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Effect of Piperazine (PIP) Concentration And Reaction Time on The Formation of Thin Film Composite Forward Osmosis (FO) Membrane

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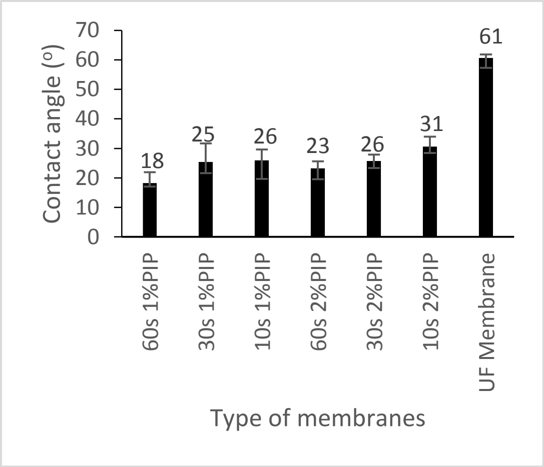
Graphical abstract



Abstract

Nowadays, wide applications of forward osmosis (FO) technology have been huge attention in solving the water shortage problems. Hence, the performance of thin film composite (TFC) forward osmosis membrane via interfacial polymerization (IP) was studied. 2% and 1% w/v of piperazine (PIP) and 0.15% w/v of trimesoyl chloride (TMC) were reacted with 3 different reaction time (60s, 30s, and 10s). The fabricated membranes were then characterized by FTIR, contact angle measurement and FESEM. Pure water flux, humic acid rejection (represent NOM) and salt leakage were evaluated to obtain the best polyamide FO membrane. The results demonstrated that polyamide FO membranes fabricated with 2% w/v possess a higher hydrophilic properties compared to 1% w/v. In addition, regardless of monomer concentrations, at longest reaction time (60s), there is no significant change in water flux. Membrane fabricated at 60s of reaction time exhibited water flux of 1.90 LMH and 1.92 LMH for 2% w/v and 1% w/v of PIP concentrations, respectively. The same trend also observed for humic acid rejection (93.9%-94.6%). The salt leakage test revealed that the minimum salt reverse diffusion (0.01-0.02 GMH) could be achieved for membrane fabricated at longest reaction time of 60s for both PIP concentrations. As conclusion, manipulating monomer concentrations and reaction time is the main key to obtain an optimal polyamide layer with high membrane performance covering higher water flux, higher removal of humic acid and lower reverse salt diffusion.

Keywords: Polyamide membrane, forward osmosis, water flux, humic acid rejection, salt leakage

1.0 INTRODUCTION

High demand for fresh and clean water has seen rapid growth due to the ever-increasing human population and industrial needs. Therefore, the work to find other alternatives for new resources of fresh water and water treatment will need special attention from researchers and engineers. One of the emerging solutions for the water scarcity problem is the membrane technology. Forward osmosis (FO) is a process that uses membrane technology which may be the viable technology to be applied in desalination and water treatment process.

Osmosis is a physical separation process that applies osmotic pressure, by which allowing the separation process to occur. This new emerging membrane technology, forward osmosis, utilizes osmotic pressure. The mechanism behind the osmotic pressure which is also known as natural driven force is generally due the differences of two solution concentration (feed and draw solution). Osmotic pressure create a driving force that allow permeate to pass through the semi permeable membrane. The great prospect of this technology was demonstrated in these industries like in chemical [1], liquid food processing [2], pharmaceutical products [3] and environmental indutries [4].

Unlike reverse osmosis (RO) that uses high driven pressure to to separate permeates from solution, FO uses osmotic pressure to effect pass of permeate through the membrane. In addition, FO has huge advantages, the process is much simpler to operate, low cost [5] and lower energy consumption [6]. Although the concept of forward osmosis has been exploited by human beings since early of mankind where the salt functioning as preservating agent, there are still a lot of research scope that needs to be explored.

Nowadays, in osmosis studies, there are a lot of researches that focusing on the synthesis, characterization and performance of the membrane. It can be seen that, most currently develop FO membranes are thin film composite membrane. This trend is due to the dense layer create on top surface of the membrane. Even though the FO membrane industries have develop commercial FO membrane known as Cellulose Triacetate (CTA) FO membrane, yet, their performances are limited by low permablity result, poor salt rejection and higher risk of potential to vulnerable by microorganism [6,7]. There are many factors influence the performancce of the membrane. The type of monomers use to create a layer of composite on top of the membrane is one of the factor that must be study.

There were limited references from previous researches that focusing on composite forward osmosis membrane that specifically study on effects of monomers to composite FO membrane. Latest research present the synthesis of thin film composite using interfacial polymerization (IP). Yusof *et al.* synthesized polyamide layer by using m-phenyldiamine (MPD) and trimesoyl chloride (TMC) as their monomers. Their study focused on the synthesis, characterization and study on the performance of the polyamide FO membrane in term of water flux and reverse salt diffusion but it was limited to the same monomers (MPD and TMC) throughout the research with different monomers reaction time [8]. The same membrane modification by Gan *et al.* on top of the active layer by adding some blending polymer into their membrane casting plays significant roles on the performance of the FO membrane. Their research was limited to same monomers where they used a polysulfone membrane as their base membrane through out the research [9].

In this work, an attempt has been made to synthesize and modify on the active layer on polyethersulfone (PES) membrane as the base membrane with monomers. Piperazine (PIP) and trimesoyl chloride (TMC) were reacted using interfacial polymerization (IP) method on active layer of the membrane. The main focus of this works is to synthesize, characterize and study the performance of the thin film composite FO membrane. The modification on the membrane surface that fulfills the criteria of the best performance membrane will give the most suitable indication of membrane to be used in FO applications.

2.0 METHODOLOGY

Chemicals

A commercial flat sheet membrane of polyether sulfone (PES 50) membrane was used as a base membrane purchased from AMFOR INC (China). The surface modification on the top surface layer of PES membrane was conducted by the interfacial polymerization reaction of two monomers, Piperazine (PIP) and trimesoyl chloride (TMC). Both monomers were supplied by Across Organics and Merck Sdn Bhd, respectively, where piperazine (PIP) is with >99.0% purity and trimesoyl chloride (TMC) is with >98.0% purity. N-hexane with >99.0% purity was supplied from Merck which function as the solvent for TMC monomer. Five different concentrations of sodium chloride solutions, NaCl (0.5M, 1.0M, 1.5M, 2.0M, and 2.5M) used as draw solution were purchased from Merck. As for the feed solution, 15mg/L of humic acid (HA) solution from Fluka was used in this experiment.

Membrane Preparation

A thin film composite forward osmosis membrane was synthesized by interfacial polymerization method. 2% w/v aqueous piperazine (PIP) and 0.15% w/v of trimesoyl chloride (TMC) were reacted to synthesize a polyamide layer on top of the commercial PES membrane. First, the PIP solution was immersed for 30 minutes on the active layer of the PES membrane before draining the excess of PIP solution on the membrane. After that, the TMC solution was immersed on the active layer of the membrane for three different reaction times of 10s, 30s, and 60s to allow the reaction of both monomers. After draining the excess monomer, the membrane was dried in fume hood for a day. Finally, the thin film composite of FO membrane then stored in pure water at cool temperature (8 $^{\circ}$C) to prevent the bacteria growth on the FO membrane. Hence, the experiment was repeated by using a different concentration of PIP monomer of 1% w/v of aqueous PIP solution.

Membrane Characterization

The performance of the membrane can be analyzed through the membrane characterizations. Three characterization tests has been made which are membrane morphology, contact angle and chemical analysis using Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy.

Morphology of thin film composite FO membrane was observed via a Field Emission Scanning Electron Microscope, FESEM (JSM-7800F). Liquid nitrogen was used to fracture the FO membrane before being tested in the FESEM.

Contact angle was used for membrane hydrophilicity analysis. The contact angles were measured by Contact Angle Geniometer where Milli-Q ultra-pure water was used as the probe liquid at room temperature. The ultra-pure water was dropped at 15 different spots on the active layer of membrane to minimize the experimental error and average value of contact angle was recorded.

FTIR testing was used to study the materials on active layer of the FO membrane.

Forward Osmosis Process

The performances of thin film composite FO membrane was evaluated via a lab-scale FO cross flow filtration system unit as shown in Figure 1, which is a similar method and system reported by Widjojo *et al.* [10]. The solution velocity was kept constant at 0.11 Lmin^{-1} during the experiment process. The temperature for both solutions also was kept constant at room temperature ~ 24°C during the experiment.

FO process consisted of two compartments which are feed and draw solution. 15 mg/L of HA and 0.5M of NaCl were prepared as feed and draw solution, respectively. Both solutions were diluted in ultra-pure water in two different 1000mL beakers. The draw solution was placed on a stirrer to keep the draw solution stirred during the experiment. Meanwhile, the feed solution was placed on a digital balance to record the liquid mass changes of draw solution via data logging system. The active layer of the membrane faced the feed solution side and support layer faced draw solution side while the membrane was placed vertically in membrane cell of lab scale FO system. As reported by Wei *et al.*, the orientation of the membrane influenced the membrane performance in term of higher water flux and higher solute rejection when the polyamide layer was faced a humic acid solution [11].

The initial and final mass changes of feed solution were recorded at time intervals of 5 minutes until the FO experiment was completed (1 hour). The duration of experiment for every concentrations (0.5M, 1.0M, 1.5M, 2.0M and 2.5M) of draw solution were fixed at 1 hour. After completed 1 hour of the experiment, the mass changes of feed solution were recorded for the calculation of the water flux. The method and formula of calculating water flux was mentioned Mehrparvar *et al.* works, is derived in formula below [12].

$$Water\ flux, J_w = \frac{\Delta V}{A\,\Delta t} \tag{1}$$

where, ΔV is volume of water permeate through the FO process (L), Δt is 1 hour, time taken for FO experiment (hr), and A = effective membrane surface area (m^2). The mass changes recorded of feed solution was converted into volume to calculate the water flux using equation 1.

For humic acid solute rejection, the initial and final concentration of humic acid was recorded by using a wavelength of humic acid, 254nm and Hitachi Ratio Beam Spectrophotometer (U-1800) with a Hellma 10mm cell made of Quartz SUPRASIL. In order to get the value of HA concentration of draw solution and feed solution (in mg/L), the concentration in absorbance value calculated by the UV-Vis spectrophotometer can be further derived using standard curve. The concentration of HA in both solutions (in mg/L) was then inserted in HA solute rejection (%) equation as stated in equation 2.

$$Rejection, R = \left[1 - \left(\frac{C_d}{C_f}\right)\right] \times 100\% \tag{2}$$

where the Cd and Cf are concentration of humic solutes in the draw solution and feed solution, respectively.

Salt solute rejection was determined by measuring the conductivity of feed solution. The conductivity measurement on feed solution is based on the standard concentration-conductivity curve. The salt solute rejection or salt leakage, Js in g m^{-2} hr^{-1} (GMH) from draw solution to the feed solution was determined by the increasing of conductivity level in feed solution using conductivity measurement meter and derived in equation 3

$$Salt\ leakage, J_s = \frac{\Delta(C_t V_t)}{A\,\Delta t} \tag{3}$$

where C_t are the salt concentration and V_t are volume of feed solution at the end of the FO tests, respectively.

3.0 RESULTS AND DISCUSSION

Membrane Characterization

Figure 1 shows the morphology (top surface and cross section) of the 2% w/v of PIP FO membrane and the commercial PES membrane

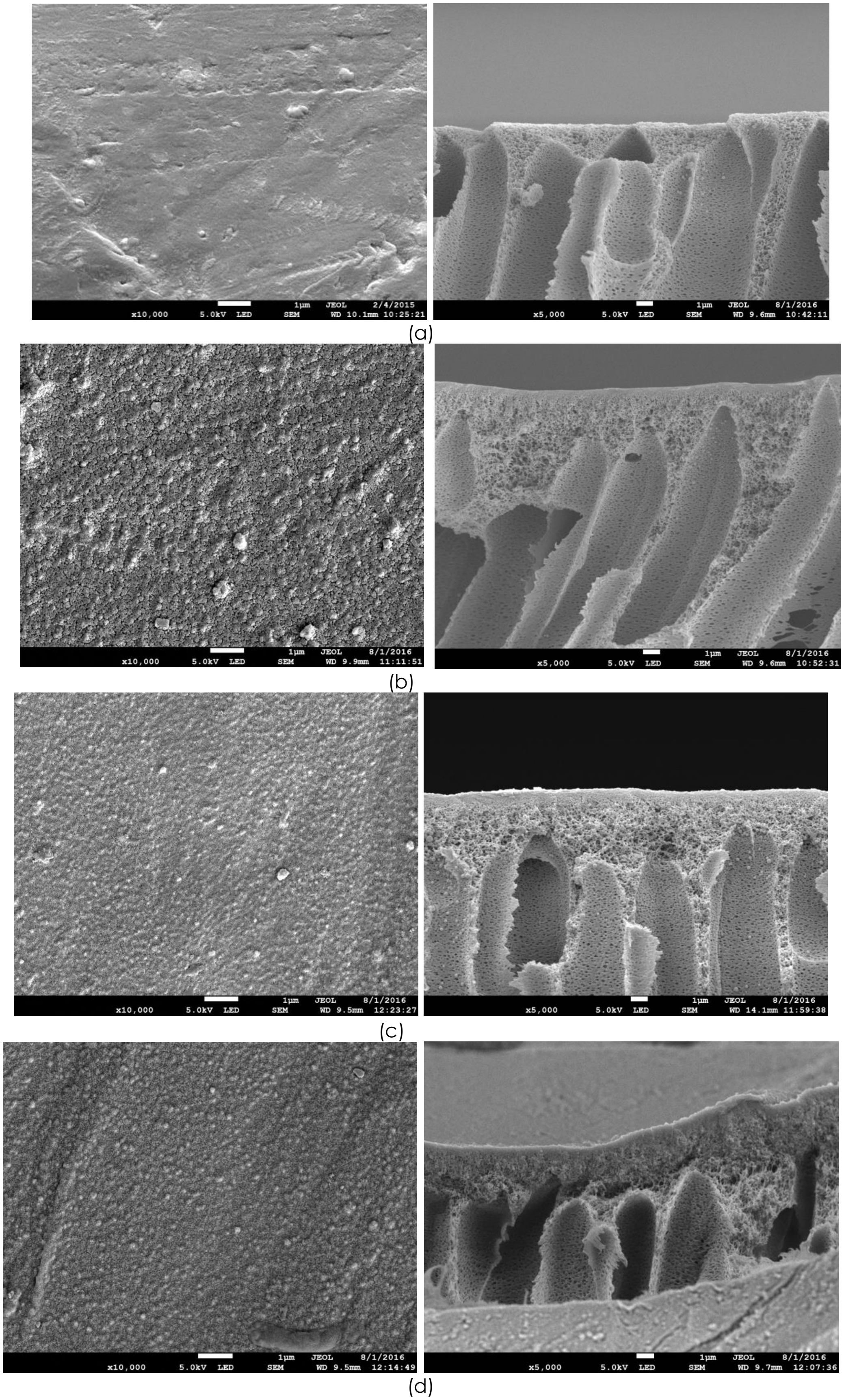


Figure 1 FESEM figures of the top surface (left, 10kx) and cross section (right, 5kx) (a) PES membrane and 2% w/v of PIP at three different reaction time, (b) 60s, (c) 30s, and (d) 10s

As shown in Figure 1, the top surface of the membrane, thin film composite membranes have rougher surface than PES membrane. It can be observed that "Circle-like" morphologies formed on top of three composite membranes compared to PES membrane which exhibits a smooth surface. The "Circle-like" morphology on 60s FO membrane also have a denser structure compared to 30s and 10s membranes. In terms of morphology, it can be observed that, composite membrane have a thick layer on top of the active layer surface. The 60s composite membranes exhibit a thicker layer of polyamide compared to 30s and 10s composite membranes. A layer of polyamide formed when the reaction between monomers (PIP and TMC) reacted via interfacial polymerization.

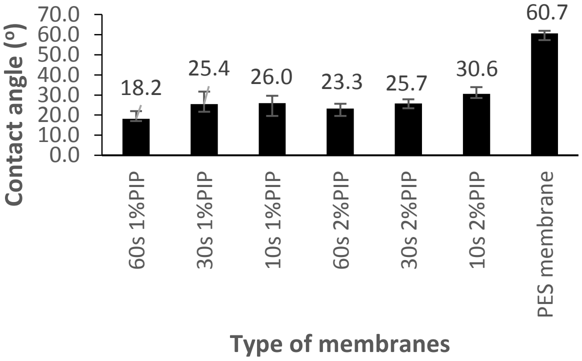


Figure 2 Contact angles measurement

Contact angle measurements further indicate that FO membrane with higher concentration of PIP has lower contact angle. As indicated in Figure 2, 1% w/v of PIP with 60s of reaction time recorded a lower contact angle (18.2°) compared to 2% w/v of PIP membrane (23.3°) with the same reaction time. Generally, the FO membrane with longest reaction time, 60s recorded a lower contact angle compared to 30s and 10s membrane. Figure 2 shows that 1% w/v of PIP with 60s of reaction time recorded the lowest contact angle reading (18.2°) compared to 30s and 10s membrane, respectively. In addition, PES membrane recorded a much higher contact angle reading compared to the composite membranes shows that the presence of composite layer or polyamide layer enhances the hydrophilicity of the membrane. The varying contact angle is probably due to the formation of composite layer from the reaction of two monomers, PIP and TMC on top of the membrane active layer.

Figure 3 shows the ATR-FTIR spectra analysis on both PES and thin film composite FO membrane (2% w/v of PIP). The spectrum of the active layer of both membranes shows peaks attributed to the active layer on the membranes. Circle indicate the peaks that are specific reaction occur on the membrane. The spectrum displays the characteristic peaks of C=O stretching amide peaks indicates the composite polyamide layer on 1667 cm^{-1}. Other than that, the peaks of aromatic ring and C-N stretching of amide also being display on 1602 cm^{-1} and 1522 cm^{-1}, respectively. Based on the peaks shown in Figure 3, it strongly suggest the likelihood that polyamide layer are well formed on the active layer of the FO membranes.

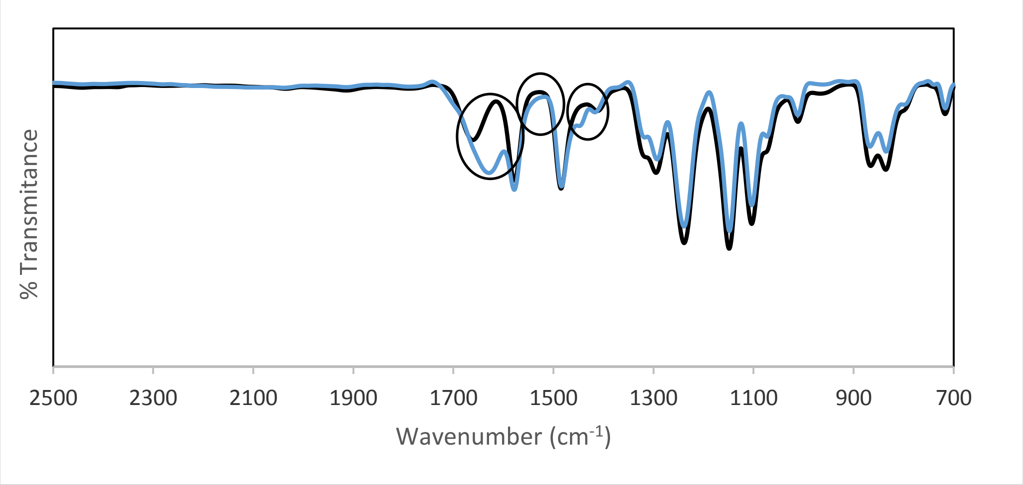


Figure 3 ATIR-FTIR spectrum of the PES membrane (black curve) and composite FO membrane (blue curve)

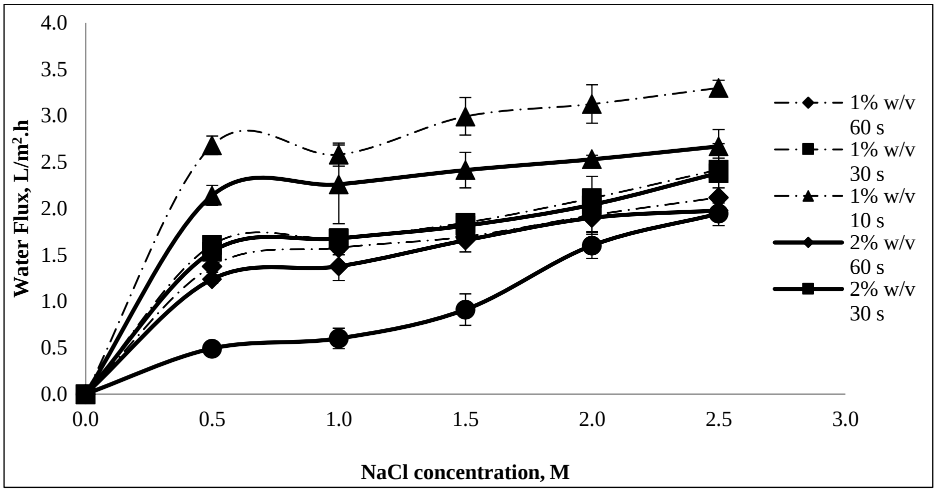


Figure 4 Water flux for different type of membranes

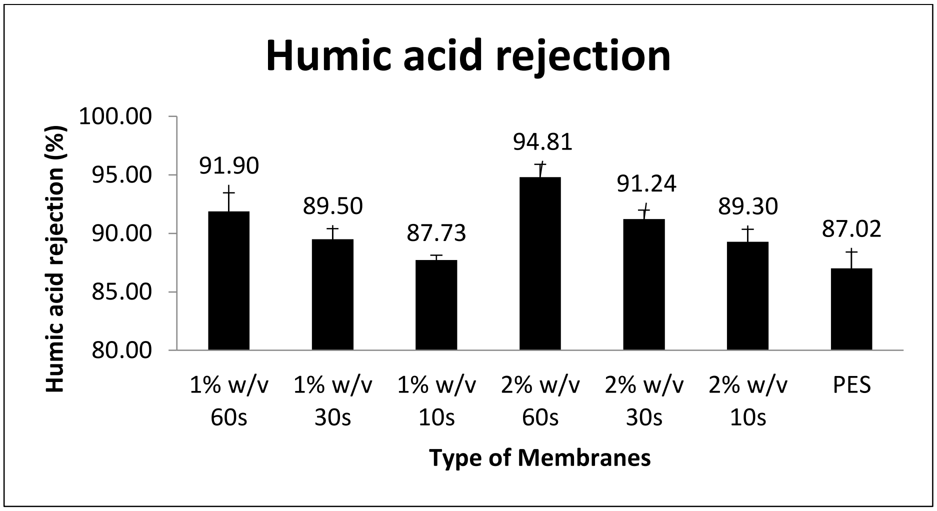


Figure 5 Humic acid rejection at 2.5M of NaCl solution

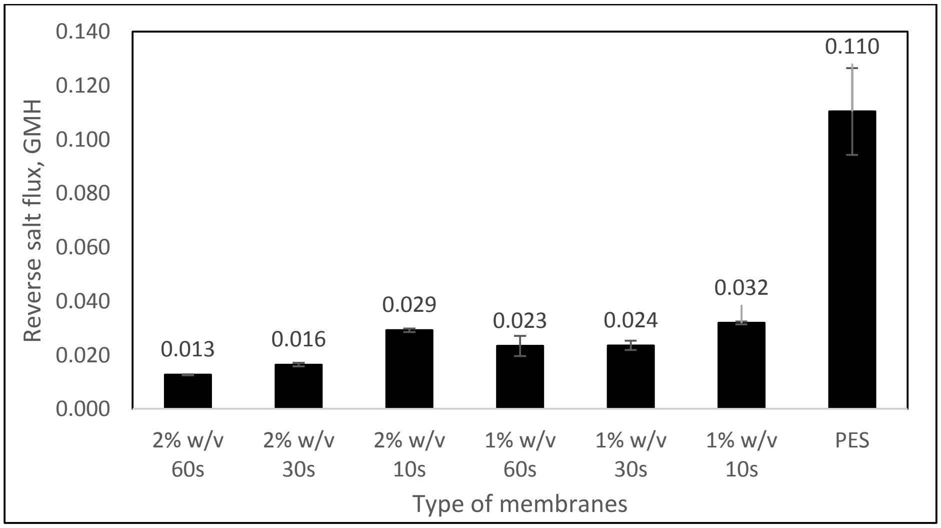


Figure 6 Reverse salt flux (GMH) at 2.5M of NaCl solution

Membrane Performances

The performances of the membranes were based on the water flux in FO system, the humic acid solute rejection and the reverse salt analysis. In this research, seven types of the membrane have been analyzed for its performance. The membranes are a PES membrane with six different types of TFC FO membranes produced by using two different monomers (1% and 2% w/v of PIP) where both reacted with 0.15% w/v of TMC at three different reaction time (60s, 30s and 10s).

The water flux for each membranes tested in FO lab scale system were summarized in Figure 4. Based on the Figure 4, the water flux of membranes increased with the increasing of NaCl concentration. The increments of NaCl concentration builds up osmotic pressure that will lead to osmosis process to occur through the membrane. The water from concentrated (draw) solution will pass through the membrane into the less concentrated (feed) solution. In terms of monomer concentration on the membranes, it shows that FO membrane with 1% w/v of PIP recorded a higher water flux compared to other membranes. The thickness of the polyamide layer form via interfacial polymerization reaction between monomers influenced the water flux to pass through the membranes. The more formation of dense polyamide layer due to the higher concentration of PIP resulted a less water transport through the membrane. A lower concentration of PIP (1% w/v of PIP) resulted a higher water flux recorded compared to lower water flux by higher concentration of PIP (2% w/v of PIP) with 3.3 $Lm^{-2}h^{-1}$ 2.7 $Lm^{-2}h^{-1}$ at 2.5M of NaCl, respectively. In addition, the reaction time between monomers also affected the water flux of membranes. The membranes produced by a longer reaction time exhibits a lower water flux. The formation of polyamide layer is expected to be thicker and dense when the reaction time increased hence exhibited a lower water flux [13]. Generally, the concentration and reaction time of monomers are significantly affecting the membrane performance.

Other than water flux, this study also focused on the humic acid rejection. The humic acid rejection of membranes at 2.5M of NaCl were summarized in Figure 5. By referring to Figure 5, it shows that modified thin film composite membrane recorded a higher HA solute rejection compared to commercial PES membrane. It obviously shows that the composite FO membrane with higher concentration of PIP (2% w/v of PIP) and longest reaction time of monomers (60s) resulted in a higher solute HA rejection compared to lower concentration of PIP (1% w/v of PIP) and shorter reaction time of monomers (30s and 10s) membranes. The thickness and dense polyamide layers formed on the active layer of the membrane gives a significant impact to the HA solute rejection. The higher concentration and longer reaction time of monomers also formed a smaller pore size. Previous research from Jalanni *et al*. also reported the same findings on their nanofiltration (NF) system where the variation of monomers reaction time improved their membranes performance in term of water flux and HA rejection [14].

In order to measure the performance of the membrane, salt leakage is an indicator used to measure the FO membrane performance [15]. Salt leakage is a reverse salt activity due to the osmotic pressure created by the differences of two solution in FO system which flow along with water through the FO membrane. The salt were flowed with water from draw to feed solution and this will affect our membrane performances in term of salt rejection. Figure 6 summarized the reverse salt activity on the FO and PES membranes. The figure clearly shows that composite FO membranes have a lower reverse salt flux compared to PES membrane. The thickness and dense polyamide layer on top of the membrane has reduced the pore size which limit the reverse salt activity to pass through the membrane.

The concentration of PIP also give a significant role in modification of the polyamide layer. The increase in monomer concentrations will lead to a denser polyamide layer which reduces the pore size produced and prevent the salt activity from draw solution to pass through the membrane into the feed solution. Han *et al.* reported the same finding on reverse salt flux on composite FO membrane but different monomers were used (MPD and TMC). The research used seven different concentrations of monomers which would give a significant impact to reverse salt activity on their FO system [9].

4.0 CONCLUSION

In this study, the characterization and performance of the thin film composite FO membrane and PES membrane were successfully studied. According to the results, the modified membranes, thin film composite FO membranes has shown an excellent improvement from the commercial PES membrane in terms of water flux, humic acid rejection and reverse salt flux. The presence of polyamide factor enhance the hydrophilicity where the contact angle indicates that thin film membrane recorded a lower contact angle (18.2° – 30.6°) compared to PES membrane (60.7°). The same trends has been shown in humic acid rejection and reverse salt fluxes. The results have indicated that the variation of concentration and reaction time of monomers improved the separation FO process. The higher concentrations of PIP resulted in a significant result of water flux plus higher humic acid rejection and lower reverse salt flux. The modification of the membranes with additional of monomers also affect the membrane morphology and improved the hydrophilicity of the membranes. Further research and improvement is recommended especially on the effect of fouling on the modified FO membranes in terms of membrane performances and FO filtration process, respectively.

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References

[1] Baker, E. C., Sullivan, D. A., and Regional, N. 1983. Development of a Pilot-Plant Process for the Extraction of Soy Flakes with Aqueous Isopropyl Alcohol. *Journal of the American Oil Chemists' Society*. 60(7): 1271-1277

[2] Garcia-castello, E. M., Mccutcheon, J. R., and M. Elimelech. 2009. Performance Evaluation Of Sucrose Concentration Using Forward Osmosis. *J. Memb. Sci*. 338: 61-66.

[3] Chung, T., Zhang, S., Yu, K., Su, J., and Ming, M. 2012. Forward Osmosis Processes : Yesterday, Today And Tomorrow. *Desalination*. 287: 78-81.

[4] McCutcheon, J. R., McGinnis, R. L., and Elimelech, M. 2006. Desalination By Ammonia-Carbon Dioxide Forward Osmosis: Influence Of Draw And Feed Solution Concentrations On Process Performance. *J. Memb. Sci.* 278: 114-123.

[5] Reddy, K.V. and Ghaffour, N. 2007. Overview Of The Cost Of Desalinated Water And Costing Methodologies. *Desalination*. 205: 340-353.

[6] McGinnis, R. L. and Elimelech, M. 2007. Energy Requirements Of Ammonia-Carbon Dioxide Forward Osmosis Desalination. *Desalination*. 207: 370-382.

[7] Emadzadeh, D., Lau, W. J., and Ismail, A. F. 2013. Synthesis Of Thin Film Nanocomposite Forward Osmosis Membrane With Enhancement In Water Flux Without Sacrificing Salt Rejection. *Desalination*. 330: 90-99.

[8] Amirul, M., Yusof, M., Nizam, M., Seman, A. and Hilal, N. 2016. Development Of Polyamide Forward Osmosis Membrane For Humic Acid Removal. *Desalin. Water Treat.* 3994: 1-5.

[9] Han, G., Chung, T. S., Toriida, M. and Tamai, S. 2012. Thin-Film Composite Forward Osmosis Membranes With Novel Hydrophilic Supports For Desalination. *J. Memb. Sci.* 423-424: 543-555.

[10] Widjojo, N., Chung, T.-S., Weber, W., Maletzko, C. and Warzelhan, V. 2011. The Role Of Sulphonated Polymer And Macrovoid-Free Structure In The Support Layer For Thin-Film Composite (TFC) Forward Osmosis (FO) Membranes. *J. Memb. Sci.* 383: 214-223.

[11] Wei, J., Liu, X., Qiu, C., Wang, R. and Tang, C. Y. Influence Of Monomer Concentrations On The Performance Of Polyamide-Based Thin Film Composite Forward Osmosis Membranes. *J. Memb. Sci.* 381: 110-117.

[12] Mehrparvar, A., Rahimpour, A. and Jahanshahi, M. 2014. Modified Ultrafiltration Membranes For Humic Acid Removal. *J. Taiwan Inst. Chem. Eng.* 45: 275-282.

[13] Yang, F., Zhang, S., Yang, D. and Jian, X. 2007. Preparation And Characterization Of Polypiperazine Amide/PPESK Hollow Fiber Composite Nanofiltration Membrane. *J. Memb. Sci.* 301: 85-92.

[14] Jalanni, N. A., Abu Seman, M. N. and Faizal, C. K. M. 2013. Investigation Of New Polyester Nanofiltration (NF) Membrane Fouling With Humic Acid Solution. *Jurnal Teknologi.* 65: 69-72.

[15] Emadzadeh, D., Lau, W. J., Sisakhat, M. R., Ilbeygi, H., Rana, D., Matsuura, T. and Ismail, A. F. 2015. Synthesis, Modification And Optimization Of Titanate Nanotubes-Polyamide Thin Film Nanocomposite (TFN) Membrane For Forward Osmosis (FO) Application. *Chemical Engineering Journal*. 281: 243-251.