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The effect of polymer concentration on electrospun PVDF membranes for desalination by direct contact membrane distillation

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Abstract: Membrane separation technology holds great potential in advancing desalination and water/wastewater treatment to improve the efficiency of impurities removal as well as to augment water supply. Various membrane based technologies are currently being applied for these purposes. Among the current membrane-based technologies, the MD process presents many attractive features compared to others. MD is a low pressure, non-isothermal membrane separation process with a hydrophobic microporous membrane which offers a solution for the treatment of concentrated solutions that are not viable for reverse osmosis. An increasing array of research is being conducted to fabricate novel membranes in order to optimize the performance of the MD process. Different parameters such as pore size, porosity and thickness affect membrane performance during the MD process. Electrospining method for fabrication of membranes allows for controlling of mentioned properties. In this study, by taking into consideration that the polymer concentration has the significant effect on the resultant nanofiber diameter and electrospun nanofibrous membrane (ENM) structure, different Polyvinylidene fluoride (PVDF) membranes with different fiber diameters and physical properties were obtained by varying polymer concentration from 20 to 24.5 wt%. Fabricated membranes were tested for desalination by direct contact membrane distillation (DCMD). The bead-free nanofiber with diameter of 240 nm obtained at 20 wt% concentration of polymer solution and increasing PVDF concentration lead to an increase of fiber diameter to 464 nm. Results of DCMD operation show that by increasing concentration of polymer solution, the permeate flux decreases. For all membranes the salt rejection ratio was more than 99.9%.

Key words: PVDF Concentration, Electrospun nano-fiberous membranes, Desalination, Membrane distillation

1. INTRODUCTION

Increase in demand for fresh water has become one of the most significant challenges nowadays. Swift growth of population alongside with industrial and agricultural activities has caused the need for water. Predictions demonstrate that the demand continues to rise up to 40% of today's need in 2030 (Shirazi et al. 2016).

As regards that saline water is very abundant, considerable amount of research has been done in order to supply fresh or agricultural water from these resources. Technologies based on membranes have played a significant role in desalination and purification of water and wastewater. Among these technologies, Membrane Distillation compared to other approaches has showed some substantial aspects (Khawaji et al. 2008). This process is appropriate for desalination of saline water that is impossible to purify by other membrane methods such as reverse osmosis. Membrane distillation (MD) is a non-thermal membrane technology which has been introduced for over 50 years and still requires development for industrial application. Driving force for membrane distillation is vapor pressure which is cause by temperature difference alongside the membrane (Tijing et al. 2014).

Membrane used for MD should be hydrophobic and porous so that it prevents pore wetting by aqueous feed. Furthermore, membrane should also have high porosity, appropriate pore size with narrow distribution and high thermal and chemical resistance. These specifications can be met by proper material and fabrication method (Essalhi and Khayet 2014).

Electrospinning process has been used to produce nano-fibers for over 20 years now. Newly, some membranes applied for MD processes have been made of nano-fibrous membranes (ENMs), which have some proper aspects for application in membranes distillation process such as high hydrophobicity, high void volume fraction (i.e. very large surface area to volume ratio), high surface roughness and low thermal conductivity (low thermal conductivity due to elctrospun nano-fibrous causes high efficiency for the MD process), interconnected inner structure and good mechanical resistance (Liao et al. 2013).

In this paper, with regards of the fact that polymer concentration has a significant effect on the final diameter of nano-fiber, performance of fabricated nano-fibrous membranes with various fibers' diameters in direct contact membrane distillation for saline water desalination has been investigated. In fact, the main objective of this article is to inquire the effects of fibers' diameter on the permeation rate of nano-fibrous membranes. At the beginning, various concentrations of polyvinylidenefluoride (PVDF) were electrospun in efficient conditions. The concentration in which we achieved the bead-free nano-fiber with smallest diameter was opted as the suited concentration for fabrication. Afterwards, to investigate diameter alterations, four solutions with different concentrations in the range of 20%wt to 24.5%wt were electrospun. Conclusions of the stated alterations will be thoroughly discussed in conclusion part.

2. MATERIALS AND METHODS

2.1 Materials

Polyvinylidene fluoride (PVDF) with average molecular weight of 146000 grams per mole and granule shape was used as polymer. N,N-dimethylacetamide(DMAC) and acetone purchased from merck, were used to form the polymer solution which have density of 0.94 and 0.791 grams per cubic centimeter respectively. Lithium chloride (LiCl) purchased from merck was used as an additive to increase the conductivity of the polymer solution.

2.2 Preparation of polymer solution

Preparation of solution was done by adding different weights of PVDF polymer to the mixture of dimethylacetamide and acetone by the weight ratio of 6 to 4. Amount of 0.004 wt% of Lithium chloride results in increase of conductivity and improves dope electro-spin ability. Afterwards, the solution was placed on stirrer for 6 hours to become completely homogenous and transparent.

2.3 Electrospining of PVDF membranes

Firstly, the solution is inserted in a glass syringe. Then, by applying the most efficient condition, feed rate of 1 ml/hr, voltage 2 kV, 21 cm distance between the needle and collector, electrospining process was began. After the fabrication, membranes were dried in oven at 80 °C for 30 min.

2.4 Direct contact membrane distillation (DCMD)

Performance of the membrane with an effective area of 50 cm^2 was tested by the DCMD apparatus. DCMD apparatus has two containers. In this work, distilled water and a solution containing salt and water with the concentration of 42 g/l (approximately concentration of The Persian Gulf seawater) were used as permeate and feed respectively. During experiment concentration of salt in both solutions was measured by a conductivity meter. Then, the membrane is placed in module between two hot and cold chambers. Temperatures of the feed and permeate are held at 60 and 20 °C respectively. Volumetric flows of both streams are 1.4 l/min and the pressure of the both sides is controlled at 0.2 bar. Both containers are placed upon balance to record the mass difference in a computer connected to them.

3. CHARACTERIZATION OF ELECTROSPUN MEMBRANE

To examine the surface of the nano-fibrous membrane, field emission scanning electron microscope was used. At first, samples were sprayed with gold vapor for 80 seconds to form a thin layer of gold on the surface of the membrane. To analyze the fiber diameter imagej software was used. To obtain the average diameter of the nano-fibers, 100 different fibers are measured and their average is reported.

To calculate the thickness of the nano-fibrous layers ACCUD IP54 digital micrometer was used.

4. RESULTS AND DISCUSSIONS

4.1 SEM images of the ENMs and effects of the PVDF polymer concentration

Firstly to determine the proper concentration, different polymer concentrations have been (18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%) electrospun. In the first and second columns of the figure 1 field emission scanning electron microscopic images of nano-fibrous surface of PVDF in two different sizes are shown. According to images, a mixture of nano-fibers and beads form the structure of electrospun layer from the solutions which had the polymer concentrations of 18wt% and 19wt% in the same conditions. Formation of beads is in conjunction with surface tension, polymer concentration, solution viscosity, net charge density and electrical conductivity. Solutions with low viscosity turn into droplets more easily while exiting the jet and they are more likely to from beads. As can be seen in the figure 1 despite beads presence, electrospun nano-fibers in low concentrations also are discontinuous. Therefore, with gradually increasing the polymer concentration, beads density decreases and finally bead-free and continuous electrospun nano-fibers achieved from higher concentrations than 20wt%. This phenomenon is related to the entanglement of polymer chains which are controlled by average polymer molecule weight, distribution of molecular weight, polymer concentration and solution viscosity. In a low polymer concentration solution chain overlap does not exist, but when the concentration is increased the polymeric chains begin to overlap and entangle each other. Hence, for stability of the jet and nano-fiber formation proper entanglement of polymeric chains is necessary. According to results, when the polymer concentration is higher than 20wt%, solution density and overlapping of the polymeric chains/polymer is increased dramatically. As a result, 20wt% concentration was selected as the appropriate concentration for electrospinning of the first membrane. Other membranes were elecrospun with the step of 1.5 wt%; other membranes' concentrations for electrospinning were 21.5 wt%, 23 wt% and 24.5 wt%.

4.2 Characteristics of the ENMs

FESEM images of PVDF nano-fibers' surface with two different scales are shown in Figure 2. Results from measuring average diameter of nano-fibers are reported in table1. It was illustrated that with altering concentration from 20 wt% to 24.5 wt% average diameter of nano-fibers is increased. Higher polymer concentration in electrospinning process causes stronger viscoelastic force compared to electrostatic force. Therefore, it brings about higher resistance of solution to bending and stretching of jet's fluid when it flows from needle to collector. Because nano-fibers are formed by evaporation and solidification of polymer fluid, their diameter mostly is related to the amount of polymer in jet and its size. Generally, the higher the polymer solution concentration is used, the thicker nano-fibers are formed.

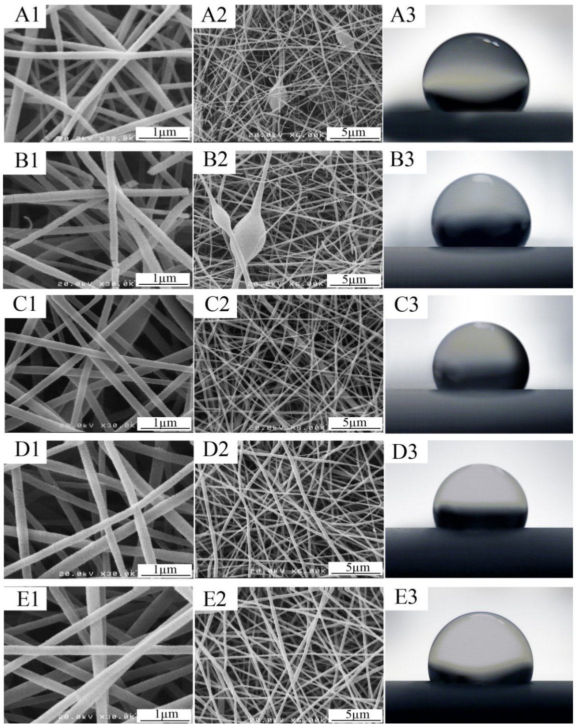

Figure 1. FESEM images and water angle contact of nano-fibrous layer of PVDF were provided from different solution concentrations (A1, A2, A3: solution 18 wt%, B1, B2, B3: solution 19 wt%, C1, C2, C3: solution 30wt%, D1, D2, D3: solution 21 wt%, E1, E2, E3: solution 22 wt%)

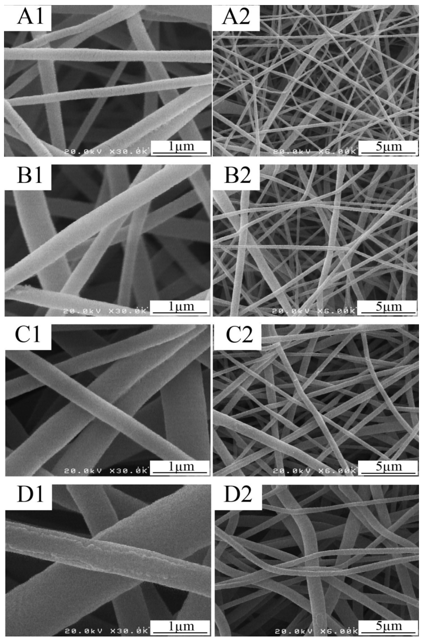

Figure 2. FESEM images and water angle contact of nano-fibrous layer of PVDF were provided from different solution concentrations (A1, A2: solution 20 wt%, B1, B2: solution 21.5 wt%, C1, C2: solution 23wt%, D1, D2: solution 24.5 wt%)

To compare the performance of the membranes, they must have the same thickness. However with the increase of PVDF concentration in the polymer solution an increase in the thickness of the membranes was observed. According to table1, the thickness of the M24-5 is considerably different from other membranes. When the fiber diameter is small, it is more prone to dissipate the electric charges to metallic collector and the repulsion among fibers will be reduced favoring a tightly packed ENM structure with thin thickness. To investigate the effect of nano-fiber diameter on the flux of the different membranes, effect of thickness should be eliminated. So, real flux is divided by the membrane thickness in order to obtain the normalized flux according to thickness. This topic is discussed in more details further.

Table 1. Nano-fibers' diameters and Membranes' Thickness

Concentration of the solution (wt%)	Membrane code	Diameter of nano-fiber (nm)	Thickness (µm)
20	M20	198±50	150±12
21.5	M21-5	221±75	215±14
23	M23	327±112	280±8
24.5	M24-5	465±145	348±16

4.3 Performance evaluation of the nano-fibrous PVDF in DCMD

As stated before, to eliminate the effect of the membrane's thickness when measuring flux, transmitted and real flux is divided by the membrane's thickness for each sample. This allows us to investigate the effect of normalized flux only with respect to concentration alterations for membrane fabrication. Figure 3 illustrates the amount of normalized flux divided by the thickness for nano-fibrous fabricated membranes by PVDF solution against different concentrations. As can be seen, with the increase of the solution concentration used for fabrication, the amount of the flux is reduced. As stated before, diameter of the nano-fibers is ranged from 197 nm (sample M20) to 465 nm (sample M24-5). Presence of thicker nano-fibers causes pores with smaller diameters and finally leads to the reduction in flux. Besides, with the increase of the nano-fibers' diameter, porosity is decreased. Structure of thicker fibers allows less empty space between them. As a result, the porosity is decreased. In general, this can be stated that with the increase of the PVDF concentration of the solution and forming thicker nano-fibers, pore diameters and porosity are decreased because of the reasons stated and as a result the amount of the transmitted flux is decreased.

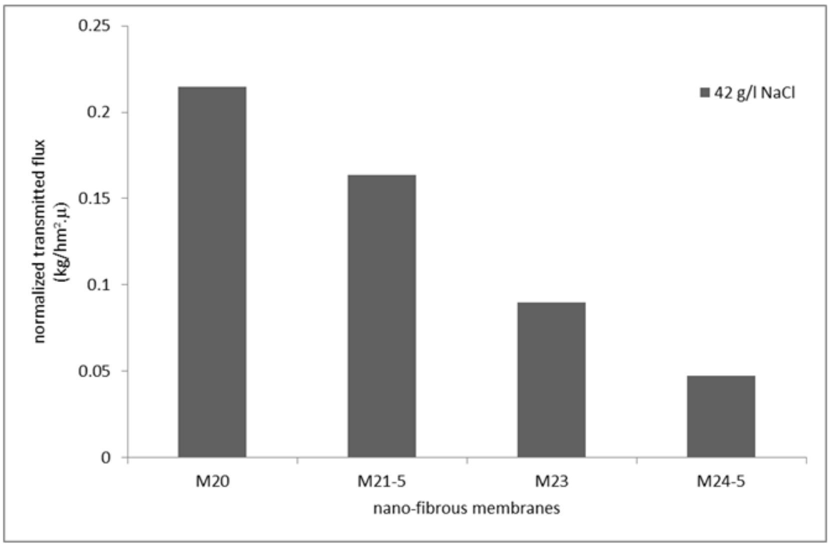

Figure 3. Transmitted flux of the PVDF fabricated electrospun membranes with different solution concentrations in DCMD

Figure 4 shows the amount of the salt rejection of the membranes. This parameter is determined by the equation:

$$\alpha=(1-C_p/C_f)*100 \quad (1)$$

in which **α** shows the salt rejection, C_p is salt concentration in the permeate side and C_f is the salt concentration in the feed side. As we can see, this parameter is obtained 99.9 percent for all membranes which shows the independence from polymer concentration and as a result nano-fibers' diameter.

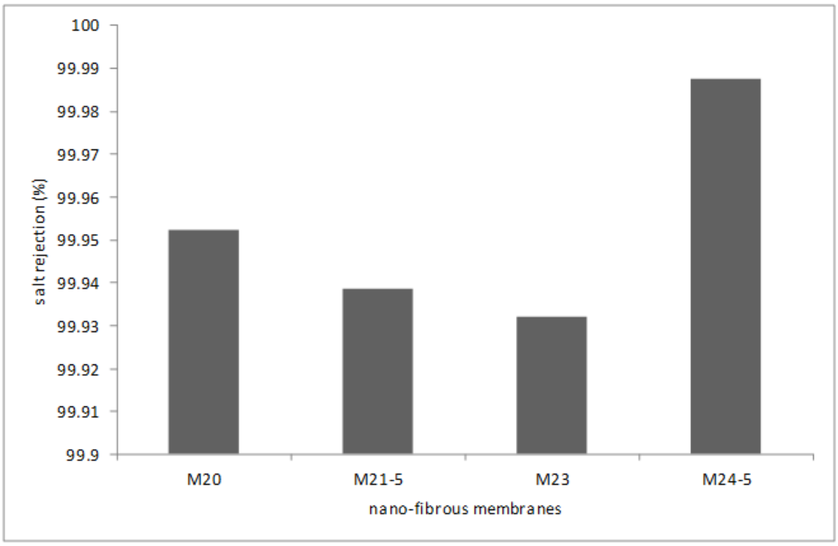

Figure 4. Comparison of desalination parameter of PVDF membranes fabricated by different solution concentrations

5. CONCLUSION

At first, different concentrations of the PVDF polymer solution with dimethyl acetamide and aceton is provided and they are electrospun in the most efficient conditions. Then, properties of the nano-fibrous layers such as nano-fibers' diameter in order to use them in DCMD are investigated. Among 5 different PVDF concentrations provided (18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%), nano-fibrous resulted from 20 wt% concentration has continuous fibers and bead-free with thinnest diameters possible. Therefore, this amount is considered the most appropriate concentration for electrospinning the first membrane. Afterwards, structures of electrospun membranes with different concentrations (20 wt%, 21.5 wt%, 23 wt%, 24.5 wt%) were examined. Performance of membranes with different nano-fibers' diameters were compared with each other. Results from DCMD test showed that with altering the concentration and consequently changes in nano-fibers' diameter, caused by the decrease in porosity and also decrease of pore diameter, leads to reduction in flux. On the other hand, increase in the pores' diameter results in increase of the overall thickness and mechanical and thermal resistance.

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