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Superhydrophobic Electro-spun Nano Fiber PVDF/SNP Membrane for Water Desalination

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Abstract

Electro-spun polyvinylidene fluoride (PVDF) nano fiber membranes were prepared and compared with PVDF casted membranes prepared by the phase inversion method. The membranes were modified in two steps to obtain super-hydrophobicity: acid treatment followed by silanization using a low-surface-energy fluoroalkyl silane (FAS). The modified membranes were tested for water desalination using a vacuum membrane distillation system. The porosity, water contact angle, and surface morphology of the membranes were examined. The porosity of the electro-spun modified nano fiber membrane (EMNM) was 94% compared to 81% for the cast modified membrane having the same composition. The EMNM showed a significant hydrophibicity of 150° compared to 119.3° for the casted modified membrane. The EMNM proved also superior to the casted modified membrane with respect to water flux, 41 lit/m^2.hr versus 25 lit/m^2.hr and salt rejection of 99.2% versus 92.7%.

Keywords: Electrospinning; Phase inversion; Nano fiber membrane; Superhydrophobicity; Vacuum membrane distillation; Desalination.

1. Introduction

Water scarcity is currently one of the most pressing and increasingly addressed environmental issues. The challenge of supplying clean drinking water, aggravated by population increase, climate change, and industrialization, has become one of the most pressing issues of our time [1]. It is expected that the growing global population, industry and urbanization, would aggravate the fresh water in crisis in many areas [2]. The quality of the few remaining freshwater sources has significantly deteriorated as a result of water pollution due to wastewater discharge into surface water bodies causing illnesses and fatalities [3, 4]. This instigated increased reliance and research in the area of desalination technology [5].

Desalination can be accomplished using a variety of methods, including electrochemical desalination cells, thermal distillation, and selective membrane technology [6]. Thermal distillation (TD) techniques [7] range between thermal vapor compression, multi-stage flash distillation (MSF), and multi-effect distillation (MED). The most commonly used selective membrane technology for producing fresh water from brackish water or seawater is reverse osmosis (RO) [8]. Its main disadvantage is flowing restrictions due to fouling and scaling issues, as well as its relatively high energy consumption. Membrane distillation (MD) received significant attention in the past two decades as freshwater is recovered from hypersaline sources using low-grade heat energy to power the filtration process [9]. It has been efficiently applied in desalination, wastewater treatment, and separation of volatile organic solvents [10].

MD is a non-isothermal separation process relying on microporous hydrophobic membranes. The less volatile solutes remain in the feed while the evaporated vapor molecules from the heated feed pass through the membrane and condense on the lower pressure permeate side [11]. An MD membrane should have high hydrophobicity, high void volume fraction (porosity), low pore tortuosity, low thermal conductivity, narrow pore size distribution, good scaling resistance properties, and be robust enough for prolonged operation [10, 12]. However, obtaining a membrane that combines high productivity and high salt rejection is still one of the most important challenges facing the membrane distillation process. More research is needed for the development of durable, high-flux, high-rejection, and energy-efficient membranes [13].

The polymers used most widely to produce membranes for MD applications are polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE) and polytetrafluoroethylene (PTFE) [14]. Recent investigations concentrated on enhancing the properties of membranes made from these well-established materials by adding chemicals to the membrane matrix to reduce thermal conductivity or to boost hydrophobicity [11, 15]. In order to produce high-performance composite membranes, a variety of transition metal oxides, including silicon dioxide (SiO_2), aluminum dioxide (Al_2O_3), magnesium oxide MgO, zinc oxide (ZnO), and zirconium dioxide (ZrO_2), have been investigated as nano fillers. One of the major metal oxides that is frequently utilized to create mixed matrix membranes is silicon dioxide nano particles (SNPs) [16].

Phase inversion, stretching, interfacial polymerization, electrospinning, and track-etching are the most widely utilized

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methods for the production of polymeric membranes [17]. The methods used in this research for producing polymeric membranes are phase inversion and electrospinning. The phase inversion technique forms polymeric membranes as thin film sheets or hollow fibers by submerging a homogenous polymeric solution in a water bath, which controls the process of turning the solution from a liquid to a solid phase [18]. Electrospinning has become a viable method for creating nano fibrous membranes [19]. The electrospinning process is highly flexible, relatively inexpensive, and enables easy arrangement of the different nano fibers into 3D networks with varying thicknesses in spite of the instabilities of the electrified jet caused by the electric field [20]. Electro-spun nano fibrous membranes (ENMs) are interesting options for the MD process because of their high porosity, interconnected structure, pore size, and thickness adjustability [21]. ENMs also have high mechanical resistance, good ratio of surface to volume, and easily soluble functional groups that increase their hydrophobicity [22, 23].

ENMs have been modified using a variety of pre and post techniques to decrease pore size and increase surface hydrophobicity while preserving higher permeate flows [24, 25]. By functionalizing ENMs with nano particles (NPs), hierarchical surface structures can be created, increasing surface roughness and producing a large number of air pockets, which increases hydrophobicity [26]. There are several methods to introduce the nano particles including adhesive deposition or dip coating, mixing with the electrospinning dope solutions, and electrospraying the nano particles while electrospinning the membranes [27]. For membrane superhydrophobicity, a membrane with low surface energy and high surface roughness is more effective. Fluoro alkylsilane (FAS) compounds have low surface energy and a hydrophobic fluoroalkyl group at one end. These compounds can be applied to membranes or nano particles to create a superhydrophobic surface which enhances the MD process.

In the present work, hydrophobic modified PVDF/SNP membranes were prepared. An indirect modification technique was used to help the hydrophobic fluoroalkyl group to graft more effectively and steadily onto the membrane surface. Several analytical methods were used to characterize and evaluate the modified membranes including scanning electron microscopy (SEM), mechanical properties, contact angles, pore size distribution and porosity measurement. The prepared membranes performance was assessed in a vacuum membrane distillation system for water desalination.

2. Materials and Methods

2.1. Materials

A commercial water insoluble polyvinylidene fluoride (PVDF) powder is used to prepare the hydrophobic porous membrane, having a density of 1.78 g/cm^3 (Alfa Aesar Inc, Germany). 1-Methyl-2-Pyrrolidinone (NMP), Mwt 99 g/mole and 99% purity was used as the solvent without further purification (Sigma Aldrich, USA). N, N-dimethyleformamide (DMF) (purity ~99.7%) was procured from Fisher Scientific, Germany. Lithium chloride (LiCl), 99% purity, was used as a modifying agent to act as a non-solvent additive to the casting solution (Sigma Aldrich, USA). Ethylene glycol (EG), assay 99%, boiling range 149-199^{o}C, (Fisher Scientific, Germeny). Silicon dioxide (SiO_2) nano powder (SNP) (purity ~99.5%, particle size: 10-20 nm) was obtained from Sigma Aldrich USA. FAS compound 1H,1H,2H,2H -Perfluoroocyltriethoxysilane, 97% was obtained from Thermo Scientific, product of China. Hydrochloric acid (HCl) and hexane were obtained from El Nasr Pharmaceutical Chemicals Co. and Piochem respectively. Isopropanol, 99% purity, Mwt 60 g/mole, density 10 g/mol (ROTH Company, Germany).

2.2. Dope solution preparation

The dope solution was prepared by dissolving the dried PVDF powder in a mixture of 90% DMF and 10% NMP by volume with the addition of 1% by weight EG. The PVDF solution was prepared by dissolving 14 wt.% PVDF in the solvent mixture and stirring for 6 hours at 70°C. 2 wt.% of SNPs were ultrasonically mixed in the solvent mixture at ambient temperature for half an hour. This solution was then combined with a separately produced PVDF dope solution as shown in **Figure 1**. To improve the electro-spinability and conductivity of the dope solution, a trace quantity of LiCl (0.004 weight percent) was added [28]. The dope solution prepared was degassed at room temperature for one day. To guarantee uniform dispersion of the nano particles, the dope solutions were also sonicated for ten minutes before the electospinning procedure.

2.3. Preparation of the cast membranes

Phase inversion was used to prepare the cast membranes using a polymeric dope solution. A liquid solution was poured onto the glass plate and a film of casting solution spread with a wet-casting thickness of 300 μm using a doctor knife tool at room temperature. After casting, coagulation was carried out by placing the membrane in a water bath to evaporate the solvent thus leaving a thin uniform polymeric membrane sheet. When the membrane came into contact with water, it became opaque, indicating that the polymer in the solution had coagulated and precipitated. The formed membrane was dried in open air at room temperature before testing.

2.4. Electrospinning setup

The electrospinning process was carried out at a high voltage to create the composite polymeric nano fiber [20]. As seen in **Figure 1**, a typical electrospinning setup consists of up of three main parts: (1) Needle of small diameter; (2) high voltage power supply; and (3) aluminum foil collector. High voltage was applied to a polymer solution jet that was electrically charged. The jet stretches before it reaches the collector, after which the solvent evaporates and the polymer solidifies as nano fibers on the collector [3, 29].

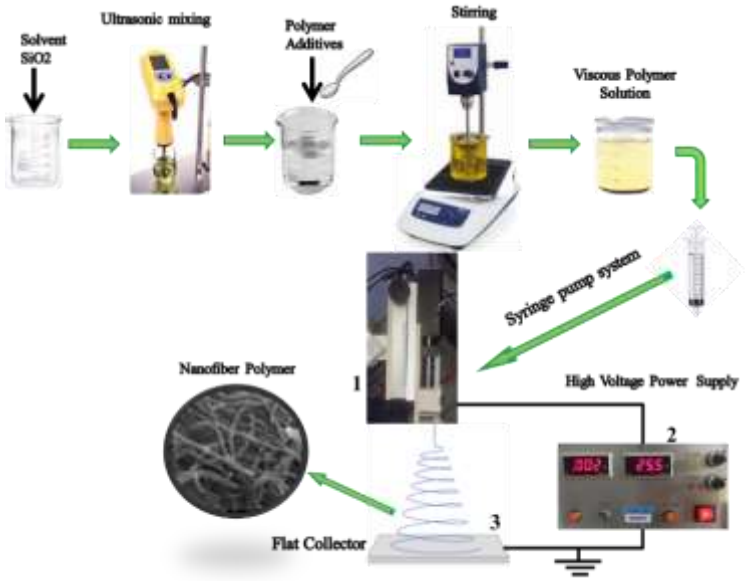

Fig.1. Illustrative diagram of Preparation dope solution and nano fiber preparations via. electrospinning setup**.**

2.5 Preparation of the electrospun nano fiber membranes

For fabrication, an electrospinning machine (Nano NC) utilized a high voltage generator, a flat collector, and a syringe pump. A stainless-steel needle (23G X 1 in. accuracy, Becton-Dickinson & Co., Franklin Lakes, NJ) was positioned vertically 15 cm above the flat collector, and the 12 ml tip plastic syringe (Luer Lock, HENKE-JECT, Germany) was connected to it. The flat collector was covered with an aluminum foil on which the fibers deposited. Since the needle was attached to a high voltage (20–30 kV) source, the electrostatic field between the needle tip and the flat collector caused the solution to deform as soon as it exits the needle.

The electrostatic force between the flat metal collector (negative side) and the needle tip (positive side), causes the distortion of the polymer solution into a conical shape known as a Taylor cone, from which a fiber jet is released. This fiber jet is elongated and stretched. The solvent is evaporated along the tip-collector distance (TCD) path and fibers are deposited on the 25×25 cm flat collector surface. The fiber mat was removed from the foil after it had formed, allowed to dry at room temperature, and then stored in a desiccator until it was used. The spinning process was carried out in a closed chamber under the following conditions: a flow rate of 1 ml/h, a temperature of 25 ± 5 °C, and a humidity of 30 ± 5%. The same set of electrospinning parameters and operating conditions were used to produce each membrane. **Figure 2** is a schematic representation of the electrospinning system.

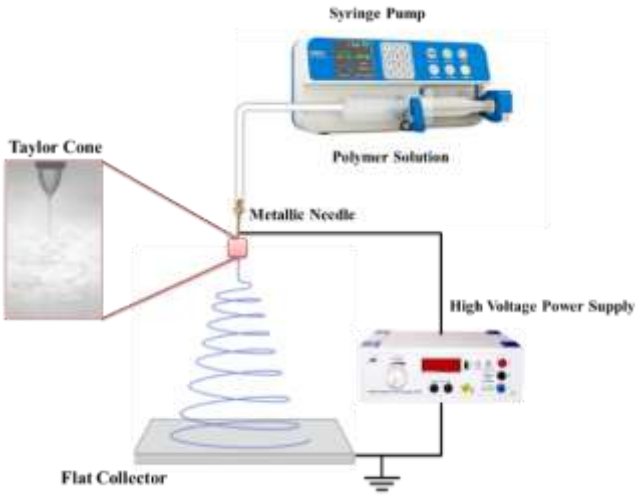

Fig. 2. Schematic representation of the electrospinning system.

2.6. Surface modification of cast and nano fiber membranes

This study used a two-step modification technique. In order to strengthen the free Si–OH groups for bond formation in the

following phase, the manufactured membranes were first treated with a 1 M hydrochloric acid solution at 60°C for 1 hour [30]. The membranes were then rinsed three times with distilled water and dried at room temperature. The second step involved submerging the membranes for eight hours at room temperature in a hexane solution containing 1% v/v FAS to fluorinate the membrane surface. After rinsing the fluorinated membranes with hexane to get rid of the extra FAS, the membranes were left to dry overnight. The two types of membranes were modified using the same modification process. **Figure 3** shows the membrane fabrication and modification steps.

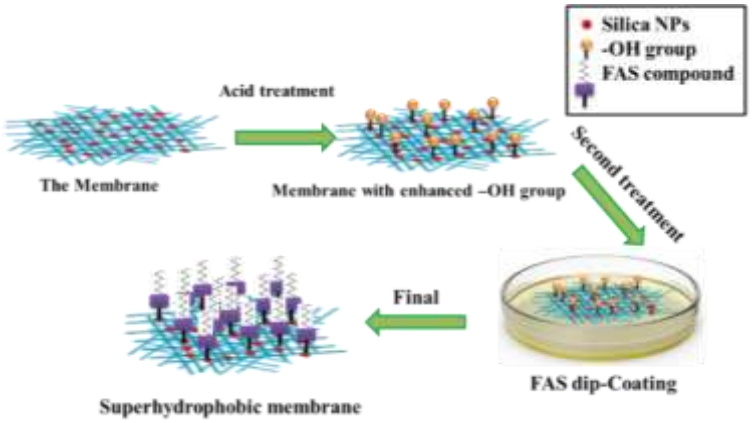

Fig. 3. Composite membranes fabrication and modification steps.

2.7. Membrane Characterization

2.7.1 Scanning Electronic Microscopy (SEM)

Using field emission SEM (JEOL 5410), NRC, Egypt [31], images of membrane samples were acquired in order to ascertain the shape of the surface structure. All samples had a tiny layer of gold sputtered on them to create a conducting face prior to SEM analysis. The accelerating voltage used for imaging was 20 kV [18]. The SEM was coupled with an energy-dispersive X-ray device (EDX) to identify the surface composition of the membrane. To provide electrical conductivity gold sputtering was applied to the dry samples.

2.7.2 BET Surface Area

The nitrogen adsorption/desorption process known as Brunauer-Emmett-Teller (BET) was used to gain insight into the pore-level of the membrane. For a full day, the membrane sample was surface activated by degassing it at 60°C and 2-10 bar vacuum. Subsequently, the sample cell was moved to a Bel Sorp Max device (Japan) to determine its nitrogen adsorption-desorption isotherm at the temperature of liquid nitrogen. Using the NLDFT method, the pore size distribution is then calculated, and the specific surface area is estimated from the isotherm.

2.7.3 Porosity

Using the gravimetric approach, the porosity of each membrane sample was determined [11]. This approach used an electronic weight balance to weigh membrane samples that were both fully wetted and dried, and the following equation (1) was used to determine the porosity:

$$\text{Porosity, } \epsilon = \frac{(W_w - W_d)/\rho_l}{(W_w - W_d)/\rho_l + W_d/\rho_l} \quad (1)$$

Where Ww and Wd represents the weights of the wet and dry membrane samples, respectively, in grams, ρ_p is the polymer density (g/m^3), and ρ_l is density (g/m^3) of iso-propyl alcohol. Each membrane was tested at least three times.

2.7.4 Water Contact Angle (WCA)

A contact angle measuring instrument (OCA 15EC, NRC, Egypt) was used to measure the water contact angle of the produced membranes in order to determine their wettability. For each membrane sample, the contact angle was considered to be the average measured in three separate locations [9].

2.8. Membrane performance using vacuum membrane distillation (VMD)

The prepared membranes were evaluated and assessed for application as hydrophobic porous membranes using the VMD unit at the National Research Centre, Egypt shown in **Figure 4**. The membrane was fixed in a specially constructed membrane cell (effective area 100 cm^2) for the VMD test, which was connected to the feed and permeate sides via silicon tubes. An aqueous salt solution (3.5 wt% NaCl) was added to the feed tank, which was then heated to 70°C by a continuously stirred hot plate (MSH-20D, DAIHAN Scientific co, Korea). The heated feed was circulated at 15 cm^3/s using a peristaltic pump (YT600-1JKZ35, longer pump co, China) across the membrane cell. Using a vacuum pump (1 bar) (vacuum pump- SH-V40,

SH SCIENTIFIC, Korea), water vapor removed from the permeate side was condensed in a tube condenser cooled by water at 10 °C. The flux and conductivity of the condensate/permeate were measured every 30 minutes. In order to maintain a consistent feed concentration, the same volume of distilled water was added to the feed tank.

The rate at which the mass and salinity (conductivity) of the permeate changed was used to calculate the VMD permeate flux and salt rejection. The water permeation flux was determined from equation (2):

$$J = \frac{\Delta W}{A \times \Delta t} \quad (2)$$

Where J is the permeate flux, lit/ (m^2 h), W is the volume of distilled water, lit, A is the membrane area (m^2), and the time (h). Salinity was measured by a portable conductivity meter (AD 8000, Adwa instrument, Romania). The salt rejection was recorded at different salt concentrations of feed and permeates. The salt rejection (SR) is obtained assuming that the salt concentration to its electrical conductivity using equation (3): where Cp is the final salt concentration (conductivity) of the permeate stream and Cf is the initial salt concentration (conductivity) of the feed. The salt rejection was calculated from

$$SR = \frac{C_f - C_p}{C_f} \times 100 \quad (3)$$

Fig. 4. Schematic of the lab scale VMD unit.

3. Results and Discussion

3.1. Membrane Morphology

Electrospinning is a widely recognized and adaptable method for fabricating membranes having high porosity and enhanced hydrophobicity [32]. Because of its porous structure and three-dimensional (3D) network, the ENMs have a large surface area and surface functions that can be further modified [33]. In this study, membranes were fabricated using two different methods namely electrospinning and phase inversion. Every membrane sample was examined under a scanning electron microscope to examine its intricate surface shape and formation.

Figure 5, 6 shows the SEM images of the ENMs (Pe_1, Pe_2) fabricated before and after modification. It is evident that the ENMs displayed an entangled nanostructure with nanonets, as well as randomly oriented 3D woven membranes. Furthermore, it is evident that the nano fibers include beads [34]. Before modification, the Pe_1 membrane was found to have a homogeneous fiber diameter and a smooth surface, indicating that the electrospinning parameters were well optimized [35].

The results show that the modified ENM is composed of a regular network system with nodes which improve membrane separation performance in MD. The Pe_2 membrane after modification incorporated FAS compound and appeared relatively rough on the surface because of the deposition of the nano particles on the nano fibers. Also, there was some aggregation of nano particles. Numerous studies have documented nano particle aggregation within nano fibrous composite membranes, which is a common restriction associated with nano particles due to their tiny size and high surface energy [36]. Nevertheless, the inclusion of nano particles in the polymer solution causes bead formation during fabrication, which improves the hydrophobicity and surface roughness of the membrane [37].

The Pe_2 was then selected for additional analysis through EDX. To find the elements in this membrane, line scanning was done on its cross-section as shown in **Figure 6**. This EDX image showed the elements silica (Si), carbon (C), oxygen (O), and fluorine (F). The detected elements depict PDVF polymer and hydrophobic modified nano fiber membrane with silane solution.

The elemental compositions, in the modified membranes, were measured. It was noted that elemental peaks with 36.58 wt. %, 54.75 wt%, 2.97 wt. %, and 5.7 wt. % were observed corresponding to the carbon, fluorine, oxygen and silica. It implies that the nanoparticles were activated and their free Si–OH groups were increased through this acid treatment. Also, the alkyl-silane group of FAS was successfully crosslinked with the Si–OH group of SNP.It is noted that the C and F elements account for the highest proportion of elements on the sample surface, because the body polymer PVDF is made of hydrocarbon compounds [38, 39].

Figure 7 shows the SEM images of the cast membranes (Pc_1, Pc_2) fabricated using the phase inversion technique before and after modification. It is evident that the size of the macrovoids decreases for membrane Pc_2 after modification. Therefore, the modification steps make the membrane denser with a narrower pore size and resulting in a smoother surface morphology. This improves the performance of membrane due to increased salt rejection [40].

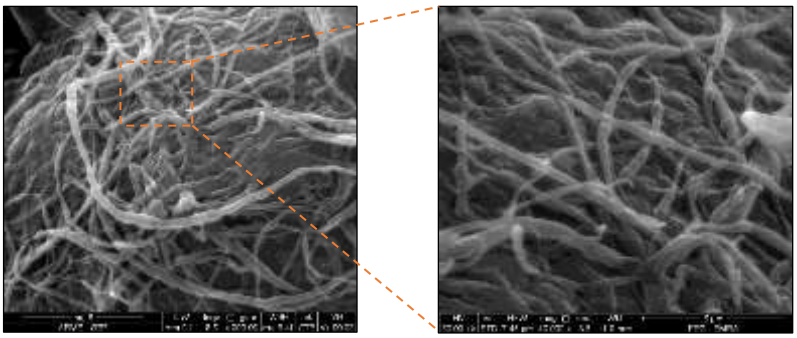

Fig. 5. SEM micrographs for electrospun nano fiber membranes before Pe_1. The images on the right are a magnification at 40000 x of the indicated areas.

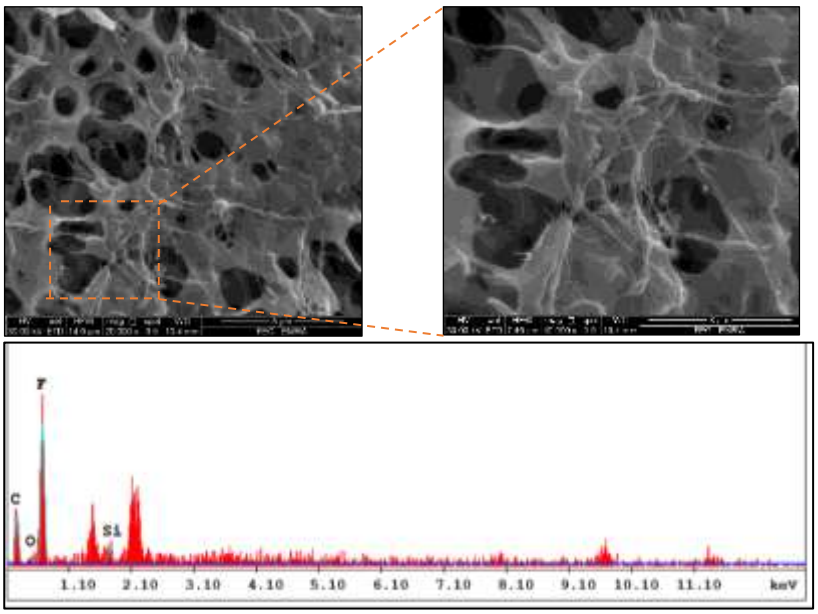

Fig. 6. SEM micrographs and EDX for electrospun nano fiber membranes after modifications Pe_2. The images on the right are a magnification at 40000 x of the indicated areas.

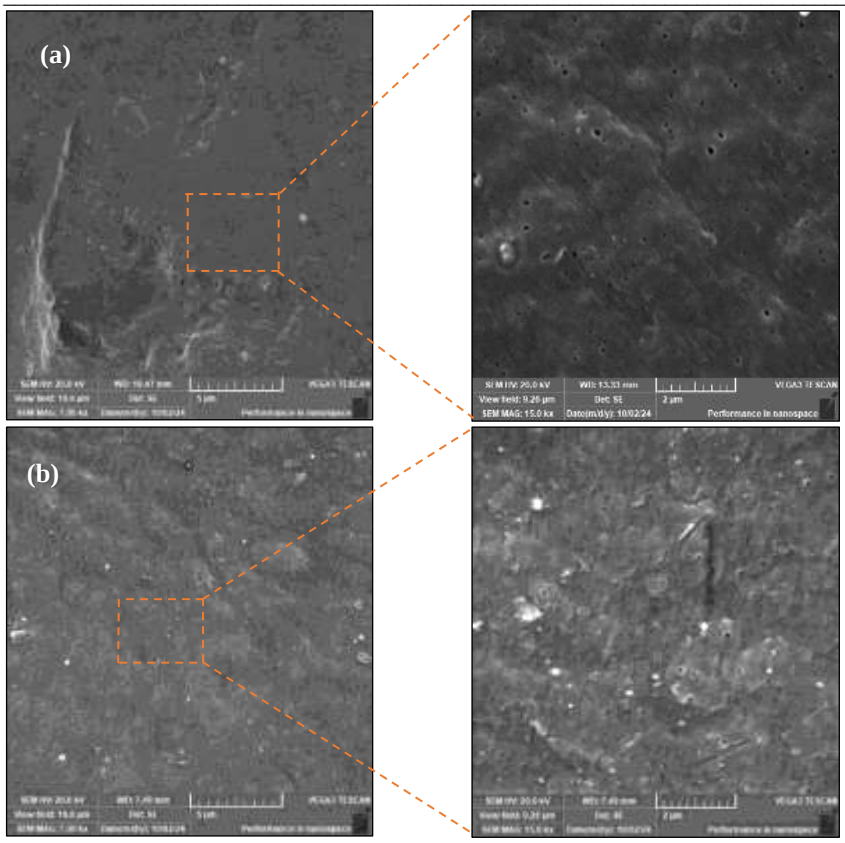

Fig. 7. SEM micrographs for cast membranes before and after modifications (a) Pc_1 and (b) Pc_2. The images on the right are a magnification at 15000 x of the indicated areas.

3.2. Pore size distribution

Pore size distribution is another membrane property that is crucial for determining the effectiveness of membranes in water desalination [41]. With a restricted pore size distribution as the target, the perfect nano fibrous membrane is to enable high permeability and superior separation efficiency [24, 42]. **Figure 8** presents the pore size distribution of the prepared membranes after modification. It is evident that the distribution of pore sizes narrowed around the mean pore size of 7.2 nm and 10.5 nm for Pc_2 and Pe_2, respectively. The increase in average pore size from Pc_2 to Pe_2 membrane leads to an increased permeability. This also increases the rejection efficiency of membrane [43].

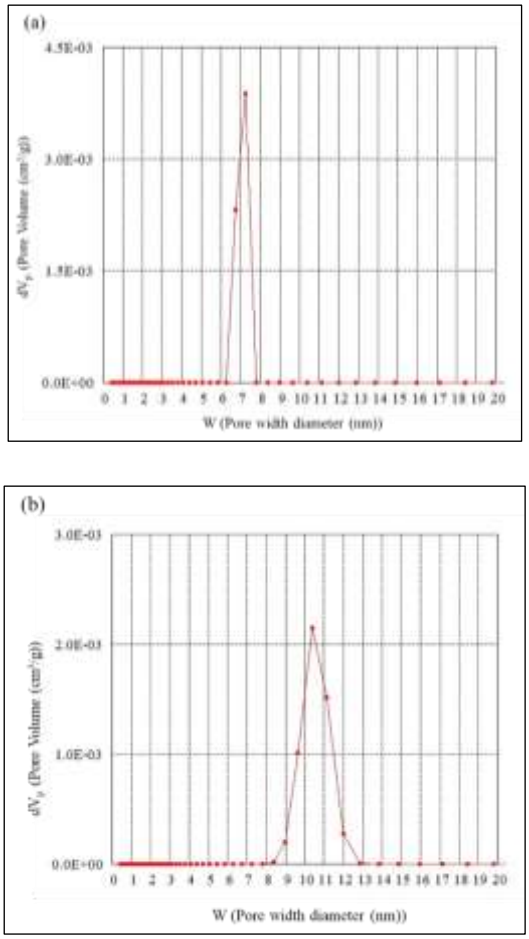

Fig.8. Pore size distribution histograms on the surfaces of modified membranes: (a) Pc_2 and (b) Pe_2.

3.3. Porosity

In membrane distillation systems, porosity is a critical characteristic that determines the membrane performance. The concept of high porosity is used to develop the perfect nano fibrous membrane with high permeability and superior separation efficiency [42]. While having a large porosity is ideal for achieving high penetration rates, this also raises the danger of wetability and decreases the membrane's acceptance efficiency [43]. The prepared nano fibrous membrane Pe_2 after modification possess several salient characteristics including excellent porosity of ranging between 74% and 94%. The measured porosity of the fabricated electrospun nano fiber membranes increased from (83% for Pe_1) to (94% for Pe_2) after modification of membranes. The measured porosity of the cast membranes increased from (74% for Pc_1) to (81% for Pc_2) after modification of the membranes.

3.4. Water contact angle and membrane hydrophobicity

Hydrophobicity is a desirable membrane property for the MD process since it decreases wettability resulting in a high rejection rate [44]. Prior findings for surface roughness indicate a clear correlation between the contact angle and surface roughness. It has been reported that nano fiber membranes with the lowest water contact angle also had the highest surface roughness. This means that higher surface roughness is associated with a higher hydrophobicity of the nano fiber surface [45]. In the present work, the water contact angle (WCA) of all membranes varied between 60 and 150 degrees. **Figure 9** shows the images of the contact angle of the various membranes. It is seen that the WCA of Pc_1 and Pc_2 flat sheet membranes increased from 61.3 to 119.3 after modification while the WCA of the nano fiber membranes Pe_1 and Pe_2 increased from 100.7° to 150°. This increase in the WCA is attributable to the increased membranes' surface roughness after modification [28, 46].

Figure 10 compares the WCA of cast and nano fiber membranes before and after modification. Compared to other membranes prior to alteration, the modified Pc_2 and Pe_2 membranes demonstrated a significantly enhanced contact angle; as a result, the electrospinning approach was able to produce super-hydrophobicity in Pe_2. Comparing the modified membrane to the smooth nano fibers of PVDF membrane, the increased surface roughness produced by SNPs and the better attachment of hydrophobic silane groups onto its surface are what give it its super-hydrophobicity [11, 13]. This may attributed to the acid

pre-treatment step which strengthens the OH group on the silica nano particles and intensifies the condensation process between the OH group of SNPs and the Si–O-alkyl groups of silane compound [25, 47]

Additionally, it can be shown that the electrospun membranes have larger contact angles compared to the cast membranes when electrospinning and phase inversion are compared. Therefore, electrospun membranes are more hydrophobic than the membranes produced by the phase inversion process.

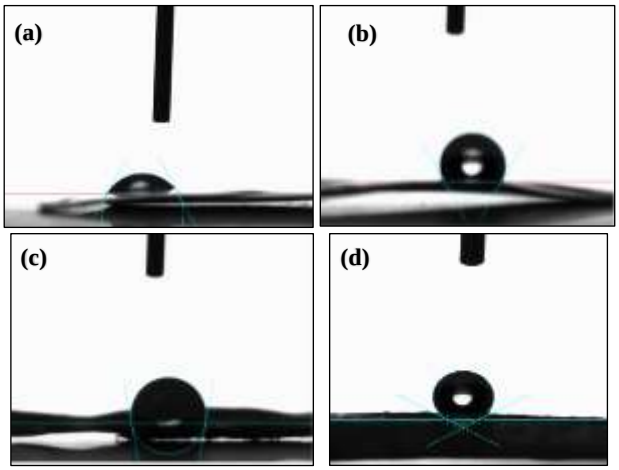

Fig. 9. Image of Water contact angle for the produced membranes (a) Pc_1, (b) Pc_2, (c) Pe_1, (d) Pe_2.

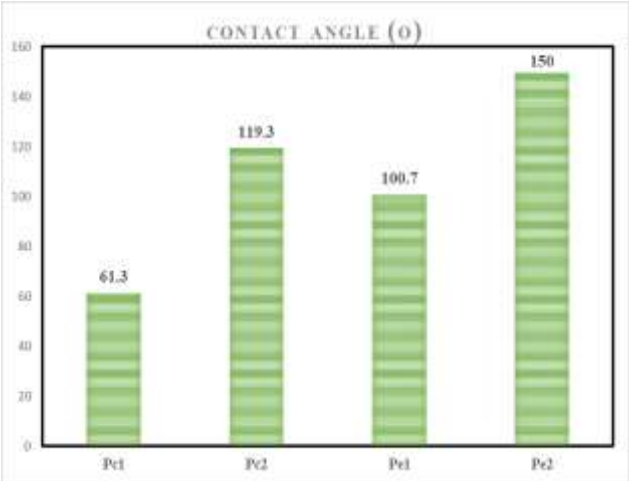

Fig. 10. Water contact angles of all membranes with and without modification.

3.5 VMD performance of the prepared membranes

The membrane requirements for membrane distillation are high flux and high salt rejection (SR). The VMD experiments were conducted for a feed solution having a concentration of 3.5 wt% NaCl at a flow rate of 15 cm^3/s and a temperature of 70°C with a permeate side vacuum pressure of about 1 bar. After 30 minutes, the weight of the permeate and salt rejection were recorded. Figure 11 compares the water permeate flux for the cast membranes before and after modification. It is seen that the water permeate flux was 17 $kg/m^2.h$ for (Pc_1) which is lower than that of (Pc_2) (25 $kg/m^2.h$). The increased porosity of the redesigned cast membrane is responsible for this increase in permeate flux. The salt rejection for (Pc_1) before modification was 86.3%, and was lower than 92.67% for (Pc_2) after modification. Figure 11 also presents the permeate flux and salt rejection of the electrospun nano fiber membranes before and after modification. (Pe1) gave a permeate flux of 32 $kg/m^2.h$ and a salt rejection of 94.6%. The above figures increase up to 41 $kg/m^2.h$ and 99.2%respectively after modification for (Pe_2). This is explained by the increased porosity and hydrophobicity on the surface of (Pe_2).

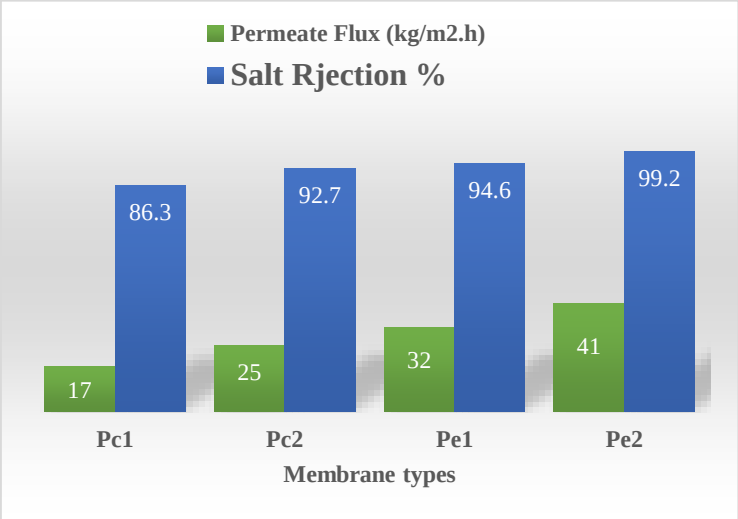

Fig. 11. Membrane performance in VMD experiments for water permeate flux and salt rejection of the prepared membranes.

4. Conclusions

The present study compared the suitability of two PVDF membranes fabricated by two different techniques to be used in vacuum membrane distillation for sea water desalination. Cast PVDF membranes were prepared by phase inversion and nano fiber PVDF membranes were prepared by electrospinning. Both membranes were subjected to a two-step surface modification process including acid treatment and fluorosilanization using FAS. The acid treatment increased the free Si–OH group thus providing for more FAS crosslinking sites. The modified electrospun nano fiber membrane gave better hydrophobicity with a WCA of 150° versus 119.3° for the modified cast membrane. The porosity of the modified membranes was 94% for the ENMs, while it was 81% for the cast membrane.The VMD tests undertaken also indicated a superior permeate flux and salt rejection for the modified ENM of 41 lit/m^2.hr and 99.2% compared with 25 lit/m^2.hr and 92.7% for the modified cast membrane. This indicates the suitability of the prepared modified superhydrophobic ENMs for VMD desalination application.

5. Conflicts of interest

There are no conflicts to declare

6. References and Bibliography

[1] Curto, D., V. Franzitta, and A. Guercio, A Review of the Water Desalination Technologies. Applied Sciences, 2021. 11(2): p. 670.
[2] Sanaeepur, H., Amooghina, A.E., Mahdi, M., Shirazi, Pishnamazi, M., and Shirazian, S., Water desalination and ion removal using mixed matrix electrospun nanofibrous membranes: A critical review. Desalination, 2022. 521: p. 115350.
[3] Mousa, H. M., Hamdya, M., Yassin, M. A., El-Sayed Seleman, M. M., and G.T. Abdel-Jaber, Characterization of nanofiber composite membrane for high water flux and antibacterial properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022. 651: p. 129655.
[4] Sosiati, H., F. Ramadhan, and M.B.N. Rahman, Fabrication and Characterization of PVC-Based Nanofiber Membranes for Water Filtration Application. Semesta Teknika, 2023. 26(1): p. 78-85.
[5] Essalhi, M., Khayet,M., Tesfalidet,S., Alsultan,M., and Tavajohi,N., Desalination by direct contact membrane distillation using mixed matrix electrospun nanofibrous membranes with carbon-based nanofillers: A strategic improvement. Chemical Engineering Journal, 2021. 426: p. 131316.
[6] Servi,A., Liu, A., Gleason, K.K, and Rutledge,G.C.,Desalination by Membrane Distillation using Electrospun Polyamide Fiber Membranes with Surface Fluorination by Chemical Vapor Deposition. ACS Appl Mater Interfaces, 2015. 7(15): p. 8225-32.
[7] Al-Furaiji, M.H. and K.R. Kalash, Desalination by Membrane Distillation Using Electrospun Membranes. Journal of Engineering, 2019. 26(1): p. 35-42.
[8] Kumarage, S., I. Munaweera, and N. Kottegoda, A comprehensive review on electrospun nanohybrid membranes for wastewater treatment. Beilstein J Nanotechnol, 2022. 13: p. 137-159.
[9] Yao, M., Tijinga,L.D., Naidua, G., Seung-Hyun, K., Matsuyamac, H., Faned, A.G., and Shona, H.K., A review of membrane wettability for the treatment of saline water deploying membrane distillation. Desalination, 2020. 479: p. 114312.
[10] Essalhi, M. and M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun nano-fibers: Effects of polymer concentration and desalination by direct contact membrane distillation. Journal of Membrane Science, 2014. 454: p. 133-143.

[11] Yadav, P., R. Farnood, and V. Kumar, Superhydrophobic modification of electrospun nanofibrous Si@PVDF membranes for desalination application in vacuum membrane distillation. Chemosphere, 2022. 287(Pt 2): p. 132092.
[12] Tijing, L.D., June-Seok, C., Lee, S., Seung-Hyun, K., and Shona, H.K., Recent progress of membrane distillation using electrospun nanofibrous membrane. Journal of Membrane Science, 2014. 453: p. 435-462.
[13] Ahmed, F.E., B.S. Lalia, and R. Hashaikeh, A review on electrospinning for membrane fabrication: Challenges and applications. Desalination, 2015. 356: p. 15-30.
[14] Zahmatkeshan, M., et al., Polymer Based Nanofibers: Preparation, Fabrication, and Applications. 2018: p. 1-47.
[15] Nady, N., N. Salem, and S.H. Kandil, Preparation and Characterization of a Novel Poly(vinylidene fluoride-co-hexafluoropropylene)/Poly(ethersulfone) Blend Membrane Fabricated Using an Innovative Method of Mixing Electrospinning and Phase Inversion. Polymers (Basel), 2021. 13(5).
[16] Sagitha, P., Reshmi, C.R., Sundaran, Suja P., and Sujith, A., Recent advances in post-modification strategies of polymeric electrospun membranes. European Polymer Journal, 2018. 105: p. 227-249.
[17] Zhou, T., Yaoa, Y., Xiang, R., and Wuc, Y., Formation and characterization of polytetrafluoroethylene nanofiber membranes for vacuum membrane distillation. Journal of Membrane Science, 2014. 453: p. 402-408.
[18] Diwan, T., Abudi, Z.N., Al-Furaiji, M.H., and Nijmeijer, N., A Competitive Study Using Electrospinning and Phase Inversion to Prepare Polymeric Membranes for Oil Removal. Membranes (Basel), 2023. 13(5).
[19] Castro-Muñoz, R., A critical review on electrospun membranes containing 2D materials for seawater desalination. Desalination, 2023. 555: p. 116528.
[20] Deka, B.J., Lee, E.J., Guo, J., Kharraz, J., and An, A.K., Electrospun Nanofiber Membranes Incorporating PDMS-Aerogel Superhydrophobic Coating with Enhanced Flux and Improved Antiwettability in Membrane Distillation. Environ Sci Technol, 2019. 53(9): p. 4948-4958.
[21] Tang, Y., Cai, Z., Sun, X., Chong, C., Li, M., and Xu, J., Electrospun Nanofiber-Based Membranes for Water Treatment. Polymers (Basel), 2022. 14(10).
[22] Yalcinkaya, F., A review on advanced nanofiber technology for membrane distillation. Journal of Engineered Fibers and Fabrics, 2019. 14: p. 155892501882490.
[23] Liao, Y., Chun-Heng, L., Miao, T., Rong, W., Anthony, F.G., Progress in electrospun polymeric nanofibrous membranes for water treatment: Fabrication, modification and applications. Progress in Polymer Science, 2018. 77: p. 69-94.
[24] Li, X., Yu, X., Cheng, C., Deng, L., Wang, M., and Wang, X., Electrospun Superhydrophobic Organic/Inorganic Composite Nanofibrous Membranes for Membrane Distillation. ACS Appl Mater Interfaces, 2015. 7(39): p. 21919-30.
[25] Dong, Z.-Q., Ma, X.-H., Xu, Z.-L., and Gu, Z.-Y., Superhydrophobic modification of PVDF–SiO2 electrospun nanofiber membranes for vacuum membrane distillation. RSC Advances, 2015. 5(83): p. 67962-67970.
[26] Ke, H., Feldman, F., Guzmana,P., Cole,J., Wei, Q., Chua, B., Alkhudhiri, A., Alrasheed, R., and Hsiao, B.S., Electrospun polystyrene nanofibrous membranes for direct contact membrane distillation. Journal of Membrane Science, 2016. 515: p. 86-97.
[27] Tijing, L.D., Woo, Y.C., Yao, M., Ren, J., and Shon, H.K., 1.16 Electrospinning for Membrane Fabrication: Strategies and Applications. 2017: p. 418-444.
[28] Jiao, L., Yana, K., Wangb, J., Linb, S., Bic, F., Zhangb, L., Low surface energy nanofibrous membrane for enhanced wetting resistance in membrane distillation process. Desalination, 2020. 476: p. 114210.
[29] Aguilar-Costumbre, Y., Lambert, J.A., Meléndez-Lira, M.A.,and Escobar-Barrios, V.A., Preparation of Membranes Based on Polysulfone (PSU) and Graphene Oxide (GrO) by Electrospinning. 2017: p. 23-30.
[30] Yohai, L., Giraldo, H.M, Procaccini, R., Pellice, S., Laxman, K.k., Duttab, J., and Uheida, A., Nanocomposite functionalized membranes based on silica nanoparticles cross-linked to electrospun nanofibrous support for arsenic(v) adsorption from contaminated underground water. RSC Adv, 2019. 9(15): p. 8280-8289.
[31] Borchers, A. and T. Pieler, Programming pluripotent precursor cells derived from Xenopus embryos to generate specific tissues and organs. Genes (Basel), 2010. 1(3): p. 413-26.
[32] Khayet, M. and R. Wang, Mixed Matrix Polytetrafluoroethylene/Polysulfone Electrospun Nanofibrous Membranes for Water Desalination by Membrane Distillation. ACS Appl Mater Interfaces, 2018. 10(28): p. 24275-24287.
[33] Makanjuola, O., I. Janajreh, and R. Hashaikeh, Novel technique for fabrication of electrospun membranes with high hydrophobicity retention. Desalination, 2018. 436: p. 98-106.
[34] Al-Attabi, R., Morsia, Y., Kujawskid, W., Kongb, L., Schütze, J.A., and Dumée, L.F., Wrinkled silica doped electrospun nano-fiber membranes with engineered roughness for advanced aerosol air filtration. Separation and Purification Technology, 2019. 215: p. 500-507.
[35] Huang, Q.-L., Huang, Y., Xiao, C.-F., You, Y.-W., and Zhang, C.-X., Electrospun ultrafine fibrous PTFE-supported ZnO porous membrane with self-cleaning function for vacuum membrane distillation. Journal of Membrane Science, 2017. 534: p. 73-82.
[36] Makanjuola, O., S.F. Anis, and R. Hashaikeh, Enhancing DCMD vapor flux of PVDF-HFP membrane with hydrophilic silica fibers. Separation and Purification Technology, 2021. 263: p. 118361.
[37] Seyed Shahabadi, S.M., Rabieec, H., Seyedib, S.M., Mokhtared, A., and Branta, J.A., Superhydrophobic dual layer functionalized titanium dioxide/polyvinylidene fluoride- co -hexafluoropropylene (TiO 2 /PH) nanofibrous membrane for high flux membrane distillation. Journal of Membrane Science, 2017. 537: p. 140-150.
[38] Manoharan, R.K, Ayyaru, S. and Ahn, Y-H., Auto-cleaning functionalization of the polyvinylidene fluoride membrane by the biocidal oxine/TiO2 nanocomposite for anti-biofouling properties, New J. Chem, © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique, 2019, DOI: 10.1039/c9nj05300j.

[39] Juliandri, Rukiah, E. E. Ernawati, R. S. Handika and M. Nasir, Nanocomposite Sulfonated PVDF-TiO2 Membranes as a Potential Alternative for Nafion, World Scientific News 107 , 2018. p.150-159
[40] Panda, S.R., Bhandaru, N., Mukherjee, R., and De, S., Ultrafiltration of oily waste water: Contribution of surface roughness in membrane properties and fouling characteristics of polyacrylonitrile membranes. The Canadian Journal of Chemical Engineering, 2015. 93(11): p. 2031-2042.
[41] Lee, E.-J., An, A.K., Hadi, P., Lee, S., Woo, Y.C., and Shon, H.K., Advanced multi-nozzle electrospun functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (TiO2/PVDF-HFP) composite membranes for direct contact membrane distillation. Journal of Membrane Science, 2017. 524: p. 712-720.
[42] Nthunya, L.N., Gutierrez, L., Verliefde, A.R., and Mhlanga, S.D., Enhanced flux in direct contact membrane distillation using superhydrophobic PVDF nanofibre membranes embedded with organically modified SiO2 nanoparticles. Journal of Chemical Technology & Biotechnology, 2019. 94(9): p. 2826-2837.
[43] Manorma, Ferreira,I., Alves, P., Gil, M.H., and Gando-Ferreira, L.M., Lignin separation from black liquor by mixed matrix polysulfone nanofiltration membrane filled with multiwalled carbon nanotubes. Separation and Purification Technology, 2021. 260: p. 118231.
[44] Aijaz, M.O., Karim, M.R., Othman, M.H.D., and Samad, U.A., Anti-fouling/wetting electrospun nanofibrous membranes for membrane distillation desalination: A comprehensive review. Desalination, 2023. 553: p. 116475.
[45] Ren, L.-F.,Liu, C., Xuc, Y., Zhang, X., Shao, J., and He, Y., High-performance electrospinning-phase inversion composite PDMS membrane for extractive membrane bioreactor: Fabrication, characterization, optimization and application. Journal of Membrane Science, 2020. 597: p. 117624.
[46] Hamta, A., Ashtian, F.Z., Karim, M., Safikhan, A., Manipulating of polyacrylonitrile membrane porosity via SiO2 and TiO2 nanoparticles: Thermodynamic and experimental point of view. Polymers for Advanced Technologies, 2020. 32(2): p. 872-885.
[47] Mirhosseini, H., Shamspur, .T, Mostafavi, .A, Sargazi, G., novel ultrasonic reverse micelle-assisted electrospun efficient route for Eu-MOF and Eu-MOF/CA composite nanofibers: a high performance photocatalytic treatment for removal of BG pollutant. Environmental Science and Pollution Research, 2021. 28: p. 4317–4328.