied as surface functional groups. Amino groups, in particular, are highly active in the formation of strong complexes with metal ions because they contain nitrogen atoms [2,4,6]. These complexes are formed via the chelation process [3,4].

In 1934, electrical forces were first used to produce polymeric filaments [11]. Consequently, this method, called electrospinning, was utilized to spin polymeric fibers. The typical electrospinning setup includes a high voltage power supply, a polymer solution injector (syringe), and a metal collector. A high voltage is applied to the solution, resulting in deformation the drop of solution (conic form) at the syringe tip. Above a critical voltage, the electrical force at the surface of the drop overcomes the solution surface tension. In this process the polymer solution is stretched and elongated into fibers (or nanofibers) and is collected as a non-woven mat [7,12–15]. The produced nanofibers have interesting properties, such as a high porosity, small interfibrous pore sizes, high gas permeability, and most importantly a large surface area per unit

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mass, in comparison to conventional microfibers. As a result, electrospinning has been given a great deal of attention in the past decade. Many nanofibers are now studied for their applications toward nanocomposites [16], tissue engineering [17,18], sensors [19], protective clothing and fine filtration [20–23], and adsorptive membranes [7,24,25].

The presence of a large specific surface area is one of the most effective factors in adsorptive membranes [7,25]. Thus, spun polymeric nanofibers could be used as adsorptive membranes [7,26].

Polyacrylonitrile (PAN), a common and inexpensive commercial product, has been studied for the production of nanofibers via electrospinning [8]. This adsorbent, which is fabricated using PAN fibers, has been recognized as a highly efficient materials for the removal and recovery of metal ions, which is especially true for dilute solutions because of the high adsorption capacity, fast adsorption equilibrium, high recycling rate, and low cost. Furthermore, PAN fibers have desirable chemical resistance, thermal stability, low flammability, and good mechanical properties [2–4,6–8,27–28].

Deng et al. [6] prepared PAN microfibers that are modified by amine groups to remove of Cu(II) and Pb(II) ions from water. Saeed et al. [7] studied the use of amidoximated PAN nanofibers for ion adsorption. Therefore, the preparation of aminated PAN nanofiber membranes could be applicable for the adsorption of metal ions.

In the present work, PAN nanofibers were produced using the electrospinning technique. Subsequently, these nanofibers were modified with diethylenetriamine. Analysis of the resulting attenuated total internal reflection (ATR) spectra confirmed the amination of the PAN nanofibers surfaces. The grafting yield was calculated by gravimetric methods. The optimum condition was determined to yield the maximum grafting of amine groups to PAN with no reduction in sample flexibility. Subsequently, the adsorptive membrane was applied to adsorb the copper ions from an aqueous solution. Atomic absorption spectroscopy was used to measure the copper ion concentration in the solution. Thermodynamic parameters were calculated. The surface morphology of these fibers was studied using a scanning electron microscope (SEM) and an atomic force microscope (AFM). The results revealed a five times higher efficiency for the prepared nanofiber membranes over microfibers.

2. Experimental

2.1. Chemicals

Polyacrylonitrile fiber made by copolymers (93.7% acrylonitrile and 6.3% methylacrylate with $M_v = 70,000$ g/mol) was purchased from Isfahan Polyacryl Inc. (Iran). The average diameter of the PAN fibers was 23 μm . Dimethylformamide (DMF), diethylenetriamine (DETA), sodium carbonate (Na_2CO_3), and copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were all supplied by Merck. Distilled water was used for all preparation and washing stages.

2.2. Apparatus and instrumentation

An attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer, Equinox 55, from Bruker (Germany), was used to analyze the chemical and/or physical interactions over the wave number range of 400–4000 cm^{-1} . The surface morphologies of the Au-coated PAN and aminated PAN nanofibers were studied using an SEM, VEGA-II form Tescan (United States). Changes in the surface morphology both before and after copper adsorption were analyzed using an AFM (Dualscope/Rasterscope C26, DME, Denmark). A model 939 Unicam atomic absorption spectrophotometer was

used to determine the copper ion concentration. The pH levels were measured with a pH-meter from Hach Co. (United States).

2.3. Electrospinning of PAN nanofibers

PAN/DMF solutions, with concentrations of 10 and 12 wt%, were prepared by stirring at room temperature for 24–30 h to obtain a homogeneous solution. The electrospinning setup consisted of a 1-ml glass syringe with a needle tip (0.51 mm diameter), a syringe pump (New Era Pump System, NE1000), a ground electrode (aluminum sheet), and a high voltage power supply (Gamma High Voltage Research, RR60) which could generate positive DC voltages up to 60 kV. The applied voltage between the tip of needle and collector was 20 kV and the distance from the tip to the collector was 15 cm. The feeding rate of the polymer solution was 200 $\mu\text{L}/\text{h}$. The electrospinning process was carried out under ambient conditions, and the PAN-nanofibers (PAN-nFs) were collected on aluminum foil in the form of non-woven mat. The electrospinning conditions were selected based upon previous research conducted in our group [15].

2.4. Preparation of the adsorptive membrane

The PAN-nFs were immersed in a mixture of diethylenetriamine (31.515 g), sodium carbonate (catalyst; 1 g), and distilled water (100 ml) in a 250-ml beaker. The reaction was carried out at three different values for each of the following parameters: time, temperature, and fiber diameter. Afterwards, the fibers were rinsed with distilled water until a pH level of 7 was reached. These were subsequently dried at 80 $^\circ\text{C}$ in an oven. In total, 17 batches were treated using the same method. The repeatability of this method was characterized by repeating the test three times [29]. Table 1 gives the reaction conditions and the conversion percents, as well as other properties.

The degree of nitrile group conversion (to an amine group) was calculated by gravimetry. Therefore, the weight of the membrane was measured before and after the modification process. The conversion percent of the amine group on PAN was calculated as follows [17]:

$$\text{Graft yield}(\%) = \left(\frac{w_g - w_0}{w_0} \right) \times \frac{M_0}{M_1} \times 100 \quad (1)$$

where w_0 and w_g denote the weight of the original and grafted PAN nanofibers in grams, respectively, M_1 is the molecular weight of diethylenetriamine ($w = 103$ g/mol), and M_0 is the molecular weight of the acrylonitrile monomer ($w = 53$ g/mol).

2.5. Adsorption equilibrium experiments

All adsorption experiments were performed batch-wise. In adsorption equilibrium experiments, the adsorption equilibrium time and adsorption capacity of the aminated PAN nanofibers and microfibers was determined. First, the adsorption equilibrium time (t_e) for the functionalized nanofibers and microfibers were determined. This step was carried out via AAS analysis by measuring the copper ion concentrations over time. The initial copper ion concentration was 590 ppm. Sample concentrations were measured at 10, 20, 30, 60, 120, 180, 240 and 1440 min. Then, samples of aminated PAN nanofibers and microfibers (with the same total areas) were added to 100 ml of a copper sulfate solution that was at a concentration of 384 ppm. The solution was stirred at 120 rpm at 25 $^\circ\text{C}$. At the adsorption equilibrium time (t_e), the copper ion concentration was measured using AAS. The amount of adsorbed copper (mg/g) was calculated as follows [12]:

$$q(\text{mg/g}) = \frac{(C_0 - C_f)V}{M} \quad (2)$$

Table 1
Reaction conditions and appearance properties of aminated PAN nanofiber mats.

Experiment no.	Fiber diameter (nm)	Time (min)	Temperature (K)	Conversion (%)	Appearance properties
1		60	358	8	Soft-light yellow
2		60	368	28	Soft-pale orange
3		90	363	39.5	Rigid-pale orange
4		120	358	41	Rigid-pale orange
5		120	368	60	Brittle-white
6	110	90	358	30	Soft-pale orange
7		120	368	44	Rigid-pale orange
8		60	363	20	Soft-pale orange
9		120	363	42	Rigid-pale orange
10		90	363	34	Rigid-pale orange
11	205	90	363	33.5	Rigid-pale orange
12		90	363	35	Rigid-pale orange
13		60	358	0.05	Soft-light yellow
14		60	368	0.6	Soft-light yellow
15		120	358	0.35	Soft-light yellow
16		120	368	6	Soft-light yellow
17		90	363	0.5	Soft-light yellow
23,000					

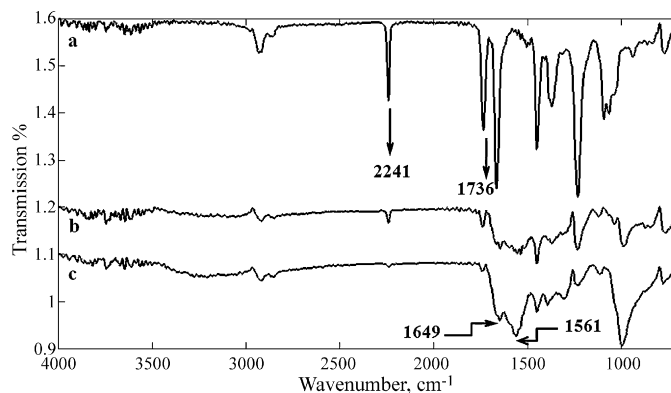


Fig. 1. ATR-FTIR spectra of the APAN nanofiber mats at different average diameters: (a) raw PAN, (b) 205 nm, and (c) 110 nm.

group ($-\text{CO}-\text{NH}_2$; Scheme 1) and then reacted with diethylenetriamine. Additionally, the $\text{C}=\text{O}$ peak of an ester at 1732 cm^{-1} was reduced due to chemical reactions of the amine groups with the methylacrylate comonomer [7].

The ATR spectra confirmed the amination of PAN nanofibers. The corresponding chemical mechanism, during amination with different conversions, is proposed as shown in Scheme 1. The nitrile group peak was found to disappear, as shown in Fig. 1(c). Hence, conversion was almost complete. Therefore, a high-conversion mechanism is proposed, as shown in Scheme 1, for when the acrylate group ($-\text{OCH}_3$) leaves in the form of methanol. At the end of the reaction, the initial copolymer would be converted to a homopolymer if the conversion efficiency was 100%. The results show that the amine and amide groups of the APAN fibers reacted with the carbon of the carbonyl and nitrile groups.

3.2. Optimization of the amination conditions

Table 1 shows the results of the conversion for the conducted experiments and the appearance of modified membranes. At first, the nanofiber mats appeared to be quite flexible and white in color. However, their appearance changed during the course of the conversion process. Depending on the reaction condition, the color of the fibers was observed to change from white to light yellow and then to pale orange. The high conversion ($>45\%$) to a white fiber color may be due to the degradation of the nitrile group. This color change may be a result of the long heating time of this step, where temperatures reached higher than 353 K . With increasing degrees of nitrile group conversion, the nanofiber mats became fragile. A high conversion ($>45\%$) was found for this process, making the resulting mats less capable of adsorbing $\text{Cu}(\text{II})$ ions from solution. This observation is consistent with previous reported results [7,27].

During the grafting process, the nanofiber mats were also observed to contract in size. It is known that nanofibers are under severe drawing tension during the electrospinning process. Therefore, this contraction could be attributed to the relaxation of the drawn nanofibers. These types of polymers are known to be in a high-energy metastable state while in the wet heating process. The polymers ultimately relax to a lower energy state, and then the nanofibers contract [27].

The conversion of the nitrile group in PAN was increased with increasing reaction time and temperature, because an increase in temperature significantly accelerates the amination reaction of the PAN nanofibers, which may be attributed to the endothermic nature of the reaction. This increase was observed using thermodynamics calculations, which are presented in a subsequent section of this paper.

where q is the amount of adsorbed copper (mg/g), V is the solution volume (L), M is the amount of added adsorbent (g), and C_0 and C_f are the initial and final copper ion concentrations (mg/L), respectively. In the investigation of the effect of pH levels on metal adsorption, the initial copper ion concentration in the solutions was 590 ppm . The solution pH values were varied between 2 and 6.

3. Results and discussion

3.1. ATR-FTIR study of the amination process

In this study, ATR-FTIR spectroscopy was used to record chemical changes in the polymer structures of interest. Using this information, the surface modification mechanism of the amine group could be identified. The ATR-FTIR spectra of the raw and aminated PAN nanofiber mats at different average diameters are shown in Fig. 1. The PAN spectra (curve a) exhibited the absorption peaks of a stretching vibration at 2241 cm^{-1} ($\text{C}\equiv\text{N}$), 1736 cm^{-1} ($\text{C}=\text{O}$), and $1200\text{--}300\text{ cm}^{-1}$ ($\text{C}-\text{O}$), which suggests that the PAN was a copolymer of acrylonitrile and methylacrylate. A peak at 2241 cm^{-1} was observed in the ATR-FTIR spectra of the aminated PAN (APAN) fibers (curves b and c) and was related to the $\text{C}\equiv\text{N}$ group. This peak decreased in intensity when a new $\text{N}-\text{H}$ group was introduced to the surface of the PAN-nFs. At the same time, the peaks at 1561 and 1649 cm^{-1} were assigned to the bending vibration band of the amine $\text{N}-\text{H}$ group and the stretching vibration band of the amide $\text{C}=\text{O}$ group, respectively. This analysis was based on the obtained ATR results and other references [2,6]. Therefore, it is suggested that the nitrile group of the PAN was first hydrolyzed into an amide

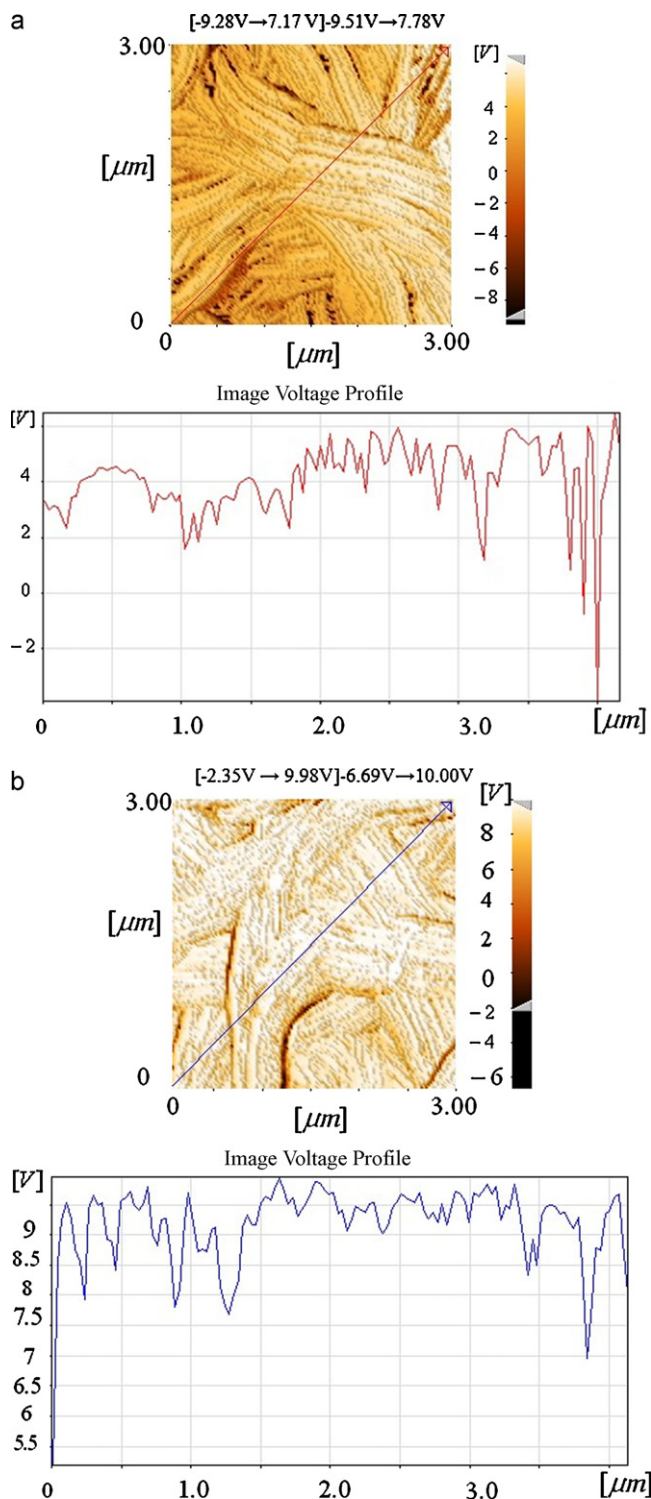


Fig. 3. AFM topography images and profiles (a) before Cu(II) adsorption and (b) after Cu(II) adsorption.

ther noticeable increase in copper ion adsorption. It has been shown that Cu^{2+} reaches maximum adsorption at pH levels between 5 and 6. This is due to the high H^+ concentration present at lower pH values. It is known that hydronium ions compete with metal ions during adsorption. Furthermore, adsorbed hydrogen ions repel metal ions. Moreover, at high pH levels (e.g., 7–12) the hydrolysis of Cu(II) ions in the form of $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, and $\text{Cu}(\text{OH})_3^-$ takes place [6,8]. Therefore the pH range was set between

5 and 6 for subsequent investigation of the adsorption of copper ions.

3.5.2. Effect of contact time

Fig. 6 shows the results of copper ion adsorption onto the APAN nanofibers (30% conversion) and microfibers (6% conversion) as a function of time (for 3 h). The amount of Cu(II) adsorption onto the APAN nanofiber mats increased rapidly in the first 20 min and then levelled off. However, for the microfibers the adsorption rate was three times slower. The adsorption process for the nanofibers was observed to be fast.

Equilibrium values for Cu(II) ion adsorption onto APAN nanofibers and microfibers were attained in 20 and 60 min at quantities of 102.12 and 22.78 mg/g, respectively. Therefore, the nanofibers exhibited a final adsorbed value that was over five times larger than for the microfibers. Furthermore, the nanofibers demonstrated an adsorption rate that was three times faster compared to the microfibers. Notably, the microfibers were functionalized using a longer time and higher temperature, which could be related to an increase in the number of adsorption sites for APAN because of its higher specific surface area [8]. Consequently, the smaller diameter of the nanofibers resulted in a higher adsorption capacity.

3.6. Adsorption isotherms

Fig. 7(a) presents the equilibrium adsorption amounts of Cu(II) ions onto APAN nanofiber mats after the equilibrium time (obtained from Fig. 6 at 20 min) as a function of equilibrium concentration. The adsorption of Cu(II) ions was determined to initially increase with increasing concentration and was then found to reach equilibrium. This initial increase could be related to the large number of chelating amine sites that were present on the APAN nanofibers, as well as the high specific surface area of the nanofibers. At equilibrium, an adsorption isotherm can be constructed as a relation of the adsorbate concentration at the surface and in the solution at a given constant temperature. Isotherm data should accurately fit into different isotherm models, to produce a suitable model for additional process studies [30]. The Langmuir and Freundlich isotherms were applied to the obtained results. These equations are as follows, respectively:

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (3)$$

$$Q_e = K C_e^{1/n} \quad (4)$$

where Q_m is the maximum metal uptake (mmol/g); b is the Langmuir constant, which is related to the binding energy (L/mmol); C_e is the equilibrium concentration (mmol/L); K and n are the Freundlich constants, which indicate adsorption capacity (mmol/g) $(\text{L/mmol})^n$, and adsorption intensity, respectively.

Eqs. (3) and (4) were used to fit the experimental adsorption equilibrium data for copper ions.

As shown in Fig. 7(a), the Langmuir model was able to describe the adsorption isotherm results of the APAN nanofiber mats for Cu(II) ions better than the Freundlich model. Based on these models, important parameters were calculated, as shown in Table 2.

According to the Langmuir model, adsorption takes place at specific homogeneous sites; once a sorbate occupies a reaction site, no further adsorption can occur at this site. Thus, the adsorption of copper ions takes place via the formation of a monolayer [10].

The reported value for the maximum adsorption of Cu(II) ions onto APAN microfibers is 0.495 mmol/g [6]. However, this value could not be fundamentally compared with the current study data because the experimental conditions for the functionalization step were significantly different in this study.

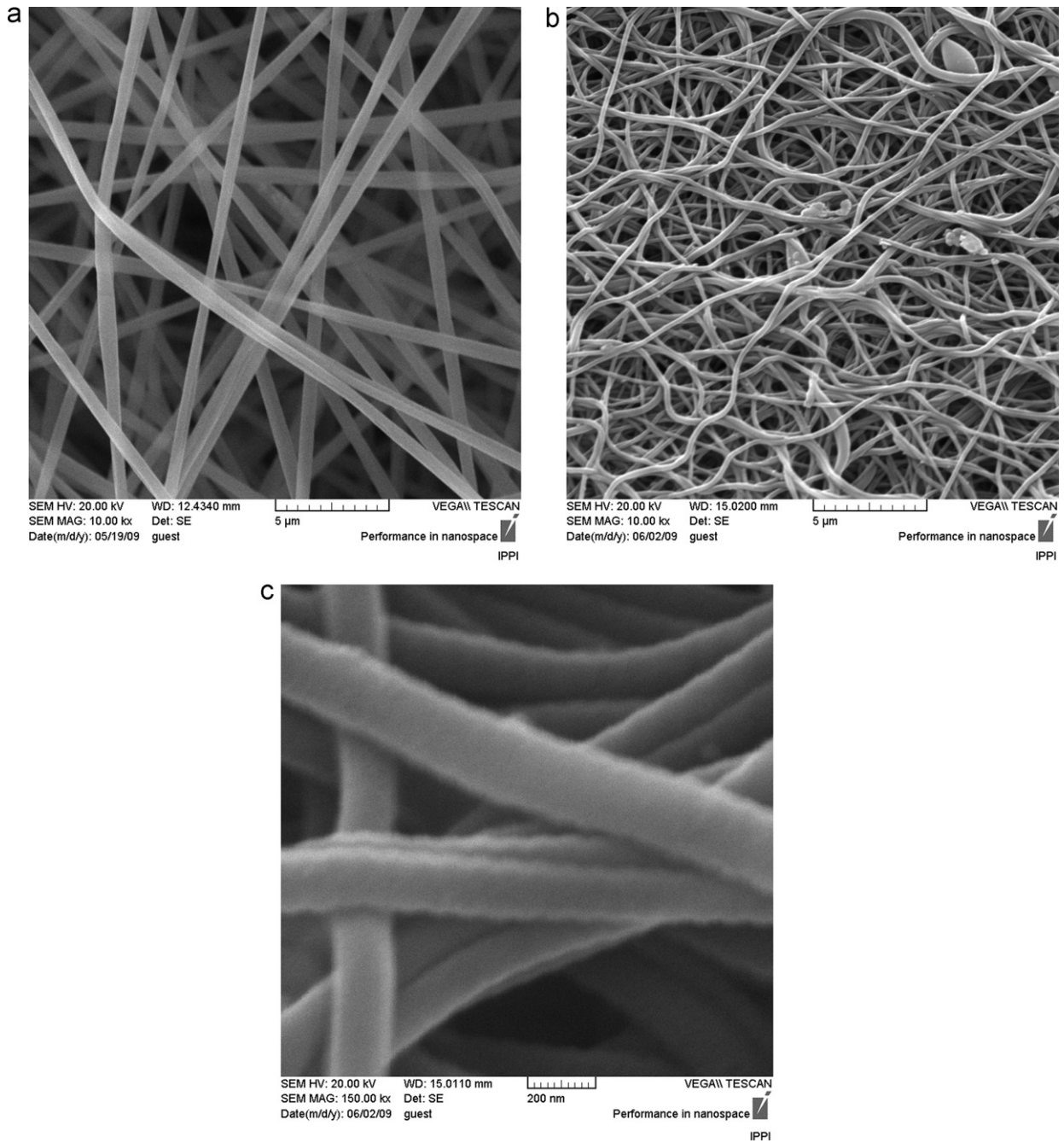


Fig. 4. SEM micrographs of (a) PAN nanofibers, (b) APAN nanofibers and (c) enlarged APAN nanofibers.

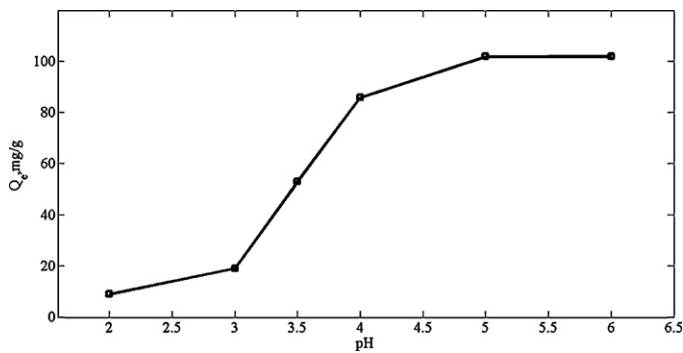


Fig. 5. Effect of solution pH on the adsorption of copper ions on the APAN nanofibers (30% conversion, $t = 1$ h, $C_0 = 590$ ppm).

Moreover, using the Langmuir parameters shown in Table 2, the dimensionless separation factor R_L could be calculated. This factor is a criterion of the tendency between sorbate and adsorbent [9].

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The R_L value is classified into categories including $R_L > 1$, $0 < R_L < 1$, and $R_L = 0$, suggesting that adsorption is unfavorable, favorable, and irreversible, respectively [31]. The R_L value decreased with increasing initial concentrations of Cu(II) ions, as shown in Fig. 8. This indicates that copper adsorption was more favorable at higher initial concentrations of Cu(II) ions [5,9].

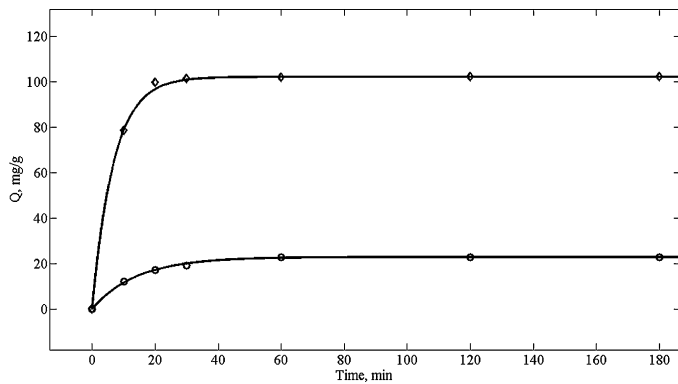


Fig. 6. Adsorption of copper ions on aminated (○) PAN microfibers (6% conversion) and (◇) PAN nanofibers (30% conversion).

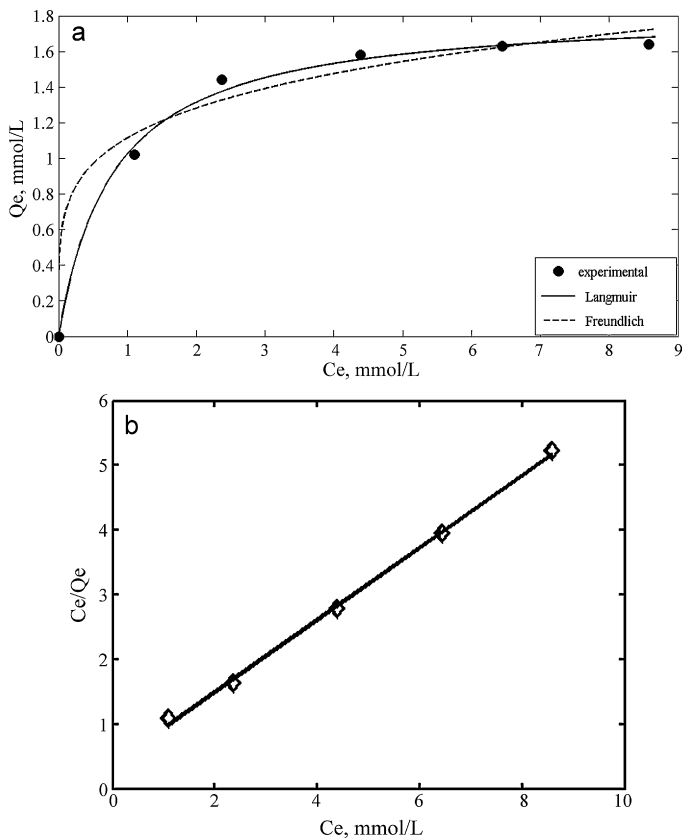


Fig. 7. Adsorption isotherms of copper ions on the (a) APAN-nF (30% conversion) fitting models and (b) Langmuir model at 298 K.

3.7. Thermodynamic parameters

The adsorption experiments were performed at temperatures of 298, 313, and 328 K. The adsorption dependency on temperature was calculated from the linearized Van't Hoff equation, Eq. (7) [30]. The Gibbs free energy change (ΔG°) is the main criterion for a spontaneous process. This value was calculated using the equilibrium constant value (b) obtained from the Langmuir model using

Table 2
Langmuir and Freundlich constants for Cu(II) adsorption on APAN nanofiber mats.

Model	Parameter	R^2
Langmuir	$Q_m = 1.835, b = 1.264$	0.9958
Freundlich	$K_f = 1.115, n = 4.9455$	0.8561

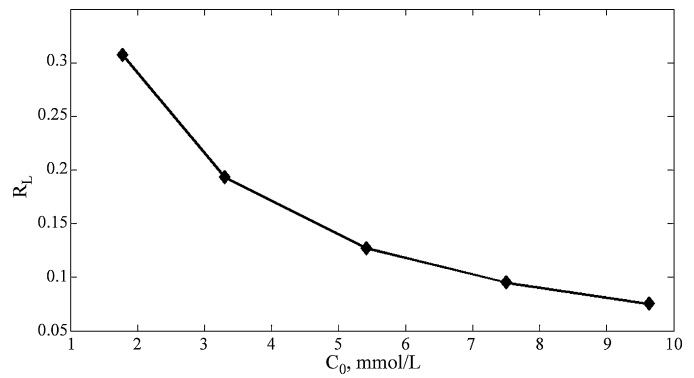


Fig. 8. R_L for the adsorption of Cu(II) ions.

Table 3

ΔG° values at different temperatures.

Temperature (K)	$\ln b$	ΔG° (kJ/mol)
298	0.234	-0.579
313	1.28	-3.33
328	1.44	-3.926

Eq. (6):

$$\Delta G^\circ = -RT \ln b \quad (6)$$

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). As presented in Table 3, all the Gibbs free energy change values were negative. This clearly confirms the feasibility of the process and the spontaneous nature of the adsorption events. The degree of spontaneity of the reaction increased with temperature, which was primarily due to chemisorption rather than physisorption [30]. The values of ΔH° and ΔS° were determined from the slope and intercept of an $\ln b$ versus $1/T$ plot, which was based on the analysis shown in Fig. 9. These values were 34.835 kJ/mol and 117.227 J/mol K, respectively.

The positive nature of these parameters ($\Delta H^\circ > 0$; $\Delta S^\circ > 0$) indicates that the process was endothermic and that, during the process, randomness was increased at the solid–solution interface. This type of increase might be due to the H_2O hydrated molecules, or the sulfate ions [28]. By definition, adsorption with a heat reaction between 20.9 kJ/mol and 418.4 kJ/mol is a chemical adsorption. Therefore, the obtained enthalpy indicates that the adsorption of copper ions on the aminated polyacrylonitrile can be regarded as a chemical adsorption event [5,32].

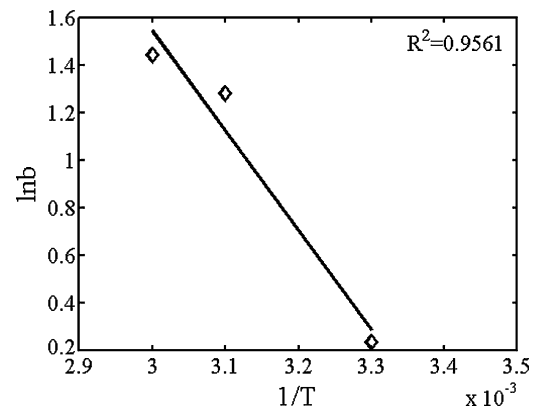


Fig. 9. The variation of $\ln b$ with $1/T$.

4. Conclusions

PAN nanofibers were produced using the electrospinning technique, where the injections of PAN and DMF solutions were carried out at 20 kV and with a 15 cm distance between the needle tip and the collector. Subsequently, amine groups were grafted onto the nanofiber and microfiber surfaces at various times and temperatures. ATR-FTIR spectra were obtained to confirm the amination of the PAN fibers surfaces. The condition that yielded the maximum amount of amine group grafting to PAN was determined so that there would be no loss in flexibility. The chelation of Cu^{2+} ions was subsequently carried out. Copper ion concentrations in the solution were measured by AAS. The nanofibers were observed to absorb metal ions three times faster than for the microfibers. The effect of pH was considered. In solution, pH values in the range of 2–6 were studied. The adsorption amounts for copper ions were found to increase with increasing pH. The value of the thermodynamic parameters ΔG° , ΔH° and ΔS° were calculated. Results of this analysis indicate that the process was endothermic. The results of this study indicate that the adsorption of copper ions on aminated polyacrylonitrile is a chemical adsorption process. The Langmuir isotherm fits the data well, proving that mono-layer adsorption occurred. Saturation adsorption capacities obtained from a Langmuir model of Cu(II) ions were higher than the reported values for APAN microfibers. The surface roughness of the fibers was studied using AFM. Increasing amounts of adsorption were found to increase the observed surface roughness. After grafting, no cracks or degradation events were seen based on SEM studies. Finally, it was found that the use of nanofibers increases the adsorption capacity and rate of copper ions. Hence, preparing APAN nanofiber membrane is a promising method that could help ensure a safe and healthy environment.

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