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Spinning of Polyacrylamidoximes by Solution Blowing Technique: Synthesis and Characterization

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Abstract: A novel route for the production of polyacryloamidoxime nano-fibers is described. The innovative solution blowing spinning technique is used for the production of polyacryloamidoxime nano-fibers. The polyacryloamidoxime was prepared by the amidoximation of the acrylonitrile groups in a non-aqueous medium (DMF) using the least possible amount of hydroxylamine. A comparison study was performed to evaluate the effectiveness of the amidoximation reaction in aqueous or non-aqueous media. As the presented method is acquiring only 0.5 g/g hydroxylamine, at 50 °C for 7 h to achieve 63.1 % conversions, also solution blowing is an alternative technique for manufacturing of micro- and nano-fibers. The morphological structure, the chemical nature as well as the dyeability of the obtained fibers are illustrated. The obtained nano polyacryloamidoxime fibers show superior adsorption ability toward copper ions. Results showed that the present work presents a promising synthesis root for spinnable polyacryloamidoxime.

Keywords: Polyacrylamidoximes, Nano-fibers, Solution blowing spinning and acrylic fibers

Introduction

In recent years, nano-fibers have attracted the attentions of many researchers due to its unique properties compared to large diameter fibers. Electrospinning is one of well know techniques that are using electric force to produce polymer filament in nanoscale [1]. In electrospinning, nano-fibers are produced from polymer solution that is stretched under electric field between the charged droplets of the polymer on the tip of a needle and the electrically charged target [2,3]. Nano-fibers characterized by their large surface area to volume ratio, good mechanical properties, and superior surface functionality [4]. However, the nano-fibers produced by electrospinning technique are obtained in a very low yield, whereas the polymer solution flow rate ranged between 1.0 m*l*/h to 5.0 m*l*/h and needle diameters ranged from 0.3 mm to 1.0 mm [5].

Recently, an innovative technique called solution blowing has been used to produce nano-fibers. This technique is characterized by its low cost, high production rates and more safe when compared to electrospinning [6]. Solution blowing spinning technique present a combination of the electrospinning, melt, and solution spinning to produce microfibers and nano-fibers [7]. Solution blowing technique depends on the high velocity of air/gas as a driving force for nano-fiber formations. Nano-fiber diameter is controlled by several spinning parameters such as; air pressure, polymer solution flow rate, polymer solution concentration, nozzle diameter, and nozzle-collector distance [6,8-11].

Polyacrylonitrile (PAN) is one of the widely used polymers among all the polymers, especially in the textile industry, because of its excellent spinnability and environmental stability [12,13]. PAN fibers mainly consist of acrylonitrile groups and few amount of acrylate groups as well as a few amount of the anionic groups (carboxyl or sulphonic), which responsible for the absorbance of the cationic dye molecules.

The reactions between (PAN) fibers and hydroxylamine were examined for the first time in the mid of 1950 to improve the fiber's properties. Chemical interaction between the CN-groups of PAN and hydroxylamine takes place in aqueous and non-aqueous medium to form polyacrylamidoximes.

It appears from many investigations that polyacrylamidoximes are a unique class of polyampholytes since the oppositely charged groups belong to the same substituent. Amidoxime groups have a high tendency to form strong complexes with a wide range of heavy metal ions such as lanthanides, actinides and transition metals [14].

Recently, a number of articles have been published describing the synthesis of macromolecules containing amidoxime groups, due to their use in the extraction of uranium as well as other heavy metals from water [15-23]. All described methods for the synthesis of a sorbent containing an amidoxime group is mostly based on incorporation of a nitrile group into a polymer matrix, then spinning of the polymer solution into nano-fibers by electrospinning technique, followed by the conversion of the nitrile group into an amidoxime group by treatment with an alkaline solution of hydroxylamine [24,25]. The drawback in all these methods is the consumption of a large amount of hydroxylamine in order to obtain the desired amount of conversion of the acrylonitrile groups into amidoxime for effective metals removal [14,19,20,26-29].

The aim of the present work is to spin polyacrylamidoximes nano-fibers using the Solution blowing spinning technique. Keeping in mind, the economic and environmental

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requirements, the conversion of the acrylonitrile groups present in the acrylic fabrics using the least amount of hydroxylamine is also an objective of the present work. The prepared fibers will be subjected to chemical, morphological and dyeability characterization also it will be challenging for the removal heavy metal ions from the aqueous medium.

Experimental

Materials

A commercial basic dyeable PAN fibers (Tg 82.6 °C, Tc 479 °C and Tm 336.4 °C, made from acrylonitrile, methyl acrylate, and itaconic acid comonomers) were supplied by Misr Mehalla for Spinning and Weaving, Egypt. The PAN fibers (P_F) were washed before treatment using a nonionic detergent (2 g/*l*) at 60ºC for 45 min thoroughly rinsed and dried at room temperature. Hydroxylamine hydrochloride from sisco research laboratory, India. Dimethylformamide (DMF) from Merck was used as a solvent. All other chemicals were a laboratory grade.

Synthesis of Polyacrylamidoximes

Hydroxylamine Solution

Dry sodium carbonate (23.8 g) was used to neutralize 50 m*l* of a 50 % hydroxylamine hydrochloride solution in dimethylformamide (DMF). The hydroxylamine hydrochloride solution was preheated to 80 °C before neutralization. When all the carbonate is added, heating is continued during another 30 min., then the solution is cooled and the precipitated sodium chloride was filtrated off.

Amidoxime Synthesis

The amidoximation reaction was performed before (non-aqueous medium) and after (aqueous medium) the spinning process via solution blowing.

In Non-aqueous Medium

For the preparation of polyacrylamidoximes, 10 g acrylic fibers are dissolved in DMF, and then mixed with different amounts of the neutralized hydroxylamine solution and further diluted with DMF until the total volume is 100 m*l*. Afterward, the solution is heated at various temperatures (30-70 °C) for different time durations (0.5-4 h).

In Aqueous Medium

10 g pure PAN nano-fibers (P_NF) obtained from the solution blowing apparatus are immersed in water, and then mixed with different amounts of the neutralized hydroxylamine solution, the total volume is 100 m*l*. The fibers were heated at various temperatures (40-70 °C) for different time durations (0.5-5 h) to obtain amidoximated nano-fibers (AP_NF).

The Conversion Degree

After reaction completion, the polymer was precipitated in an aqueous medium, and washed several times with distilled water, followed by air drying at 60 °C in an oven till constant weight is reached. The % conversion was calculated according to equation (1).

$$C_n = \frac{(W_1 - W_0)M_0}{W_0 M_1} \times 100 \qquad (1)$$

where C_n is % conversion of PAN, W_0 is the weight of the PAN before the reaction, W_1 is the weight of the PAN after the reaction, M_1 is the molecular weight of hydroxylamine (33 g/mol) and M_0 is the molecular weight of acrylonitrile (AN) monomer (53.06 g/mol).

Fiber Productions

Solution blowing apparatus is composed of air compressor, injection pump, spinning nozzle, and fiber collector (Figure 1(a)). The polymer solution (P_F or amidoximated PAN in non-aqueous medium) with a concentration of 15 wt % in DMF was pumped through a 19-gauge needle with polymer flow rate of 20 m*l*/h and the air pressure of 1.5 bars. Nano-fiber collector distance was maintained at 50 cm of the spinning nozzle. The spinning needle was located at the center of the concentric nozzle and protruded 1 mm out of the concentric nozzle. The obtained nano PAN fibers (P_NF) and amidoximated PAN nano-fibers (NP_NF) were then dried at 60 °C in an oven till constant weight.

Fibers Characterizations

FTIR Analysis

The chemical compositions of P_NF, NP_NF and AP_NF are investigated with ATR-FTIR (JASCO 4700). The scanning range was 400-4000 cm^{-1}.

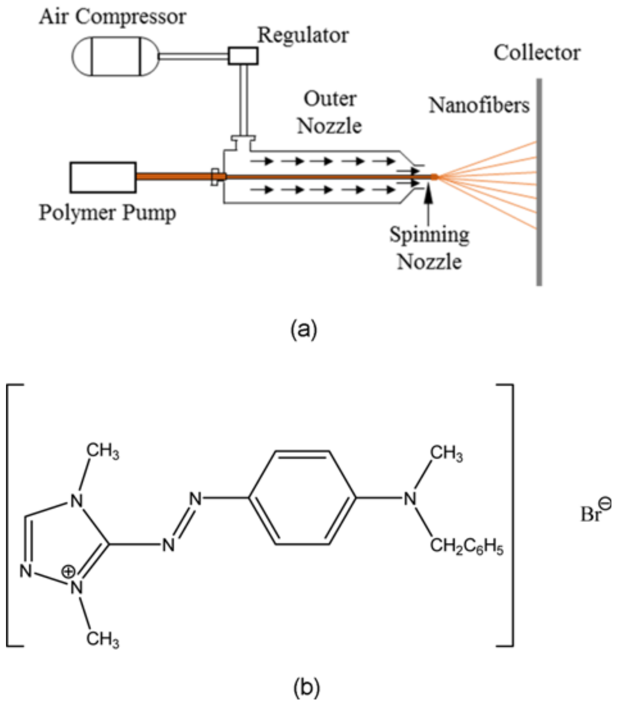


Figure 1. Schematic representation of solution blowing apparatus (a) and chemical structure of Basic Red 46 dye (b).

Scanning Electron Microscopy

The morphological structure of P_NF, NP_NF and AP_NF were mounted on aluminum stubs, and sputter coated with gold in a 150 Å sputter (coated Edwards), and examined by JEOL (JXA-840A) Electron Probe Microanalysis (Japan), magnification range 35-10,000, accelerating voltage 20 kV.

Measurement of the Nano-fibers Diameter

Nano-fibers average diameter was determined by measuring the diameter of 100 fibers that were randomly selected from the SEM micrograph and their diameters were measured using a software program. The histograms of nano-fibers diameters were plotted using the software program.

Batch Dyeing Experiment

Basic Red 46 dye (Figure 1(b)) supplied from a local textile factory was used without further purification. The accurately weighted amount of dye was dissolved in 500 m*l* distilled water and the required concentration (500 ppm) of the experimental solutions was obtained by diluting the stock solution. Dried samples of pretreated nano-fibers with 100 m*l* of 0.1 M HCl in methanolic solution (5 min) for conversion into an H-form were added separately to 50 m*l* dye solution and shaken in a water bath at 80 °C. The concentrations of dye in solution after the dyeing test were determined by (JENWAY) a UV/VIS Spectrometer at λ_{max} 530 nm for different time intervals until 180 min. The amount BR dye adsorbed was calculated using the following equation;

$$q = \frac{(Co-Ce)V}{M} \tag{2}$$

where q is the amount of sorbed dye (mg g^{-1}), Co and Ce are the initial and the equilibrium concentrations of dye (mg l^{-1}), respectively. V is the volume of the solution (L) and M is the weight of nano-fibers used (g).

Batch Metal Ions Adsorption Experiment

In metal ion removal experiment for a typical (Cu^{2+}), 1 g of nano-fibers was immersed in the metal ion solution (100 m*l*) containing 400 ppm (Cu^{2+}) at pH 6 using sodium acetate as a buffer, then shook using a Heidolph unimax 2010 shaker at 150 rpm at ambient temperature for 24 hrs. After equilibration is reached, the fibers were separated by filtration and the concentration of metal ions in the solutions was measured using atomic absorption spectroscopy (AAS) (VARIAN AA220). The adsorption amounts were calculated as follows:

$$Q\ (\text{mg/g}) = \frac{(Co-Ce)V}{M} \tag{3}$$

where Q is the adsorption amount of metal ions (mg g^{-1}), Co and Ce are the initial and the equilibrium concentrations of metal ions (mg l^{-1}), respectively. V is the volume of the solution (L) and M is the weight of nano-fibers used (g).

Results and Discussion

Conversion Degree in Non-aqueous Medium

As shown in Table 1, in a non-aqueous medium, the percentage conversion of the nitrile group in the PAN molecules into amidoxime increased along with the increases in the amount of hydroxylamine, reaction temperature and reaction time. Maximum conversion was achieved at hydroxylamine amount of 5 g at 60 °C for 7 h. For this reaction conditions, the produced solution is completely gelated and not suitable for spinning. Data of Table 1 also revealed that the conversion of 63.1 % could be attained at hydroxylamine amount of 5 g at 50 °C for 7 h and the obtained solution is viscous, not gelated and it is spinnable,

Table 1. Reaction parameters and degree of conversion in non-aqueous medium

Sample code	Amount of hydroxylamine (g)	Reaction temperature (ºC)	Reaction time (h)	Degree of conversion (%)	Form of resulted solution
$NP\_NF_{11.8}$	0.5	70	4	11.8	Normal
$NP\_NF_{33.4}$	1			33.4	Normal
$NP\_NF_{52.5}$	3			52.5	Normal
$NP\_NF_{57.9}$	5			57.9	Viscous
$NP\_NF_{64.7}$	7.5			64.7	Gelated
$NP\_NF_{22.9}$	5	70	0.5	22.9	Normal
$NP\_NF_{32.1}$			1	32.1	Normal
$NP\_NF_{47.4}$			2	47.4	Normal
$NP\_NF_{51.2}$			3	51.2	Viscous
$NP\_NF_{12.5}$	5	30	7	12.5	Normal
$NP\_NF_{27.8}$		40		27.8	Normal
$NP\_NF_{63.1}$		50		63.1	Viscous
$NP\_NF_{71.8}$		60		71.8	Complete gelation

The weight of PAN fibers is 10 g.

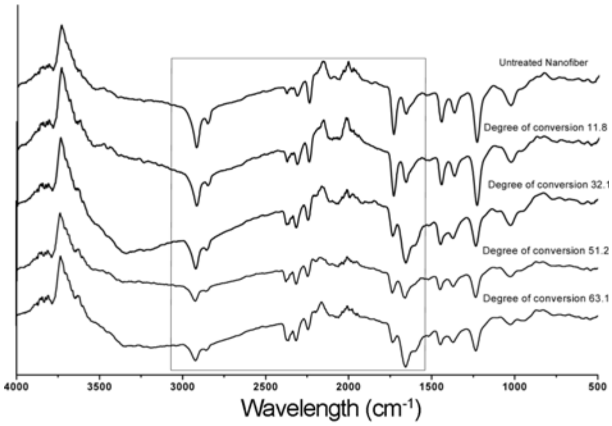


Figure 2. FTIR spectra of the pure PAN and its amidoximated form in non-aqueous medium.

while the solution obtained at hydroxylamine amount of 7.5 g at 70 °C for 4 h has nearly equal conversion degree (64.7 %) but it is gelated. The gelation could be attributed to the cyclization reaction of the produced amidoxime into glutaroimide-dioxime ring (Figure 2). The cyclization reaction is favored at high temperature and long reaction duration [23,30].

A comparison study between the amidoximation reaction in non-aqueous and aqueous media at similar reaction conditions was performed. Data of Table 2 shows the conversion degree of P_NF into polyacryloamidoxime in an aqueous medium at variable reaction conditions. As the conversion (%) depended on the amount of hydroxylamine molecule diffused from the reaction solution into P_NF, the increasing the reaction temperature and hydroxylamine amount effectively enhance the molecular diffusion of hydroxylamine into P_NF. The content of the amidoxime group also increased as the reaction time increased, because more time is available for the molecular diffusion of hydroxylamine from the solution into the nano-fibers [23, 28,31]. It's worth noting that the maximum amount of conversion that could be attained in the aqueous amidoximation reaction was 39.2 % whatever the reaction conditions used, while it was 71.8 % in the non-aqueous amidoximation, and that could be attributed to the reaction heterogeneity in the aqueous amidoximation, which hinders the effective amount hydroxylamine required for the reaction. Table 3 represents the effect of reaction parameters on the degree of nitrile conversion reported in the literature. The amidoximation reaction of nitrile group, through the reaction of PAN with hydroxylamine, have been studied. A comparison of the percentage nitrile group's conversion shows that higher hydroxylamine amount is required to attain higher conversion yield (Table 3). Also, it is clear that the present work presents a promising synthesis root for spinnable polyacryloamidoxime. As the presented method is acquiring only 0.5 g/g hydroxylamine, at 50 °C for 7 h to achieve 63.1 % conversions.

Table 2. Reaction parameters and degree of conversion in an aqueous medium (10 g PAN)

Sample code	Amount of hydroxylamine (g)	Reaction temperature (°C)	Reaction time (h)	Degree of conversion (%)
$AP\_NF_{2.1}$	0.5	70	4	2.1
$AP\_NF_{7.5}$	1			7.5
$AP\_NF_{12.6}$	3			12.6
$AP\_NF_{26.8}$	5			26.8
$AP\_NF_{39.2}$	7.5			39.2
$AP\_NF_{7.9}$	5	70	0.5	7.9
$AP\_NF_{19.2}$			1	19.2
$AP\_NF_{26.6}$			2	26.6
$AP\_NF_{32.1}$			3	32.1
$AP\_NF_{1.7}$	5	30	7	1.7
$AP\_NF_{16.5}$		40		16.5
$AP\_NF_{29.1}$		50		29.1
$AP\_NF_{35.4}$		60		35.4

Table 3. The effect of reaction parameters on the degree of nitrile conversion reported in the literature

Weight of hydroxylamine / g PAN	Reaction temp. (°C)	Reaction time (h)	Degree of nitrile conversation (%)	Reference
40	80	2	86	[28]
0.9	80	2	18.69	[33]
198.04 The mass of fibers is not mentioned	55	4	99.7	[31]
2.085	Reflux	24	Not mentioned	[14]
6.949	65	6	Not mentioned	[29]
2	70	6	Not mentioned	[27]
2.105	70	2	Not mentioned	[19]
0.5	50	7	63.1	In present work

FT-IR Study

The FTIR spectra of the P_NF and NP_NF (Figure 2) or AP_NF (Figure 3) media were consistent with the structures assigned to them. The typical structures of these polymers are depicted in Figure 4.

The FT-IR spectrum of P_NF (Figure 2) shows the characteristic absorption peak at 2242 cm^{-1} (-C≡N), 1734 cm^{-1} (C=O), 1234 cm^{-1} (C-O-C) and 1027 cm^{-1} (C-O), which indicated that the PAN was a copolymer as designated in the experimental part. The FT-IR spectrum of modified PAN (in non-aqueous medium) (Figure 2) or the modified PAN (in aqueous medium) (Figure 3) exhibited new and correlative characteristic bands of amidoxime at 1650 cm^{-1}, 1600 cm^{-1}

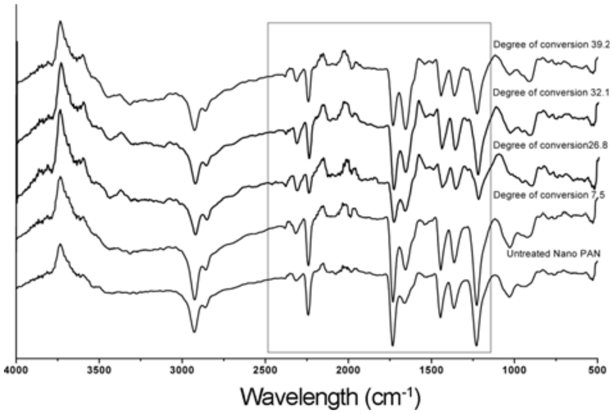


Figure 3. FTIR spectra of the pure PAN and its amidoximated form in aqueous medium.

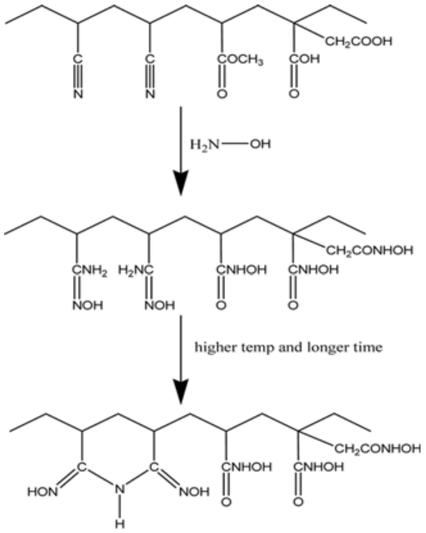
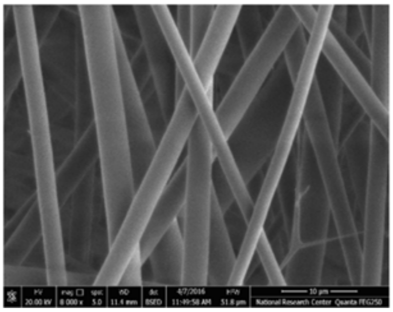
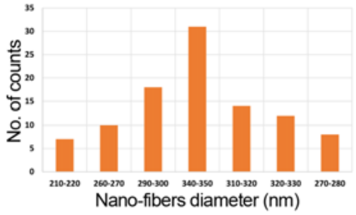
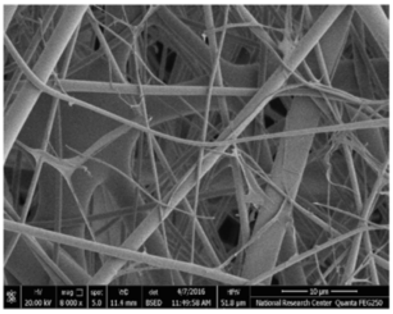
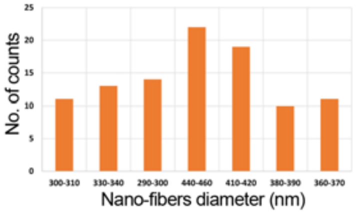
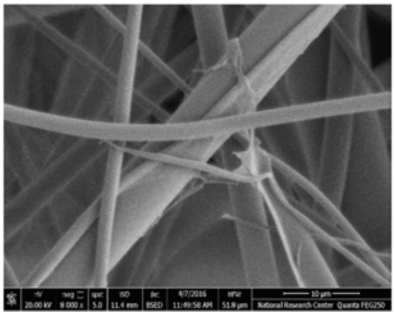
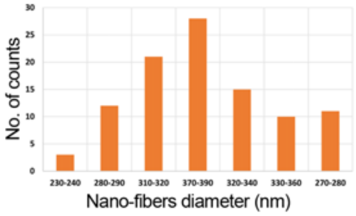


Figure 4. Chemical representation of pure PAN and its amidoximated forms.

Table 4. The optical and SEM images of pure PAN nano-fiber and the amidoximated nano-fibers in aqueous or non- aqueous medium

Fiber type	Optical images	ESM images	Fibers diameters
Pure nano-PAN			
Nano amidoximated PAN in non-aqueous medium (conversion 63.1 %)			
Nano amidoximated PAN in aqueous medium (conversion 39.2 %)			

and 950 cm^{-1}, which were attributed to the stretching vibration of C=N, N-H, and N-O, respectively [14,23,32]. The FT-IR spectra approved that the amidoxime group was introduced onto the PAN surface. It is observed that the sharp band at 2242 cm^{-1} continuously decreased in intensity, as the conversion (%) increase. Also, the same behavior was observed regarding the band at 1734 cm^{-1} (C=O ester or acidic), which decreased intensities. While the absorption bands at 1650 cm^{-1}, 1600 cm^{-1} and 950 cm^{-1}, which were attributed to the stretching vibration of C=N, N-H, and N-O respectively, were increased continuously with the increase in the conversion (%) [23]. The band in the region of 1600-1650 cm^{-1} could also be attributed to the formation of hydroxamic acid [14]. Generally, the overall characteristic changes in the FTIR spectra of PAN due to the amidoximation reaction were intensively observed due to the amidoximation reaction in the non-aqueous medium than in the aqueous medium.

SEM Analysis

Table 4 shows the optical and SEM images of P_NF, NP_NF, and AP_NF. The surface of the PAN-oxime (NP_NF and AP_NF) did not show any serious cracks or degradation and obtainable almost with similar morphology to that of P_NF. The diameter of the nano-fiber was calculated from the SEM image, and it was found that the diameter of the nano-fibers was increased in the following order (pure PAN 348 nm, AP_NF 388nm, NP_NF 454 nm). The remarkable increase in the fiber diameter of the amidoximated PAN in the non-aqueous medium is due to an increase in viscosity of the spinning solution as a result of the amidoximation reaction [20] (Table 1). Also, the slight increase in the fiber diameter of the amidoximated PAN in the aqueous medium could be understood on the basis of the surface interaction between the fibers and the hydroxylamine [31].

Dyeability

Since dyeing of fibers is considered as an important feature, therefore, a comparison study between the dyeability of the pure PAN fibers, P_NF as well as NP_NF and AP_NF. Figures 5 illustrates the dyeing kinetics (as a function of time) of basic red dye onto the PAN fibers, P_NF, $AP\_NF_{39.2}$, and $NP\_NF_{63.1}$.

Dyeing of fibers was observed to increase rapidly until 60 min. and then level off which, further suggests that the equilibrium between adsorption and desorption of dye is attained. The dyeing capacity of fibers for dye was found to increase in the order: $NP\_NF_{63.1}$ < PAN fibers < $AP\_NF_{39.2}$ < P_NF, (Figure 5). The superior ability of the nano-PAN fibers to adsorb higher amount of the dye could be attributed to the increased available active sites (carboxylic groups) onto the nano-fibers surface (i.e. increased surface area per unit volume). Furthermore, the slight enhancement in the dye adsorption by the $AP\_NF_{39.2}$ is due to the synergistic effect of the introduced oxime groups, which interact with the dye molecule through hydrogen bonding in addition to the existed carboxylic groups [31]. Also, it seems that the $NP\_NF_{63.1}$ loses its basic dyeability. The conversion of the majority of the carboxylic groups in the non-aqueous medium into hydroxamic acid could be the reason behind the deterioration in the dyeability. Those carboxylic groups are responsible for the dyeability of PAN fibers with basic dyes. This finding is consistent with the FTIR analysis (Figure 2).

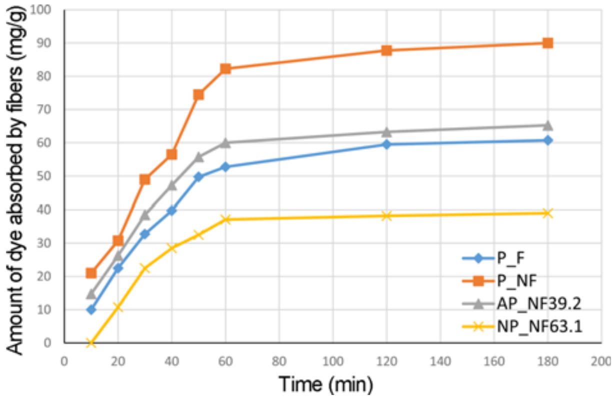


Figure 5. Dyeing kinetics of basic red 46 onto pure or modified PAN.

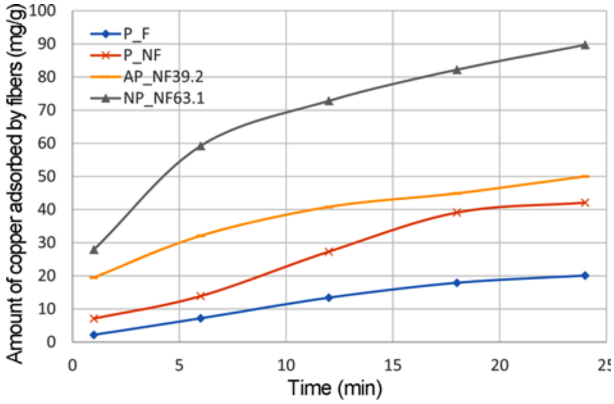


Figure 6. The effect of time on the amount adsorbed of copper ions by pure PAN and amidoximated fibers.

Adsorption of Copper (II) Ions onto Polyacryloamidoxime Nano-fibers

Amidoxime modified PAN fibers were known for its high affinity for metal ions removal from its aqueous solution [23,33-36]. The prepared polyacryloamidoxime nano-fibers in the aqueous or non-aqueous medium were challenged for the removal of Cu^{2+} ions from the aqueous medium, and compared with the ability of pure nano PAN or pure PAN.

Figure 6 shows the adsorption ability of the fibers toward Cu^{2+} in a 400 ppm solution as functions of time. The adsorption capacity of the metal increased as the time increased. The adsorption capacities (at 24 h) of Cu^{2+} onto the NP_NF$_{63.1}$, AP_NF$_{39.2}$, P_NF and PAN fibers were 89.7, 50, 42.1 and 20.1 mg/g, respectively.

The adsorption of both Cu^{2+} by both PAN fibers and P_NF could be attributed the existence of the carboxylic groups on the fiber surface, which is able to coordinate to the copper ions [37]. NP_NF$_{63.1}$ shows superior ability to adsorb copper ions over the other fibers, which emphasis on the effectiveness of the amidoxime and hydroxamic acid groups in the adsorption of copper ions.

Conclusion

The present work investigates the possibility of effective amidoximation of the acrylonitrile groups in a non-aqueous medium using the least possible amount of hydroxylamine, followed by solution blowing spinning to produce nano polyacryloamidoxime fibers. In a non-aqueous medium, the percentage conversion of the nitrile group in the PAN molecules into amidoxime increased along with the increase of the amount of hydroxylamine, reaction temperature and reaction time. The maximum conversion was achieved at hydroxylamine amount 0.5 g/g PAN at 60 °C for 7 h, but the produced solution is completely gelated and not suitable for spinning, while at 50 °C the produced solution is suitable for spinning. The maximum amount of conversion that could be attained in the aqueous amidoximation reaction was 39.2 % whatever the reaction conditions used while it was 71.8 % in the non-aqueous amidoximation. The FT-IR spectra confirm the introduction of amidoxime groups onto the PAN surface. The SEM images show that the diameter of the nano-fibers was increased in the following order (pure PAN 348 nm, AP_NF 388 nm, NP_NF 454 nm). Also, the dyeing capacity of fibers for basic red dye was found to increase in the order: NP_NF$_{63.1}$ < PAN fibers < AP_NF$_{39.2}$ < P_NF and the adsorption capacities (at 24 h) of Cu^{2+} onto the NP_NF$_{63.1}$, AP_NF$_{39.2}$, P_NF and PAN fibers were 89.7, 50, 42.1 and 20.1 mg/g, respectively.

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