

Characteristic Assessment of Stabilized Polyacrylonitrile Nanowebs for the Production of Activated Carbon Nano-Sorbents

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Abstract Polyacrylonitrile (PAN) nanofibers with average diameter of 300 nm were produced by electro-spinning. The nanofibers were stabilized at different temperatures in the range of 180–270 °C in several duration times and heating rates. Fourier transforms infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyzing techniques were employed to measure the extent of stabilization reaction. By all procedures, the ranges of temperature and duration time recommended were about 250–270 °C and 1–2 h, respectively. Increasing the activation temperature from 800 °C to 1200 °C caused porosity and pore volume development up to 60% and 0.532 cm³/g, respectively. Pore width of all samples was calculated to be about 0.7 nm confirming micro-pore structure of the produced PAN based activated carbon nanofibers. Comparing dye adsorption for different adsorbents including chitin and granular activated carbon (GAC) showed the highest efficiency for the produced activated carbon nanofibers (ACNFs).

Keywords: Polyacrylonitrile; Electro-spinning; Stabilization; Activated carbon nanofibers; Adsorbent.

INTRODUCTION

Water and air represent two environmental systems where the most pressing environmental issues persist. Water pollution and deteriorating freshwater supplies are often cited as critical global problems. It is estimated that more than 50% of nations in the world will face freshwater preparation^[1]. Dyes are one of the most complex pollution that is entering the water sources by industries. Conventional water treatment process of flocculation-filtration-disinfection is effective to remove suspended solid in raw water, and has been used for over century for water supply. However, it is disabled to remove micro-pollutants such as dye particles that may cause serious problem of water safety in raw water^[2].

Activated carbon fiber (ACF) has been widely used for water purification systems as an effective adsorbent for micro-pollutants in recent years^[1]. ACF effectively adsorbs and removes a broad spectrum of harmful substances. It has become popular for use in water purification because of its higher adsorption rate and capacities compared to the other granular adsorbents, such as GAC or powdered activated carbon (PAC)^[3]. Introducing of nano-sized porosity has been shown as an effective strategy to achieve better adsorption^[4]. On the other hand, fibrous materials have filled requests in lots of areas due to their intrinsically high surface and porous structures^[5]. In concept, coupling nano-porosity and ultrafine form of fibrous materials would lead to the highest possible specific surface area^[6]. Activated form of carbon nanofibers (CNF) is one of the most famous porous ultrafine fibers. They are new forms of porous carbon materials with a number of significant advantages over the traditional powder or granular form including higher adsorption and desorption rate and significant flexibility^[7, 8].

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The conventional preparation methods for CNFs, including vapor growth and plasma enhanced chemical vapor deposition methods, are known to be very complicated and costly^[7, 9]. Therefore, a simple and inexpensive electro-spinning process, first patented by Cooly in 1902, has been used to fabricate CNFs^[7, 10, 11]. Since the performance of carbon fibers highly depends on their precursor and the desired precursor should have high carbon content, high molecular weight and also high degree of molecular orientations, PAN-based carbon fiber seems to satisfy all of these expectations^[12, 13]. On the other hand, PAN homopolymer has been hardly used because of its poor properties and processing ability, so the monomers such as acrylic acid (AA), methacrylic acid (MAA) and methylmethacrylate (MMA) have been widely added to PAN monomer to form high performance carbon fibers^[14]. Typically, PAN-based CNFs formation method includes electro spinning, stabilization and carbonization^[15]. Activation process is used to develop specific surface area and porosity of CNFs, which can be physical or chemical. Physical activation as the most common technique, involves carbonization of precursors followed by gasification of resulting char or direct activation by CO₂ or steam^[16, 17].

Electro-spinning utilizes electrostatic forces to spin ultrafine fibers from precursor solution. The common spinning techniques can finally produce micro scale carbon fibers (diameter > 5 μm), while by employing electro-spinning of precursor solution, especially PAN, it is possible to get carbon fibers in nanoscale^[12, 18–21]. PAN precursor fibers and nanofibers need to be thermally stabilized prior to pyrolysis process to obtain high quality carbon fibers. PAN nanofibers are converted into carbon nanofibers by the sequenced processes of stabilization, carbonization and graphitization^[22]. The stabilization is intended to prevent melting or fusion of the fiber, to avoid excessive volatilization of elemental carbon in the subsequent carbonization step and thereby to maximize the ultimate carbon yield from the fiber precursor. The chemistry of the stabilization process is complex, but generally consists of cyclization of the nitrile groups ($\text{—C}\equiv\text{N}$) and cross-linking of the chain molecules in the form of —C=N—C=N— . In this process a lower temperature treatment (180–300 °C) in air (usually oxygen containing atmosphere) leads to the formation of an aromatic structure. Dehydrogenation, aromatization, oxidation and cross-linking occur as a result of the conversion of $\text{C}\equiv\text{N}$ bonds to C=N bonds, then fully aromatic cyclized ladder type structure forms. This cyclized structure is stable toward heat and is converted to turbo-stratic carbon^[23, 24]. The physical changes include color, crystallinity, entropy, density and tensile strength; whilst chemical changes include nitrile polymerization, chain scission, evolution of volatile gases (NH₃, CH₄, CO, CO₂, H₂O, and so on), and formation of carbonyl, carboxyl and peroxide groups^[25]. Also, it has been reported that during stabilization, —CH_2 and $\text{—C}\equiv\text{N}$ groups disappeared while C=C , C=N and =C—H groups formed. At the same time the color of precursor fiber changes gradually and finally turns black when carbonized^[13, 26, 27]. It is necessary to choose the optimum conditions of temperature, heating rate and oxidation period. Studies showed that optimal stabilization conditions lead to high modulus fibers (these fibers have tenacities of more than 25 g/d, module greater than 600 g/d and elongations at break of less than 5%)^[28]. Too low temperatures lead to slow reactions and incomplete stabilization, whereas too high temperatures can fuse or even burn the fibers^[20, 27].

In the current work, PAN-based carbon nanofibers are prepared using electro-spinning method. The physical, chemical and structural changes created in stabilization process assessed by various analyzing techniques include XRD, DSC and FTIR spectroscopy to measure stabilization index of electro spun PAN nanofibers after heating to obtain the desired conditions include temperature, dwell time and heating rate in order to obtain desired ACNF. Finally the produced ACNF was compared to GAC and chitin for the removal of a selected cationic dye, basic blue 41 (BB41), from its aqueous solution.

EXPERIMENTAL

Materials

Poly(acrylonitrile-co-methylacrylate) (94.6 wt%) with molecular weight of 1×10^5 g/mol received from Polyacryl Co. (Isfahan, Iran). Dimethylformamide (DMF) was purchased from Merck Company as appropriate solvent due to its solubility parameters^[29] of the PAN powder dissolving.

The Dye BB41 was purchased from Sigma-Aldrich, Milwaukee, WI. This dye is a monoazo-basic dye with C. I. No: 11105, λ_{max} equal to 610 nm, color of bright blue hue and molecular weight of 483 g/mol. It is particularly suitable for dyeing of acrylic substrates and can also be applied to some polyamide and polyester types, viscose, cotton and wool. F400 (Filtrisorb 400) was used as a typical GAC (Calgon, Pittsburg, PA).

PAN Nanofibers Production

Accurate scaled mass of PAN powder dried and stored in dessicator for 24 h was dissolved in DMF. The solutions with concentration range of 8–13 wt% were prepared by using magnetic stirrer for 1 day. Then each solution was fed into the electro-spinning set up by a 2 mL syringe pump with pumping rate of 1–2 $\mu\text{L}/\text{min}$. The Gamma high voltage was used to supply applicable voltage of 7–10 kV in the spinning distances of 15 cm for all samples. Scanning electron microscopy (SEM) was used to select the best electro-spinning conditions according to the appearances, uniformity and diameters of electro spun nanofibers. The electro-spinning setup used in this work can be found elsewhere^[30].

Thermal Stabilization of PAN Nanofibers and Activation

Stabilization of the samples was carried out under air atmosphere in a chamber furnace (Nabertherm Controller Co.) using different temperatures and dwell times ranging from 180 °C to 270 °C and 15–120 min, respectively. All runs were in discontinuous mode. Heating rate also varied from 1 to 4 K/min to obtain the best results. The range of temperatures was chosen according to the thermal behavior of PAN nanofibers got from DSC analysis.

Simultaneous carbonization and activation were performed in furnace under pure nitrogen (99.99%) atmosphere at temperatures ranging from 800 °C/min to 1200 °C/min for 1 h.

Characterization

Scanning electron microscope (Philips XL-30) was employed to get micrograph from stabilized and untreated samples. FTIR spectrometer (Nexus 670) from Nicolet Instrument Corporation was used to detect the chemical transformation as well as measuring the extent of reaction (EOR) after heat stabilization. DSC measurements were carried out using DSC 302 BAHR thermo analyses calorimeter. All samples weighed about 7 mg in aluminum pans using alumina reference and were heated in heating rate of 10 K/min. X-ray diffractometer (Philips 1140/90) with Ni filtered $\text{Co } K_{\alpha}$ radiation ($\lambda = 0.1785 \text{ nm}$) was utilized to obtain XRD patterns of PAN fibers and the fibers stabilized in different conditions. Each sample had a weight around 4 mg. The fibers were fixed straightly on the supporting glass. The scanning rate is 4°/min with a scanning step of 0.02°. The physical properties of the activated carbon nanofibers (ACNF) at different activation temperatures were evaluated by BET technique. Nitrogen adsorption at 77.2 K was conducted for determining multipoint specific surface and the basic t-plot micropore analysis using Micrometrics Tristar 3000, a surface area and porosity analyzer.

Evaluation of Adsorption Properties of the ACNF

A simple adsorption experiment was used to evaluate the dye removal capability of the produced ACNF. Adsorption experiment was carried out in a batch equilibrium technique at 25 °C. Certain amounts of the adsorbents (0.01 g of chitin, GAC and ACNF) were contacted with 45 mL of 100 mg/L dye solution in 50 mL capped bottles. The solutions were stirred using a shaker model WB14 of Memmert, Germany kept under dark conditions. At equilibrium the solutions were centrifuged using a Rotana 460R at 3500 r/min and 25 °C for 1 min. A Cintra 10 UV-Vis spectrophotometer was used for optical absorbance measurements at maximum wavelength of the dye (610 nm) to calculate the dye concentration.

RESULTS AND DISCUSSION

The PAN nanofiber and its stabilized forms were evaluated using SEM, FTIR, DSC and X-ray analysis. SEM photographs showed that the best applied voltage to obtain the uniform electrospun PAN nanofibers webs having no beads in their structure using the mentioned concentrations range was 8 kV. This is an important key factor in the subsequent heat treatment of the web for carbon and activated carbon nanofibers production. Table 1 shows the average diameters of produced PAN nanofibers in concentration range of 8%–13% under constant voltage, pumping rate and spinning distance of 8 kV, 2 $\mu\text{L}/\text{min}$ and 15 cm, respectively.

Table 1. Average diameter of prepared PAN nanofibers

Concentration (wt%)	8	10	11	13
Average diameter (nm)	78.2	121.4	367.5	1100.0

Voltage: 8 kV, pumping rate: 2 μ L/min and spinning distance: 15 cm

It has been reported that PAN nanofibers lose about 50% of their diameters during stabilization and carbonization processes^[31, 32], so concentrations of 8% and 10% seem to be inappropriate for this study because of their instability during the heating process. This was revealed in selected experiments. As it is seen in Table 1 the concentration of 13% will not provide desirable diameter due to its micro scale. Figure 1 shows SEM pictures of PAN nanofibers spun using 11% solution and its stabilized and carbonized product.



Fig. 1 SEM micrograph of (a) PAN nanofibers (solution concentration: 11%, voltage: 8 kV, pumping rate: 2 μ L/min, distance: 15 cm), (b) stabilized PAN nanofibers (Temperature: 270 $^{\circ}$ C, time: 1 h, heating rate: 1 K/min) and (c) carbonized PAN (temperature: 1000 $^{\circ}$ C, time: 1 h, heating rate: 1 K/min)

Comparing the FTIR spectra of untreated and stabilized PAN nanofibers in Fig. 2, the effects of temperature and duration time on chemical bond changes can be concluded. During stabilization, the peak at 2240 cm^{-1} related to $\text{C}\equiv\text{N}$ bond decreases intensely, indicating nitrile groups disappearing. On the other hands, new peaks around 1600 cm^{-1} and 1400 cm^{-1} engender that are related to the formation of $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds, which reveals improving the creation of aromatic and ladder like structures^[27, 32].

A common way to assess the extent of stabilization reaction (EOR) is using Eq. (1):

$$\text{EOR}(\%) = \frac{I_{1600}}{I_{2240} + I_{1600}} \quad (1)$$

where I_{2240} and I_{1600} show the intensity of peaks related to $\text{C}\equiv\text{N}$ and $\text{C}=\text{N}$ bonds, respectively. Table 2 shows the effect of temperature on the EOR. Data indicate that increasing temperature has an extraordinary effect on the extent of reaction and weight loss percentage (WL). Though temperatures in the range of 250–280 $^{\circ}$ C seem to afford good results but due to their weight loss, 280 $^{\circ}$ C is not recommended for the stabilization process (as it is presented in Table 2 there is no significant difference between EOR% of samples stabilized at 270 $^{\circ}$ C and 280 $^{\circ}$ C but the weight loss of the latter is considerable). On the other hand, EOR of the reaction indicates that, the process is nearly accomplished beyond 270 $^{\circ}$ C, hence higher temperature is not essential. Dwell time as presented in Table 3, has the same effect, but with less intensity, on EOR and WL. The dwell time between 60–120 min is optimum due to calculated EOR%. The influence of heating rate is negligible. It should be noted that because of making a brittle and cracked web handle, heating rates more than 2 K/min did not provide proper conditions for stabilization process.

Table 2. Effects of temperature on EOR and WL of stabilized nanofibers

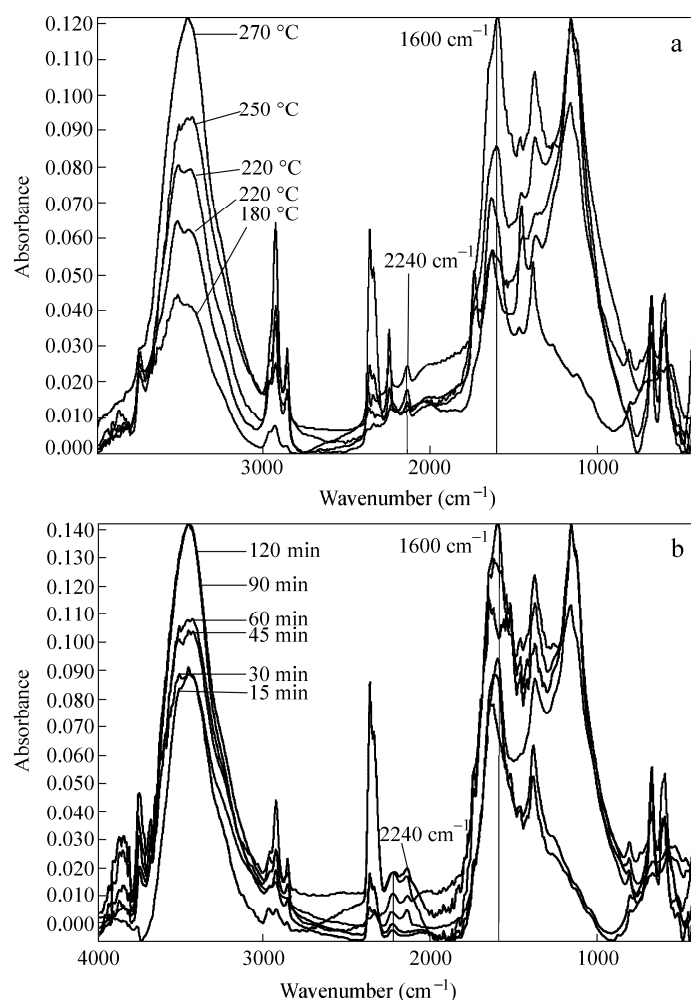
Stabilization temperature ($^{\circ}$ C)	180	200	220	250	270	280
EOR (%)	62.14	67.48	76.08	89.52	91.28	92.21
Weight loss (%)	18.0	22.3	25.8	30.0	32.1	38.4

Constant time of 1 h and heating rate of 1 K/min

Table 3. Effects of time on EOR and WL of stabilized nanofibers

Stabilization time (min)	15	30	45	60	90	120	150
EOR (%)	83.3	84.4	84.8	89.52	91.8	92.03	92.08
Weight loss (%)	19.2	25.6	26.8	28.1	30.5	32.4	37.9

Constant temperature of 250 °C and heating rate of 1 K/min

**Fig. 2** FTIR spectra of samples stabilized with different temperatures (a) and dwell times (b)

A different method for evaluating the stabilization extent is to study thermal behavior of untreated and stabilized PAN nanofibers using DSC analysis in certain heating rate^[26]. As mentioned, the DSC curve of PAN nanofibers has two exothermic peaks, the first one is related to the cyclization reactions and the latter confirms the oxidation processes. Thermally stabilized nanofibers show wider exothermic peaks with lower heights. Figure 3 shows DSC curves of nanofibers stabilized in different conditions. The conditions (times and temperatures) are selected according to higher calculated EOR.

The curves show that during stabilization, the intensity of exothermic peaks are reduced and peaks shift to lower temperatures, indicating that cyclization of the structure occurs more rapidly by increasing stabilization time and temperature. The plot area of the curves, representing the enthalpy of reaction, was decreased by completing the process. The reduction of enthalpies can be used to measure the stabilization yield, by Eq. (2)^[33].

$$SI(\%) = \left(1 - \frac{\Delta H_{OX}}{\Delta H_0}\right) \times 100 \quad (2)$$

where SI is stabilization index percentage, ΔH_{OX} is the enthalpy of oxidized PAN nanofibers and ΔH_0 is the enthalpy of raw PAN nanofibers.

Calculated SI presenting in Tables 4 and 5, shows consistency to the related FTIRs EOR. DSC analysis confirms that the most important effective parameter in stabilization extent is temperature.

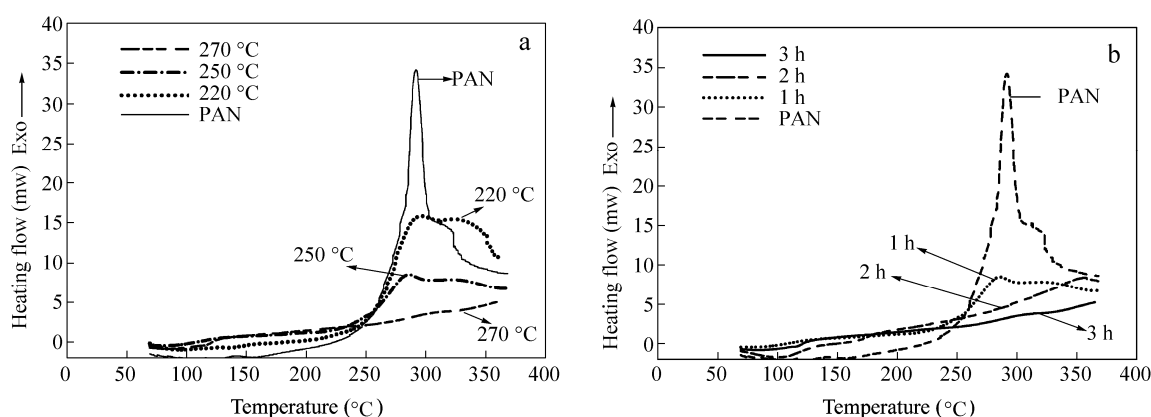


Fig. 3 DSC curves of stabilized samples in different temperatures (a) and dwell times (b)

Table 4. Enthalpy and stabilization indexes of stabilized samples at different temperatures

Samples	PAN	Stabilized PAN temperature (°C)		
		200	250	270
ΔH (J)	180.8	63.2	17.4	11.1
SI (%)	NA	65.0	90.4	93.8

Constant time of 1 h and heating rate of 1 K/min

Table 5. Evaluated parameters for stabilized samples with different dwell times

Samples	PAN	Stabilized PAN (duration time (h))		
		1	2	3
ΔH (J)	180.8	11.1	10.8	9.1
SI (%)	NA	93.8	94.0	95.1
EOR (%)	NA	91.3	92.1	93.1
Weight loss (%)	NA	32.1	36.7	42.8

Constant temperature of 270 °C and heating rate of 1 K/min

The last method has been used to measure the stabilization index was utilization of XRD patterns of untreated and stabilized nanofibers. XRD has usually been used to study the crystalline structure changes during thermal stabilization by many researchers^[14, 34]. Figure 4 shows the XRD patterns of PAN precursor fibers and the fibers stabilized at various temperatures. It's obvious that the main diffraction peak for PAN fibers occurs at around $2\theta = 17^\circ$, which is corresponding to plane (100) of a hexagonal structure. Another peak is around $2\theta = 29^\circ$ that is related to plane (110)^[35]. As mentioned before, when the PAN nanofibers is heated above 180 °C in the presence of oxygen, $C\equiv N$ bonds are converted into $C=N$ bonds as the ladder polymer is formed. In this case, a new diffraction peak in $2\theta = 25^\circ$ comes to exist; corresponding to a sheet-like structure ladder polymer. The percentage conversion of $C\equiv N$ to $C=N$ groups depends on the extent of stabilization and can be attributed to decreasing the intensity of the peak at $2\theta = 17^\circ$ and forming a broad peak at $2\theta = 25^\circ$ ^[36].

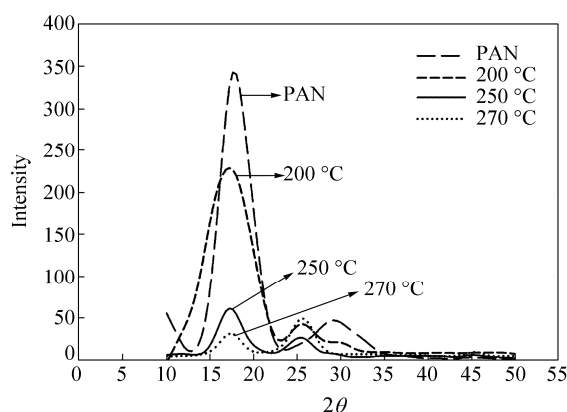


Fig. 4 XRD patterns of samples untreated and stabilized at different temperatures

Aromatization index (AI) is a useful parameter indicating the content of aromatic structures in stabilized polymer and can be obtained from XRD patterns. AI is calculated by Eq. (3)^[17]:

$$AI(\%) = \frac{I_a}{I_a + I_p} \times 100 \quad (3)$$

where, I_a and I_p are the intensity of a new peak ($2\theta = 25^\circ$) and the main peak at $2\theta = 17^\circ$.

Another way to measure aromatization index (which can indicate stabilization yield as SI and EOR) is as Eq. (4).

$$AI(\%) = \frac{I_0 - I_i}{I_0} \times 100 \quad (4)$$

where I_0 is the intensity of the diffraction peak of the original PAN nanofibers at $2\theta = 17^\circ$ and I_i is the intensity of the same peak of the stabilized nanofibers. The AI value increases with temperature or heat-treatment time during stabilization. Figure 4 shows XRD patterns of samples at different stabilization temperatures. As Table 6 shows, after stabilization at 270 °C, the yield of the reaction is enhanced to 90% and the process is nearly accomplished, so 270 °C seems to be the most efficient stabilization temperature. The evaluation methods of stabilization index that is discussed, is one of the most accurate technique that can be employed to optimize preoxidation parameters. The results obtained are similar to previous methods data.

Ko *et al.*^[17] modified this testing method and recommended that the AI value can be used to check the stabilization process and estimate the ladder structure of the polymer. A higher percentage conversion (AI value) means that the stabilized fibers have more ladder characteristics. Table 6 shows AI and SI values of the stabilized nanofibers. As a result the higher stabilization temperature yields a stabilized polymer with greater ladder content. A suitable AI value of stabilized fibers for activating is calculated to be about 50%–60%.

Table 6. AI and SI values of the stabilized nanofibers at different temperatures

Samples	PAN	Stabilized PAN temperature (°C)		
		200	250	270
SI (%)	NA	56.1	83.4	90.0
AI (%)	NA	22.0	50.0	62.3

According to the consistent confirmed results obtained by employed analyzing techniques, the conditions that contain ranges of temperature and time of 250–270 °C and 1–2 h using heating rate below 2 K/min had the maximum stabilization efficiency, so they were selected as the suitable conditions for stabilization stage prior to carbonization and activation process. Simultaneous carbonization and activation were carried out under pure nitrogen (99.99%) atmosphere at temperatures ranging from 800 °C to 1200 °C for 1 h to achieve ACNF. The

physical properties of the ACNF are presented in Table 7. As it is shown, the porosity, surface area and pore volumes increased by increasing the temperature of activation. Also it can be found that the pores can be classified as micro-ones according to IUPAC definitions.

Table 7. Surface parameters of activated carbon nanofibers obtained at different carbonization/activation temperatures

Carbonization/activation temperature (°C)	1200	1000	800
Specific surface area (m ² /g)	840	362	218
Pore volume (cm ³ /g)	0.075	0.128	0.289
Pore diameter (nm)	0.71	0.70	0.68
Porosity (%)	60.0	25.6	16.0

Finally, a regular adsorption experiment was used to evaluate the dye removal potential of the produced ACNF. Adsorption experiment was carried out with 200 mg/L of Basic blue 41 dye (a cationic dye) using batch equilibrium technique at 25 °C using powder activated carbon (AC), chitin and ACNF. Figure 5 shows dye removal efficiency for the adsorbents. It is observed that adsorption capacity of the ACNF is much higher than that of the other adsorbents making it appropriate for the dye molecule adsorption from its aqueous solution. Higher adsorption capacity can be related to the high porous structure of the produced ACNF providing physical entrapping of the adsorbate molecules. Complete evaluation of the physical and chemical properties of the ACNFs including adsorption properties is under investigation by the authors which will be reported in the next related manuscript.

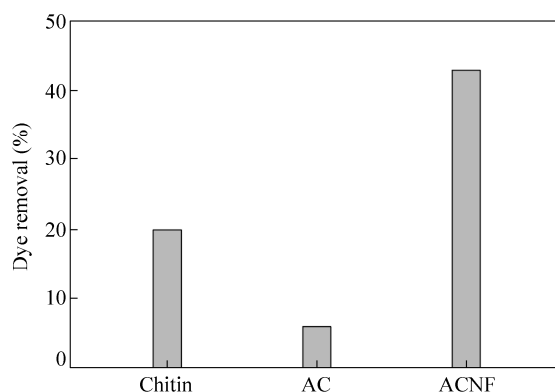


Fig. 5 Dye removal efficiency for different adsorbents

CONCLUSIONS

It is known that the quality of resulting carbon fibers depends strongly upon the degree of stabilization process during carbon nanofibers production. Hence it is important to evaluate the stabilization accurately and rapidly so as to provide information for optimizing technology parameters such as dwell time, temperature and heating rate. In this study untreated and stabilized PAN samples were evaluated using FTIR, DSC and XRD analysis. All results indicated that both dwell time and temperature of stabilization process increased the extent of reaction, but the influence of the temperature was more obvious. FTIR spectra of stabilized samples showed that the extent of the reaction was positively affected by increasing time and temperatures. In all experiments heating rate influence was negligible. In DSC curves of the samples, total enthalpy decreased by increasing the mentioned parameters, revealed improving the stabilization index. XRD patterns were also used to evaluate stabilization yield and AI value of stabilized fibers for activation was calculated to be about 50%–60%. Finally, according to the assessment of all applied methods, consistency was observed among the obtained results to propose the best process conditions. By applying optimum conditions of electro-spinning, stabilization and simultaneous carbonization and activation, using SEM, FTIR, DSC and BET techniques, ACNFs with the surface area of 840 m²/g and the porosity of 60% with micropores (average width pores of 0.7 nm) were produced in this work.

Adsorption of dye with different adsorbents showed that activated carbon nanofibers had the maximum dye removal capability. Also it is claimed that the production parameters can be arranged in the manner which is leading to the appropriate pore volume and pore size distribution for the ACNF application as molecular sieving in water pollution control.

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