Jurnal Teknologi

Full Paper

FABRICATION AND CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE COMPOSITE NANOFIBER MEMBRANE FOR WATER FLUX PROPERTY

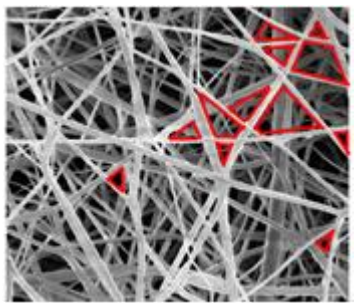
Azizul Mohd Zahari[a], Abdull Rahim Mohd Yusoff[b*], Nor Aziah Buang[a], Palanivel Satishkumar[b], M Jasmin Fathi Jasni[a], Zulkifli Yusop[b]

[a]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Centre for Environmental Sustainability and Water Security (IPASA), Research Institute for Sustainable Environment (RISE), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

Article history
Received
24 April 2015
Received in revised form
4 May 2015
Accepted
9 May 2015

*Corresponding author
rahim@kimia.fs.utm.my

Graphical abstract



Abstract

This research is about the investigation of the pure water flux property of composite polyvinylidene fluoride (PVDF) nanofibers. Electrospinning technique was used to prepare the composite electrospun nanofibers. PVDF was dissolved in N,N-dimethylformamide (DMF) solvent and blended together with activated carbon (AC) and polyvinylpyrrolidone (PVP). The nanofibers were characterized to determine the morphologies, wettability property, and its tensile strength. The fabricated nanofibers diameter was found in the range between 20 to 180 nm. The presence of AC deteriorates the mechanical properties of the nanofibers as the size of AC is larger than the external diameter of the nanofibers. The results of contact angle confirmed that the fabricated nanofiber exhibit less hydrophobic in the presence of PVP and AC. The less hydrophobic nature of proposed nanofiber might be useful for the water treatment process.

Keywords: Electrospinning, polyvinylidene fluoride, nanofibers

Abstrak

Kajian ini adalan mengenai penyiasatan sifat fluks terhadap komposit gentian nano polyvinylidene fluoride (PVDF). Electrospinning telah digunakan untuk menyediakan komposit gentian nano. PVDF telah dilarutkan di dalam N, N-dimethylformamide (DMF) dan dicampur bersama dengan karbon diaktifkan (AC) dan polyvinylpyrrolidone (PVP). Gentian nano telah dicirikan untuk menentukan morfologi, kebolehbasahan, dan kekuatan. Diameter gentian nano didapati dalam julat di antara 20-180 nm. Kehadiran AC merosotkan sifat mekanik gentian nano kerana saiz AC adalah lebih besar daripada diameter luar gentian nano. Eksperimen mengesahkan bahawa gentian nano yang direka kurang hidrofobik setelah PVP dan AC ditambah. Sifat kurang hidrofobik dimiliki oleh gentian nano yang dicadangkan adalah berguna untuk proses rawatan air.

Kata kunci: Electrospinning, polyvinylidene fluorida, gentian nano

1.0 INTRODUCTION

Electrospinning has been acknowledged as an efficient nanotechnology technique to produce nanofibers. Nanofibers has been extensively exploit for many applications such as protective clothing, electronic sensors, tissue engineering scaffolding, enzyme immobilization, and also as filter media [1–3].

Nanofibers have magnificent characteristics that capable to trap many contaminants. Porous fiber materials like nanofibers provide advantages of high water filtration efficiency. Due to many layer of interconnected nanofibers forming a fibers mat resulted in formation of pores that can be applied as a filter media.

The refinement characteristics of the nanofibers membrane via electrospinning technique can match to the scale (<0.3 µm) of the structural elements of the contaminant to be captured and the channels of the nanofibers has been acknowledged as an efficient media for the separation of many compounds [4]. This is due to unique interconnected opening cavity structure of the nanofibers membrane enables them to function well as filter media to trap the contaminants [5]. Hence, nanofibers membrane is used for the production of safe drinking water (water softening, removal of micropollutants) and also for the treatment of waste and process waters [6,7].

Polyvinylidene fluoride (PVDF) has been explored as polymer materials for the fabrication of membrane due to its outstanding properties such as high mechanical strength, chemical resistance and thermally stable. Due to its hydrophobicity, this material may be susceptible to fouling during filtration process [8]. Membrane can be fouling as solutes or particles deposited onto the surface and block the pore of the nanofibers membrane cause the performance of the nanofibers to be degraded [9]. Thus, reducing the permeability and final separation performance of the membrane, reducing the lifespan of the membranes and then causing more operation cost [8].

There are several modification approaches can be done such as surface modification and blending modification for improving the surface hydropilicity, roughness and structure [8, 10].

Polymer solution blending with fillers is the most prevalent method to prepare composite nanofibers has been widely demonstrated. According to Sawicka and Gouma (2006), electrospinning combination of polymer with composite allows control over composition and reduces the preparation time [11].

To increase both the permeability and fouling resistance, blending of PVDF with hydrophilic group of filler like PVP (which is hydrophilic in nature) was believed to gives excellent miscibility with improved pure water permeability and enhance hyrophilicity of the membrane [8,12]. In addition, PVP was commonly used as additive for membrane fabrication that functioned as pore performer and control the structure of the nanofibers [13].

In fact, until today there are unlimited researches to be done to enhance and improve the characteristics of the electrospun nanofibers to suit for different applications by addition of multiple materials. For example, carbonaceous materials have been applied in various research fields for application such as reinforcement of materials, electronic devices, and supporter of catalyst. They also can be used in a powerful adsorbent for diverse toxic and harmful compounds [14].

2.0 EXPERIMENTAL

2.1 Chemicals

Polyvinylidene fluoride (PVDF Kynar 740, Mw = 156,000 g/mol) was used as received. A charcoal activated granulated (AC, Mw = 1201 g/mol) and N,N-dimethylformamide (DMF) were obtained from QRëC. The charcoal activated was grinded and sieve to the size < 150 µm. Polyvinylpyrrolidone (PVP, Mw = 40,000 g/mol) was obtained from Sigma-Adrich.

2.2 Fabrication of PVDF and Composite PVDF Electrospun Nanofibers

In this study, polyvinylidene fluoride (PVDF Kynar 740 grade) in a form of pallets was used as a polymer to be electrospun together with additives and solvent. A 1.8 g of PVDF was dissolved in DMF to the concentration of 18% (w/v). The polymer solution was kept stirred until homogeneous at 60 oC.

After all the PVDF pellets were dissolved, the fillers were added and blended together into the polymer solution with different weight percent. The nanofibers prepared as follows: NF0 (18% PVDF with no filler), NF1 (18% PVDF with 1% AC), NF2 (18% PVDF with 1% PVP), NF3 (18% PVDF with 1% AC and 1% PVP). Before electrospinning process was done, the polymer solution was kept in the ultra sonicator bath for 1 h. The total volume loaded into the syringe for all the polymer solution is 30 mL.

Electrospinning operational parameters such applied potential energy (high voltage), working distance of the spinneret and the collector, flow rate, needle size, temperature were optimized at 18 kV, 150 mm, 1.5 mL/h, and ambient temperature respectively.

2.3 Characterization of Electrospun Nanofibers

The morphology of the PVDF nanofibers by electrospinning was observed using a scanning electron microscope (FESEM); Zeiss Supra 35VP operated at 5 kV. Before the observations, all the samples were sputter-coated with Au. The fiber diameter was analyzed from FESEM image by imageJ software (http://rsb.info.nih.gov/ij/).

The mechanical properties of the electrospun nanofibers were obtained from LRX 2.5 kN Lloyd tensile tester. A minimum of five strips of dimension 30 mm x 13 mm x thickness of each of the membrane were tested from each of the nanofibers membrane. The controlled force module was selected with speed set at 10 mm/min. The electrospun nanofibers thickness was measured using electronic external micrometer.

The static surface contact angle of the electrospun membrane was measured using contact angle analysis system by data physic OCA. A 0.5 µL droplet of distilled water was dispensed onto the membrane using a sessile drop method and the measured angle was recorded. A picture of the drop was captured after the drop set onto the sample. The contact angle could be calculated by the software through

analyzing the shape of the drop. The contact angle θ was an average of 8 measurements.

2.4 Flat Sheet Membrane System and Filtration Protocol

To determine the water permeability of the nanofibers membrane, flat sheet testing unit for direct liquid penetration was used. Figure 1 shows the flat sheet membrane testing system.

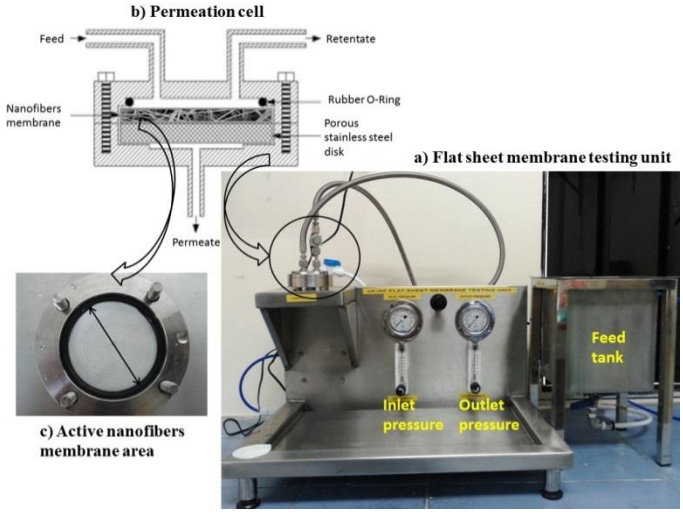


Figure 1 Components of the flat sheet membrane testing unit, a) Overall picture of the flat sheet membrane testing unit consists of feed tank, inlet and outlet pressure, permeation cell and pump at the back of the unit; b) schematic diagram of the permeation cell; c) Active nanofibers membrane area for direct liquid penetration

The fabricated nanofibers was firstly conditioned with distilled water for 24 h and dried at room temperature. Circular electrospun nanofibers membranes of 52 mm in diameter with an effective area of 21.24 cm^2 were cut out and subsequently used for flux studies.

The nanofibers membrane was undergoes compaction for stabilization for 1 h with pressure 1.5 bar, while the flux pressure was set at 1.0 bar. Flux can be calculated by the formula:

$$\text{Flux, } J = \frac{\text{Volume permeation rate, } (V/t)}{\text{Nanofibers membrane area, } A}$$

Where J is the flux (L/m^2h), V is the permeate volume (L), A is the effective nanofibers membrane area (m^2) and t is the time (h). The effective nanofibers membrane area is 21.24 cm^2.

The pure water flux was measured for every 10 min of permeate collected. Pure water experiment was continued until the flux is stable.

3.0 RESULTS AND DISCUSSION

3.1 Effects of Composite Filler towards Electrospun Nanofibers Characteristics

In the experiment, PVDF was very easy to electrospun. PVDF concentration was set constant at 18 wt% with or without fillers. The electrospinning of the PVDF and PVDF composite blend solution was greatly affected by the polymer content and composition and resulting characteristics of electrospun nanofibers as shown in Table 1.

The composition of each solution influence the dispersion and attraction of the fiber formed on the collector, thus affecting the thickness of the nanofibers. As the polymer solution was added with different filler, the concentration of the solution was increased. NF0 which is a single polymer for instance, have lower solution concentration forming a lighter nanofibers than others are randomly flew inside the electrospinning chamber besides deposited onto the collector making the thickness value for NF0 is smaller than the others. The total volume loaded into the syringe for all the polymer solutions are the same. Hence, the thicknesses of each electrospun nanofibers are comparatively can be compared. The thickness of each electrospun nanofibers is shown in Table 1.

Table 1 Properties of PVDF electrospun nanofibers

Nanofiber properties	Electrospun nanofibers			
	NF0	NF1	NF2	NF3
Average fiber diameters (nm)	123.49	101.26	108.09	106.37
Average thickness (mm)	0.47	0.56	0.58	0.57
Tensile strength (MPa)	2.4420	2.2131	2.9663	1.1391

In the electrospun nanofibers membrane, the network of interconnected fiber floss considered very complex caused complex flow path [6]. The complexities of the flow path are corresponding to the thickness of the electrospun nanofibers membrane. The thicknesses of each electrospun nanofibers are correspondent to the nanolayers of fibers formed during electrospinning.

In this research, direct liquid penetration was applied; hence the electrospun membrane was designed necessary to withstand a normal domestic water pressure for a household. The tensile properties of the electrospun nanofibers was measured and found that the addition of AC into the polymer solution reduces the mechanical properties. This may happen due to the size of the carbon loading are slightly

bigger than the internal diameter of the fiber floss. Thus, does not improve the mechanical properties of the electrospun nanofibers. Larger particles would probably deteriorate the mechanical properties of the materials.

Surface contact angle of the nanofibers membrane was measured using sessile drop observation. The surface contact angle of each nanofibers membrane is shown in Figure 2. The value of the surface contact angle of PVDF nanofibers membrane is high with the complement to the strong hydrophobicity of PVDF material to water. Usually PVDF exhibit high contact angle of ~130-140o [15,16]. Figure 2 shows a water droplet formed on the PVDF nanofibers and pointed a slightly decrease in the surface contact angle value. Addition of PVP and AC into the polymer solution improves in the electrospun nanofibers wettability property. This may help the nanofibers membrane to be less prone to fouling.

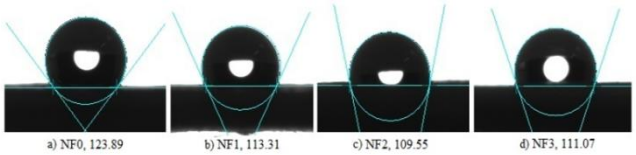


Figure 2 Micrograph of surface contact angle of electrospun nanofibers

3.2 Influence of Different Fillers Composition on Size and Morphology

At 18 wt%, NF0 single PVDF electrospun nanofibers obtained consists of beads-free fiber with uniform size due to molecular chain entanglement that prevents the breakup of the polymer jet into droplets. Electrostatic stress permit the jet to stretched and elongate to form a fine nanofibers [17].

Table 1 shows the average fiber diameters of different electrospun nanofibers membrane of PVDF, with or without fillers.

In this experiment, the concentration of the polymer solutions however is not significantly affecting much on the average fiber diameters. The fiber diameter distributions are shown in Figure 3.

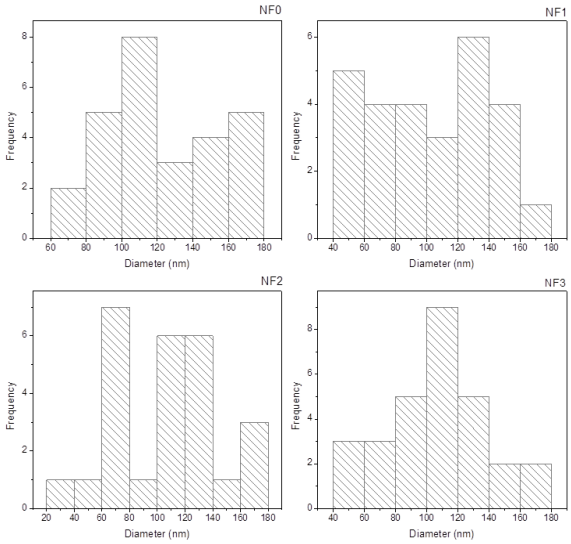


Figure 3 Fiber diameter distributions of PVDF and its composites

Representative FESEM micrograph of PVDF and its composites nanofibers matrix prepared are shown in Figure 4. From the FESEM micrograph, NF1 and NF3 polymer solution formed a beaded nanofibers due to the AC loading into the polymer solution cause the reduction of the fiber diameter an also caused the non-uniform fibers diameter but selective in a few diameter range.

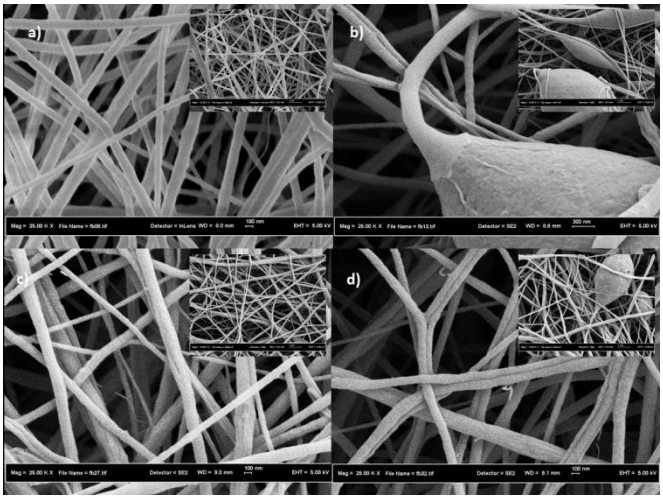


Figure 4 FESEM micrograph of (a) NF0 (PVDF), (b) NF1 (PVDF with AC), (c) NF2 (PVDF with PVP), (d) NF3 (PVDF with PVP and AC)

The beaded nanofibers are due to activated carbon loading into the polymer solution which is larger in diameter compared to the nanofibers diameter. From Figure 3, it was found that the diameter size nanofibers becoming ununiformed as the composite electrospun was fabricated. The floss diameter range of the electrospun nanofibers is 20-180

nm. The most abundant fiber diameter was at 100-120 nm found on each fabricated electrospun nanofibers.

3.3 Influence of Nanofibers Characteristics towards Permeability Performance

The performance of electrospun PVDF nanofibers membrane with/without filler was tested on the permeation cell. The permeation fluxes of fresh water are shown in Figure 5.

The NF0 nanofibers membrane shows the highest water flux rate (710.16 L/m2h) as it complement to the highest contact angle value due to its hydrophobicity characteristics.

The possible reason for this phenomenon to happen to hydrophobic PVDF membrane is because there is almost no hydrogen bonding interaction in the boundary layer between the nanofibers membrane interface and water [8]. The water is forced by pressure applied to pass through the nanofibers membrane. Water is not being absorbed by the membrane like other hydrophilic membrane. This allows NF0 to have highest flux rate.

Despite NF0 possess highest permeate flux, the repulsion of water molecules away from hydrophobic PVDF nanofibers membrane surface is an impulsive process with an entropy increasing and therefore the tendency of unwanted particles to absorb onto the membrane surface and dominate the boundary layer. Thus, this may lead to different membrane stability. NF0, NF1, NF2, NF3 reach stability at different time period (100, 150, 180, and 150 min, respectively). Nanofibers membrane is a matrix of multiple nano sheets layers were each layer have complex inter-connected fibers. Within this interconnected fibers, the cavity opening/pore were formed due to the nature of electrospinning. Structural analysis from the morphological of the electrospun nanofibers, NF1 and NF3 shows the formation of beaded fibers due to AC loading cause a greater cavity/pore from the interconnected fiber floss cause the cavity/pore are larger compared the electrospun nanofibers that does not have beaded fiber. This influences the water permeability performance of the nanofibers membrane. NF1 and NF3 nanofibers membrane fluxes rate are relatively high when compared to NF2 nanofibers membrane. The flux value for NF1 and NF3 are 467.27 L/m2h and 510.78 L/m2h respectively.

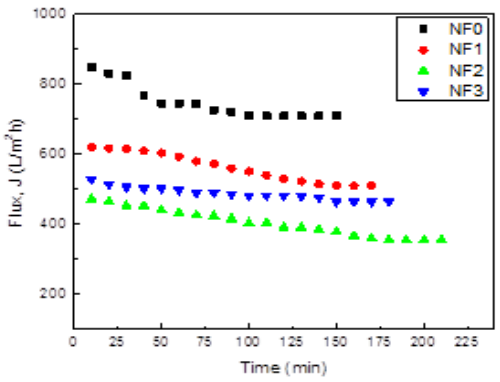


Figure 5 Pure water flux, J of different type of fabricated

NF2 possesses surface contact angle value slightly lower than the other membranes however gives lowest flux rate which is 355.07 L/m2h. There must be a little water absorption occurred on the nanofibers membrane. NF2 show the most sustainable fluxes reading due to the highest nanofibers density packing within the membrane based on the thickness value.

During electrospinning, certain nature of the technique that is understandable is that the formations of the nanofibers are random and cannot be seen in our naked eyes. The depositions of the nanofibers on the collector are arbitrary that causes the thicknesses of each place on the collector are different. Another reason is the addition of filler onto the polymer solution cause to different thickness of each nanofibers. This may lead to the different number of nano sheets layer on each part of the fiber, thus may influence the permeability performance of the membrane.

For water filtration membrane, higher flux rate are highly desirable but less prone to fouling. Higher flux rate reduces the operational time during filtration, hence save the filtration cost.

4.0 CONCLUSION

Electrospinning was used to fabricate four types of nanofibers. The characterization of prepared nanofibers membrane was studied in details. Structural analysis of the nanofibers membrane using FESEM found that the nanofibers diameter range is 20-180 nm.

Tensile strength analysis of the nanofibers membrane discovered that larger particles deteriorate the mechanical properties of the nanofibers. AC loading into NF1 and NF3 does not improve the mechanical properties of the nanofibers. Study on the AC loading into the nanofibers to the rejection and removal of contaminants will be investigated in the future.

Further investigation of the nanofibers wettability properties showed that addition of PVP and AC

improves the water contact angle value. Flux rate discovered to have a significant relationship with the contact angle value due to the interaction of nanofibers membrane with water. More hydrophobic nanofibers (NF0) membrane gives higher flux rate due to less or almost no interaction with water.

Acknowledgement

This work was financially supported by Long-Term Research Grant Scheme 4L810-(Grant No. 203/PKT/6720006), provided by Ministry of Higher Education, Malaysia. We should also thank University Teknologi Malaysia, Johor Bahru, Malaysia for facility that has been provided.

References

[1] Huang, Z. M., Zhang, Y. Z., Kotaki, M., Ramakrishna, S. 2003. A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites. *Compos. Sci. Technol.* 63: 2223-2253.

[2] Sathishkumar, P., Kamala-Kannan, S., Cho, M., Kim, J. S., Hadibarata, T., Salim, M. R., Oh, B. T. 2014. Laccase Immobilization on Cellulose Nanofiber: The Catalytic Efficiency and Recyclic Application for Simulated Dye Effluent Treatment. *J. Mol. Catal. B Enzym.* 100: 111-120.

[3] Sathishkumar, P., Chae, J. C., Unnithan, A. R., Palvannan, T., Kim, H. Y., Lee, K. J., Cho, M., Kamala-Kannan, S., Oh, B. T. 2012. Laccase-poly(lactic-co-glycolic acid) (PLGA) Nanofiber: Highly Stable, Reusable, and Efficacious for the Transformation of Diclofenac. *Enzyme Microb. Technol*. 51: 113-118.

[4] Qin, X. H., Wang, S. Y. 2006. Filtration Properties of Electrospinning Nanofibers. J. Appl. Polym. Sci. 102: 1285-1290.

[5] Feng, C., Khulbe, K. C., Matsuura, T., Tabe, S., Ismail, a. F. 2013. Preparation and Characterization of Electro-spun Nanofiber Membranes and Their Possible Applications in Water Treatment. *Sep. Purif. Technol.* 102: 118-135.

[6] Kaur, S., Sundarrajan, S., Rana, D., Matsuura, T., Ramakrishna, S. 2012. Influence of Electrospun Fiber Size on the Separation Efficiency of Thin Film Nanofiltration Composite Membrane. *J. Memb. Sci.* 392-393: 101–111.

[7] Nasreen, S., Sundarrajan, S., Nizar, S., Balamurugan, R., Ramakrishna, S. 2013. Advancement in Electrospun Nanofibrous Membranes Modification and Their Application in Water Treatment. *Membranes (Basel)*. 3: 266-284.

[8] Liu, F., Hashim, N. A., Liu, Y., Abed, M. R. M., Li, K. 2011. Progress in the Production and Modification of PVDF Membranes. *J. Memb. Sci.* 375: 1-27.

[9] Kaur, S., Rana, D., Matsuura, T., Sundarrajan, S., Ramakrishna, S. 2012. Preparation and Characterization of Surface Modified Electrospun Membranes for Higher Filtration Flux. *J. Memb. Sci.* 390-391: 235–242.

[10] Ahmad, A. L., Abdulkarim, A. A., Ooi, B. S., Ismail, S. 2013. Recent Development in Additives Modifications of Polyethersulfone Membrane For Flux Enhancement. *Chem. Eng. J.* 223: 246-267.

[11] Sawicka, K. M., Gouma, P. 2006. Electrospun Composite Nanofibers for Functional Applications. *J. Nanoparticle Res.* 8: 769-781.

[12] Kang, G., Cao, Y. 2014. Application and Modification of Poly(Vinylidene Fluoride) (PVDF) Membranes – A Review. *J. Memb. Sci.* 463: 145-165.

[13] Nasir, M., Matsumoto, H., Minagawa, M., Tanioka, A., Danno, T., Horibe, H. 2007. Preparation of Porous PVDF Nanofiber from PVDF/PVP Blend by Electrospray Deposition. *Polym. J.* 39: 1060-1064.

[14] Lee, K. J., Shiratori, N., Lee, G. H., Miyawaki, J., *et al.* 2010. Activated Carbon Nanofiber Produced from Electrospun Polyacrylonitrile Nanofiber as a Highly Efficient Formaldehyde Adsorbent. *Carbon N. Y.* 48: 4248-4255.

[15] Kaur, S., Ma, Z., Gopal, R., Singh, G. 2007. Plasma-induced Graft Copolymerization of Poly(Methacrylic Acid) on Electrospun Poly(Vinylidene Fluoride) Nanofiber Membrane. *Langmuir*. 23: 13085-13092.

[16] Feng, C., Khulbe, K. C., Matsuura, T., Gopal, R., *et al*. 2008. Production of Drinking Water from Saline Water by Air-Gap Membrane Distillation Using Polyvinylidene Fluoride Nanofiber Membrane. *J. Memb. Sci.* 311: 1-6.

[17] Sethupathy, M., Sethuraman, V., Manisankar, P. 2013. Preparation of PVDF/SiO2 Composite Nanofiber Membrane Using Electrospinning for Polymer Electrolyte Analysis. *Soft Nanosci. Lett*. 03: 37-43.