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EVALUATION OF THIN FILM COMPOSITE FORWARD OSMOSIS MEMBRANES: EFFECT OF POLYMER TYPE

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Abstract: In the forward osmosis (FO) processes, the semipermeable membranes are used. These membranes are prepared from several types of polymers. In this research, the characterizations of each polymer were studied to conversance the effect of polymer type on the efficiency of the forward osmosis process. The prepared membrane's roughness was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM) to compare the formation of the TFC polyamide selective layer on each polymer type. Also, SEM images showed the distribution of pores on the prepared membrane. Contact angle (CA) measurements explained the hydrophilic and hydrophobic properties of membrane types. Finally, Energy dispersion spectrometry (EDS) was tested to determine the type, amount, and distribution of atoms in the prepared membranes. All of these characterizations proved that the Polysulfone (PSU) polymer was the best choice in the FO process. It can be proved that by test results, the PSU membrane gave the optimal water flux and salt rejection.

Keywords: *Forward-Osmosis; polyethersulfone; Polysulfone; polyacrylonitrile; Interfacial Polymerization; Poly-amide.*

1. Introduction

Water Purification is define a process by which the contaminants are removed for the specific purpose of water production for people consumption. Desalination water is a number consecutive of processes performed to stripe all or part of the excess salts, and minerals from the water. Seawater can be desalinated for practical use such as agriculture, drinking, and industry [1]. There are several methods of desalination, the most important of which is the method of osmosis using thin films.

During this time, the reverse osmosis (RO) process is the most effective technique that can be used for the desalination of seawater [2,3]. More clearly, RO clarified as a procedure which depends on external force, where a hydraulic pressure is used to is accountable in water solutes movement through membrane [4].

Forward osmosis (FO) can be defined as an emerging technology that falls under the classification of osmotically driven membrane processes [5]. FO works depending on the difference in osmotic pressure on both sides of a semi-permeable membrane and not hydraulic pressure difference like the RO process, to extract clean water from the feed solution to the draw solution (higher osmotic pressure solution) [6]. In order to develop the forward osmosis process, a suitable membrane must be prepared

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for this process, meaning that the ideal films for FO must able to provide a towering permeability of water, highly rejection dissolved of substances, and greatly reduce the interior concentration polarization, and also has great mechanical integrity and chemical stability [7, 8].

Thin film composite (TFC) membrane has been studied recently for forward osmosis applications [9-11]. TFC a traditional membrane utilized in the FO process as a result of the need for a dense selective layer to lower the loss of draw solute from the draw solution to the feed solution [12]. TFC membranes have 2 layers, the first one known as rejection layer that only permits water to pass through and prevents salt, and a supporting layer that gives the membrane the needed mechanical integrity called support layer. Few papers about FO-TFC membranes are concerned with the development of the support layer, while the active layer has been intensively studied.

Polysulfone (PSU), Polyethersulfone (PES), and Polyacrylonitrile (PAN) polymer membranes have been paid interest among osmosis membranes research subjects. A polyamide rejection layer can be synthesized by interfacial polymerization (IP) reaction [13]. The IP reaction is occur between two monomers: 1, 3, 5-benzenetricarbonyl chloride (TMC) in the organic phase with m-phenylene diamine (MPD) in the aqueous phase of [14]. Very few previous studies compared the effect of polymer type, but some studies proved the importance of mixing two polymers (PAN adding to PES) to improve osmotic performance [15], While another study aims to increase the intrinsic peculiarities of TFC FO membrane by using combinations of PSU and PES [16], in addition, there is a study focusing on the use of new materials for copolymerization, grafting, and polymer blend [17]; however, there is a study that showed the most significant determinants of the properties that provide a membrane with superior output for forward osmosis [18] also, there is a study has significant attention for improving performances and properties of the FO membranes by studying recent developments of polymer used in making the membrane [19]. Therefore, studying the effect of polymer type on FO process performance can help to provide acceptable results.

This search aims to study the effect of support layer properties (i.e. polymer type) on the creation of the polyamide selective layer in the forward osmosis membranes. SEM, AFM, energy dispersion spectrometry (EDS), and contact angles (CA) measurements have been utilized to describe the FO membranes prepared.

2. Chemical Materials and Work Methods

2.1. Chemical Materials

Polysulfone polymer (PSU) MW=22000, Polyacrylonitrile (PAN) MW=150000, and Polyethersulfone (PES) MW=150000, were used for the fabrication of membranes supports. N,N dimethylformamide (DMF, 99.8%) with the formula $(CH_3)_2NC(O)H$ or in a simple way (C_3H_7NO), and 2,2, 4-trimethylpentane (also known as isooctane with the formula C_8H_{18}, 99%). meta-phenylenediamine (MPD, 99%), trimesic chloride (TMC, 98%). Sodium chloride was imported from China. The aqueous solutions NaCl and MPD were prepared by using Deionized water (DI water) and cleaning.

2.2. Support Layer Preparation

For all types of polymers, the support sheets were prepared by the same method. This method is called Phase Inversion (PI**).** The casting solutions equipped via dissolving 17 wt. % of each PSU, PES, and PAN in DMF, severally. All mixtures were heated to 60^0C for 6 h with stirred until clear solutions were created. Afterward, each solution

taken separately to prepare the support layer. The process required cast the solution using a home-made casting knife, the solution prevalence on clean plate (from glass) to coveted thickness. This glass with solution on the top of it, was directly immersed horizontally into the water bath making an instant creation of the supporting layer that separated from the plate through moment at room temperature. Finally, all (PSU, PES, and PAN) support sheets collected in the DI water and kept separately for 24 h at 4^{o}C.

2.3. TFC Membrane Preparation

Thin film composite forward osmosis membranes synthesized via the IP reaction between MPD aqueous solution and TMC organic solution on the top surface of the PSU, PES, and PAN sheets. To prepare the MPD aqueous solution, it was needed to dissolve 2 percent of the MPD in DI water, but TMC solution was made via dissolving 0.15 percent TMC in an organic solution of isooctane. First step is the MPD teemed onto PSU, PES, and PAN sheets in 2 min reaction time. Second step is the TMC teemed onto the sheets which contained MPD active areas on their surfaces with 1 min reaction time. Finally, all TFC membranes obtained, were dried by oven for 60^{o}C in 10 min, thereafter collected in DI water and stored at 4^{o}C for 24 h. Figure 1 illustrates the preparation steps of the TFC membrane.

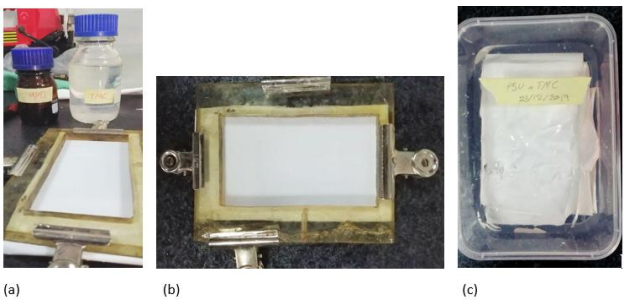


Figure 1. Steps for preparation of the TFC membrane. (a) Pour MPD solution onto PSU sheet for minutes. (b) After that pour TMC solution. (c) After left to dry, store the membrane in Deionized water before use.

2.4. Membrane Characterization

To assess the composition of the prepared membranes, we used Scanning Electron Microscope (Fesem Tescan Mira3 France) as in Figure 2. Firstly, the sample was coated with ultra- thin layer of gold. SEM was conducted by using an accelerating voltage of 10 kV and a current of 12 μA. Figure 2 also shows the Energy Dispersion Spectrometry, which was used to determine the amount and types of chemical atoms that are distributed in membranes. Figure 3 shows the Atomic Force Microscope system (Angstrom advanced Inc., 2008, U.S.A) utilized to study the roughness and the surface morphology of the prepared membranes. Tiny pieces of the prepared membranes (1x1 cm) were cut and attached on a glass substrate. The membrane surfaces were scanned with a photo size of 2500x2500 nm. Contact angles were tested in laboratories of Ministry of Science and Technology in Baghdad.

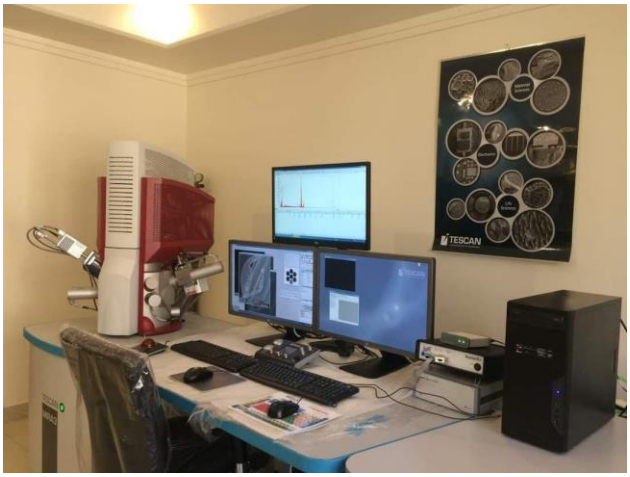


Figure 2. SEM with EDS systems.

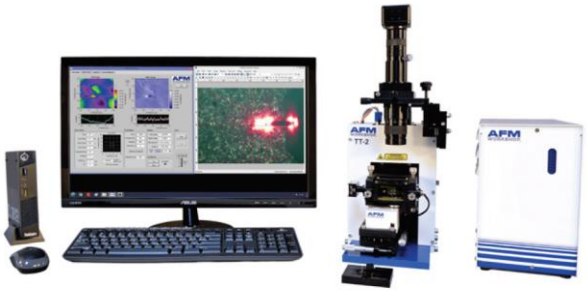


Figure 3. Atomic Force Microscope (AFM) system.

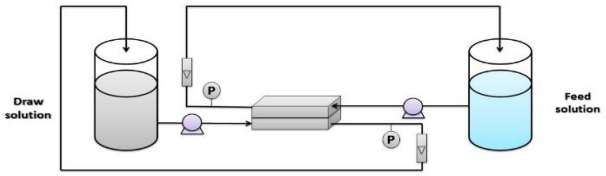


Figure 4. The FO bench-scale test system.

2.5. Testing of FO Performance

Figure 4 illustrates system adopted for the FO performance membrane testing. The bench-scale system consisting of two beakers: one was for the draw solution (1M NaCl) , and the other one used to feed solution (DI water) [20]. Pumps (need 2) from Pure-water with properties (model: 75GPD, workflow: 28LPH, volts: 24VDC) used to pumping the solutions to the cell that contain membrane. The membrane was mounted in a custom-made cell with dimensions (length = 7.6 cm, width = 2.5 cm, depth = 0.3 cm.)

To estimate Water flux use the following equation [21]:

$$J_w = \frac{\Delta V}{At} = \frac{change\ in\ volume\ (l)}{active\ area\ (m2) * \text{experiment's time (h)}}$$

Where J_w represent water flux ($Lm^{-2}\ h^{-1}$).

While the Salt flux across membrane could evaluate by surveillance changing in the conductivity of feed solution and applying the next equation [22]:

$$J_s = \frac{\Delta C V}{At} = \frac{change\ in\ feed\ concentration\ \left(\frac{g}{l}\right) * volume\ (l)}{active\ membrane\ area\ (m2) * \text{experiment's time (h)}}$$

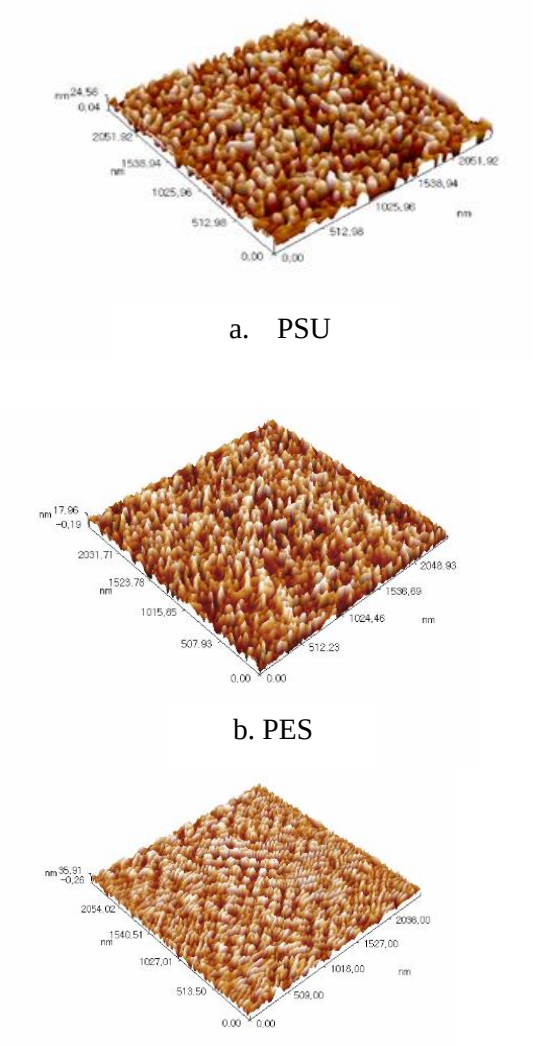
Here, J_s represent salt flux ($gm^{-2}\ h^{-1}$).

3. Results and Discussion

3.1. Membrane Characterization

3.1.1. *Atomic force microscopy (AFM)*

Three dimensional (3D) of AFM top surface images for all TFC membranes (i.e. PSU, PES, and PAN) are displayed in a scan area of 2500*2500 nm as exhibited in Fig. 5. It can also be noted that the surfaces of the polyamide layers had a hills and valleys structure with the average roughness, each type of selective layer have a different roughness from the other one. The most visible areas, i.e. the lighter ones, represent the highest areas of the membrane surface while the darker regions represent the pores of the membrane surface. Increasing these areas and porosity means increasing the surface roughness and therefore this means increasing the surface area of the membrane and this is one of the benefits of the membrane performance where the chances of a material transfer are higher. The roughness of prepared TFC membranes approximately similar to those repoted for the typical FO membrane [23] the Nanofiltration membranes [24, 25]. Otherwise, some studies that interest in the high fouling feed solution have proven that the lower roughness is the better [26].



a. PSU

b. PES

c. PAN

Figure 5. AFM images for all TFC membranes. a) PSU. b) PES. c) PAN.

3.1.2. *Scanning electron microscopy (SEM)*

SEM was executed to explore the top surface structures of TFC forward osmosis membranes as showing in figure 6. In order to understand the structure of all types of polymers, the surface properties and structures of all sheets were investigated by SEM. Therefore, figure 6A illustrated the SEM images for PSU, PES, and PAN before adding the active layer. It can be noted that the PSU has very small pores that cannot be detected by SEM, unlike the PES membrane that revealed larger pores. However, PAN SEM image shows non uniform surface. Figure 6B illustrated the SEM images for PSU, PES, and PAN membranes after adding the active layer (i.e. TFC membranes) and shows that the active regions of TFC formed on PSU membrane more than other membranes. That indicates a successful formation of polyamide selective membrane on the PSU support sheet.

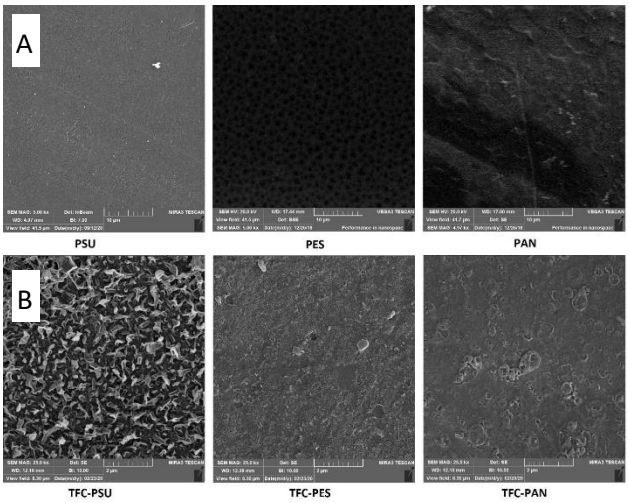


Figure 6. SEM images, (A) membranes without TFC. (B) with TFC.

3.1.3. *Contact angle (CA) measurements*

Figure 7 illustrates contact-angle measurements of PSU, PES, and PAN support membranes and the TFC membranes. As shown, Figure 7. a, c, and e for contact angle of support membranes, while pictures (b,d, and f) illustrated the contact angle for polyamide thin layers. From the images, it can be seen the difference between the contact angles for the support membranes and the TFC membranes. Table 1. Shows the value of contact angle for each type of polymers. Whenever the average value of the contact angle is small, this mean the membrane is really hydrophilic, which helps to give a better osmotic water flux performance. That because the hydrophilic property means water easily passes through the membrane's pores. But the large

contact angle indicates that the film is hydrophobic. The Hydrophobic property means that the membrane does not absorb water, which means that the pores are dry and thus reduce the performance of the water flux.

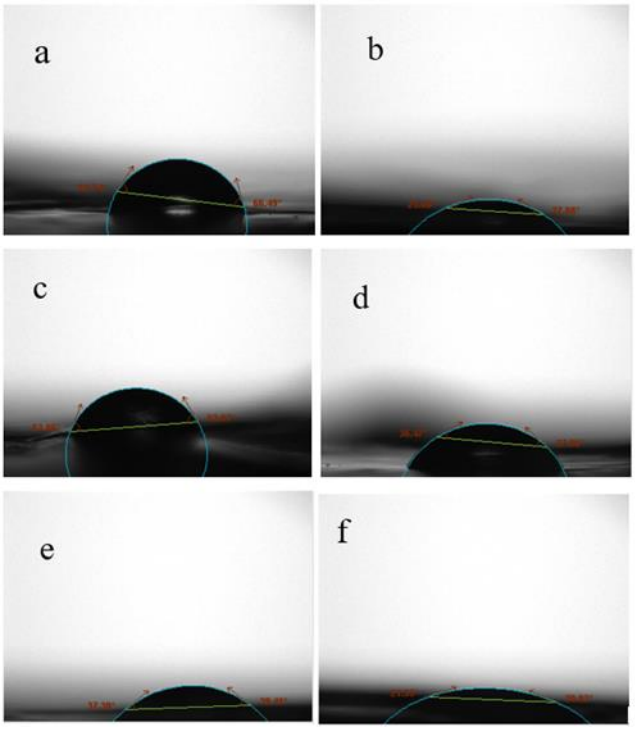


Figure 7. Contact angles. (a, b) PSU. (c, d) PES. (e, f) PAN.

Table 1. *contact value measurements before TFC polyamide selective layer*

Material	CA*
PSU	66
PES	63
PAN	32

Contact Angle*

3.1.4. *Energy dispersion spectrometry (EDS)*

Energy-dispersive X-ray spectroscopy (EDS) test was applied to study the chemical composition of the prepared membranes. In general, EDS was used to measure the relative amounts of each atom and also to determine the distribution of atoms in the membranes. Figure 8 illustrate the type and amount of each element for all types of TFC membranes (PSU, PES, and PAN).

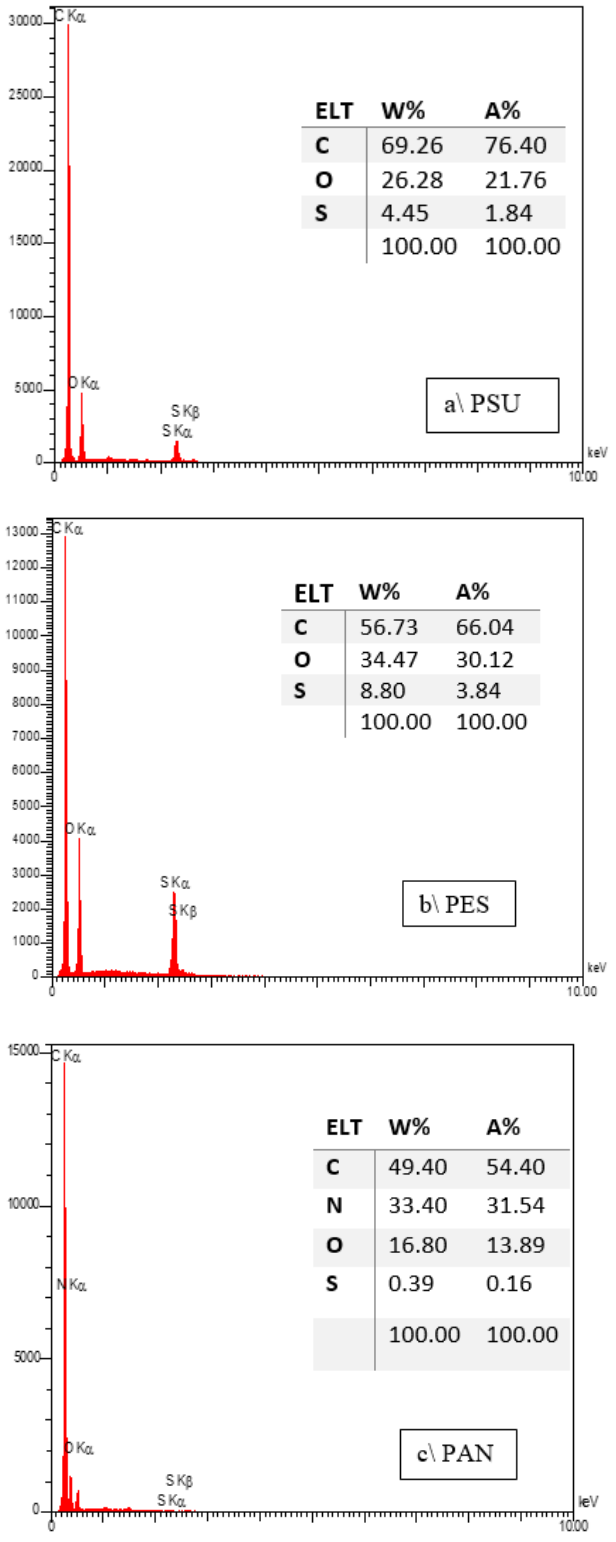


Figure 8. EDS analysis for (a.) TFC-PSU membrane, (b.) TFC-PES membrane, and (c.) TFC-PAN membrane.

3.2. Osmotic Flux Results

In order to assess the efficacy of each TFC-FO membrane, the permeate flux, and solute flux were tested. Figure 9 shows the results of water flux, and Figure 10 shows the result of salt flux for each type of polymers. Note that the highest water-salt fluxes values were for the PAN membrane. Otherwise, the PSU membrane had the average value of water flux and the lowest value for the salt flux. As for the PES membrane, the test results showed that it had the lowest value for the flow of water and the average value for salt flux. The high rejection of the TFC-PSU membrane was due to that polyamide layer was perfectly formed as was proven by the SEM test. However, the polyamide layer was not successfully synthesized on TFC-PAN membrane which explains the low rejection and the high salt flux.

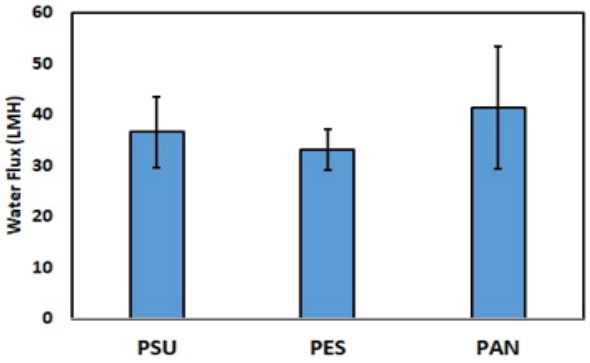


Figure 9. Water flux performance results for all types of polymers.

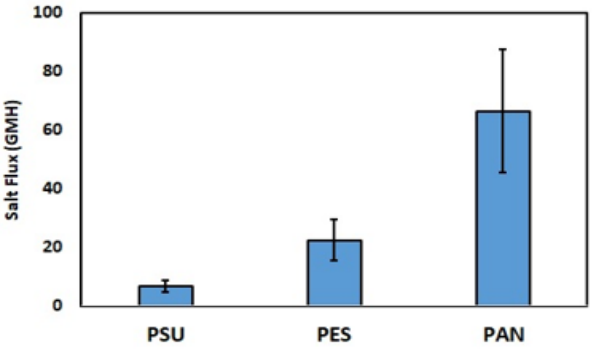


Figure 10. Salt flux performance results for all types of polymers.

4. Conclusion

This course of work illustrate how the TFC forward osmosis membranes prepared on the support layers from PSU, PES, and PAN substances (17wt %) by using IP reaction between MPD and TMC solutions to combine selective polyamide layers. The characterizations membrane were investigated. AFM images showed that the more roughness TFC membrane was PSU, and that was expected due to TFC selective layer. As mentioned previously in this study, the best polymer is the one that has the highest roughness (i.e, PSU) and gives an optimal separation performance. SEM test results of TFC forward osmosis membranes illustrate that the best reaction of IP between MPD and TMC was on the PSU polymer support layer. TFC-PSU membrane has more active areas than TFC-PES and TFC-PAN membranes. In the contact angle (CA) measurements, the results showed the hydrophilic property for each TFC-PSU and TFC-PAN forward osmosis membranes that give a better water flux performance. In order to demonstrate these important characterizations, all of the polymer types were studied in a lab-scale FO system with the DI water as the feed solution and saltwater (1M NaCl) as the draw solution to examine the performance of the membranes. The results confirmed the measured characteristics. However, osmotic flux performance results could show the better performance of water flux, and salt flux was with PSU polymer in the FO process. This study focused on comparing the three types of membranes, so it helps researchers and workers in this field to easily choose the type of membrane they need.

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Conflict of Interest

The authors confirm that the publication of this article causes no conflict of interest.

5. References

1. A. Panagopoulos, K. J. Haralambous, and M. Loizidou. (2019) "*Desalination brine disposal methods and treatment technologies - A review*," Sci. Total Environ., vol. 693, p. doi: 10.1016/j.scitotenv.2019.07.351.
2. K. Kalash, M. Kadhom, and M. Al-Furaiji. (2020). "*Thin film nanocomposite membranes filled with MCM-41 and SBA-15 nanoparticles for brackish water desalination via reverse osmosis*," Environ. Technol. Innov., vol. 20, p. doi: 10.1016/j.eti.2020.101101
3. B. Peñate and L. García-Rodríguez. (2012). "*Current trends and future prospects in the design of seawater reverse osmosis desalination technology*," Desalination, vol. 284, pp. doi: 10.1016/j.desal.2011.09.010.
4. T. Y. Cath, A. E. Childress, and M. Elimelech. (2006). "*Forward osmosis: Principles, applications, and recent developments*," J. Memb. Sci., vol. 281, no. 1–2, pp. doi: 10.1016/j.memsci.2006.05.048.
5. W. A. Phillip, J. S. Yong, and M. Elimelech. (2010). "*Reverse draw solute permeation in forward osmosis: Modeling and experiments*," Environ. Sci. Technol., vol. 44, no. 13, pp. doi: 10.1021/es100901n.
6. X. Liu and H. Y. Ng. (2014). "*Double-blade casting technique for optimizing substrate membrane in thin-film composite forward osmosis membrane fabrication*," J. Memb. Sci., vol. 469, pp. doi: 10.1016/j.memsci.2014.06.037.
7. S. Zhao, L. Zou, C. Y. Tang, and D. Mulcahy. (2012). "*Recent developments in forward osmosis: Opportunities and challenges*," J. Memb. Sci., vol. 396, pp. doi: 10.1016/j.memsci.2011.12.023.
8. J. Ren and J. R. McCutcheon. (2014). "A new commercial thin film composite membrane for forward osmosis," *Desalination*, vol. 343, pp. doi: 10.1016/j.desal.2013.11.026.
9. M. Al-Furaiji, N. Benes, A. Nijmeijer, and J. R. McCutcheon. (2019). "*Use of a Forward Osmosis-Membrane Distillation Integrated Process in the Treatment of High-Salinity Oily Wastewater*," Ind. Eng. Chem. Res., vol. 58, no. 2, pp. doi: 10.1021/acs.iecr.8b04875.
10. M. R. Chowdhury, L. Huang, and J. R. McCutcheon. (2017). "*Thin film composite membranes for forward osmosis supported by commercial nanofiber nonwovens*," Ind. Eng. Chem. Res., vol. 56, no. 4, pp. doi: 10.1021/acs.iecr.6b04256.
11. J. Ren and J. R. McCutcheon. (2017). "*Making Thin Film Composite Hollow Fiber Forward Osmosis Membranes at the Module Scale Using Commercial Ultrafiltration Membranes*," Ind. Eng. Chem. Res., vol. 56, no. 14, pp. doi: 10.1021/acs.iecr.6b04931.
12. J. J. Beh, B. S. Ooi, J. K. Lim, E. P. Ng, and H. Mustapa. (2020). "*Development of high water permeability and chemically stable thin film nanocomposite (TFN) forward osmosis (FO) membrane with poly(sodium 4-styrenesulfonate) (PSS)-coated zeolitic imidazolate framework-8 (ZIF-8) for produced water treatment*," J. Water Process Eng., vol. 33, no. October 2019, 2020, doi: 10.1016/j.jwpe.2019.101031.
13. M. J. T. Raaijmakers and N. E. Benes. (2016). "*Current trends in interfacial polymerization chemistry*," Prog. Polym. Sci., vol. 63, pp. doi: 10.1016/j.progpolymsci.2016.06.004.
14. M. Kadhom and B. Deng. (2019). "*Synthesis of high-performance thin film composite (TFC) membranes by controlling the preparation conditions: Technical notes*," J. Water Process Eng., vol. 30, no. November, pp. 0–1, doi: 10.1016/j.jwpe.2017.12.011.
15. M. E. Pasaoglu, S. Guclu, and I. Koyuncu. (2016). "*Polyethersulfone/polyacrylonitrile blended ultrafiltration membranes: Preparation, morphology and filtration properties*," Water Sci. Technol., vol. 74, no. 3, pp. 738–748, doi: 10.2166/wst.2016.252.
16. Y. Sun, L. Xue, Y. Zhang, X. Zhao, Y. Huang, and X. Du. (2014). "*High flux*

polyamide thin film composite forward osmosis membranes prepared from porous substrates made of polysulfone and polyethersulfone blends," Desalination, vol. 336, no. 1, pp. 72–79, doi: 10.1016/j.desal.2013.12.036.

17. C. Qiu, S. Qi, and C. Y. Tang. (2011). *"Synthesis of high flux forward osmosis membranes by chemically crosslinked layer-by-layer polyelectrolytes,"* J. Memb. Sci., vol. 381, no. 1–2, pp. 74–80, doi: 10.1016/j.memsci.2011.07.013.
18. G. Han, T. S. Chung, M. Toriida, and S. Tamai. (2012). "*Thin-film composite forward osmosis membranes with novel hydrophilic supports for desalination*," J. Memb. Sci., vol. 423–424, pp. 543–555, doi: 10.1016/j.memsci.2012.09.005.
19. D. Li, Y. Yan, and H. Wang. (2016). *"Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes,"* Prog. Polym. Sci., vol. 61, pp. 104–155, doi:10.1016/j.progpolymsci.2016.03.003.
20. C. Klaysom, S. Hermans, A. Gahlaut, S. Van Craenenbroeck, and I. F. J. Vankelecom. (2013). "*Polyamide/Polyacrylonitrile (PA/PAN) thin film composite osmosis membranes: Film optimization, characterization and performance evaluation*," J. Memb. Sci., vol. 445, pp. 25–33, doi: 10.1016/j.memsci.2013.05.037.
21. T. Y. Cath *et al.* (2013). "*Standard Methodology for Evaluating Membrane Performance in Osmotically Driven Membrane Processes*," Desalination, vol. 312, pp. 31–38, doi: 10.1016/j.desal.2012.07.005.
22. M.H.O. Al-Furaiji, J.T. Arena, M. Chowdhury, N. Benes, A. Nijmeijer, J.R. McCutcheon. (2018). "*Use of forward osmosis in treatment of hyper-saline water*, " Desalin. Water Treat. ,doi:10.5004/dwt.2018.22851.
23. M. Al-Furaiji, M. Kadhom, K. Kalash, B. Waisi, and N. Albayati. (2020). "*Preparation of TFC Membranes Supported with Elelctrospun Nanofibers for Desalination by Forward Osmosis*," Drink. Water Eng. *Sci. Discuss.*, no. March, pp. 1–17, doi: 10.5194/dwes-2020-9.
24. B. Mi, M. Elimelech. (2008). "*Chemical and physical aspects of organic fouling of forward osmosis membranes"*, J. Memb. Sci. 320292–302. doi:10.1016/j.memsci.2008.04.036.
25. H. Li, W. Shi, H. Zhang, R. Zhou, X. Qin. (2020). '' *Preparation of internally pressurized polyamide thin-film composite hollow fiber nanofiltration membrane with high ions selectivity by a facile coating method* ", Prog. Org. Coatings. 139 105456. doi:10.1016/j.porgcoat.2019.105456.
26. L. F. Fang, L. Cheng, S. Jeon, S. Y. Wang, T. Takahashi, and H. Matsuyama. (2018). "*Effect of the supporting layer structures on antifouling properties of forward osmosis membranes in AL-DS mode*," J. Memb. Sci., vol. 552, no. May 2017, pp. 265–273, 2018, doi: 10.1016/j.memsci.2018.02.028.