

# Performance of Forward Osmosis (FO) Membrane Fabricated from Different Molecular Weight of Polyvinylpyrrolidone (PVP) Additive

Nur Aisyah Shafie<sup>a</sup>, Mazrul Nizam Abu Seman<sup>a,b,\*</sup>, Syed Mohd Saufi Tuan Chik<sup>a</sup>, Abdul Wahab Mohammad<sup>c</sup>

<sup>a</sup>Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Persiaran Tun Khalil Yaakob, 26300 Gambang, Kuantan, Pahang, Malaysia

<sup>b</sup>Earth Resources and Sustainability (ERAS) Centre, Universiti Malaysia Pahang, Lebuhraya Persiaran Tun Khalil Yaakob, 26300 Gambang, Kuantan, Pahang, Malaysia

<sup>c</sup>Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia  
mazrul@ump.edu.my

Despite of the emergence of revolutionary Forward Osmosis (FO) technology, the membrane is hindered by the severe effect of internal concentration polarization (ICP) which generated in membrane substrate layer. In current study, polyethersulfone (PES) membranes substrate layer were fabricated via phase inversion using three different polyvinylpyrrolidone (PVP; molecular weight of 10 kDa, 40 kDa and 360 kDa) which act as a pore former agent. Using 2 wt% of aqueous *m*-phenylenediamine (MPD) and 0.15 wt% of trimesoyl chloride (TMC) in hexane, the active polyamide layer was formed on the top surface of PES substrate via interfacial polymerization to produce thin film composite (TFC) FO membrane. The performance of TFC FO membranes were evaluated and three intrinsic parameters; A, B and S were determined by mathematical model. The results attained were compared to find the optimized PVP molecular weight for FO membranes with desired performance. It was observed that FO membrane prepared with molecular weight PVP of 40 kDa exhibited excellent performance with low ICP, thus reduce the replacement of draw solute in FO application.

## 1. Introduction

Freshwater is a renewable resource but increasing population development and density have put a pressure on the ability of many local sources to meet water quantity and quality demands. Continuous population growth coupled with a vast increase in urbanization and industrialization has exacerbated water shortage in several regions of the world. Simultaneously, climate change and pollution have destabilized the ecosystem, resulting in an inadequate supply of freshwater (Unfried et al., 2022). Even though 96 % of the planet's surface is covered by salty ocean water, the fact that seawater is unfit for human consumption remains unchanged. According to a recent analysis, global water cessation will significantly raise from  $4,500 \times 10^9$  to  $6,900 \times 10^9$  m<sup>3</sup>/y by 2030 (McKinsey, 2009). Unless new means to supply and increase freshwater are found, water scarcity may cause global catastrophe in the coming years. A recent surge in membrane science and technology, however, gives reason for optimism about reducing the negative effects of this subject. Membrane technology appears to be a worthwhile and cost-effective separation technique for replenishing and recovering freshwater from a variety of inputs that address both salinity effect and pollution peculiarities (Goh et al., 2022). Over the past decades, reverse osmosis (RO) has overtaken membrane niche owing to the successfulness in desalination of seawater and wastewater treatment. Nevertheless, this pressure-driven system obstructed by the major downsides such as high energy cost, significant potential of fouling, as well as high of retentate concentration. The drawbacks lead to the emergence of novel forward osmosis (FO) membrane which proven to be more advantageous compared to RO even at molecular level. Unlike the RO membrane, FO separation using the fundamental of natural occurrence; osmotic pressure gradient and due to that, it requires less energy to execute the operation than pressure-driven membrane. However, the FO membranes suffers from the limitation of internal

concentration polarization which generates within the porous substrate layer. Many of researchers agreed that ICP is the major stumbling block in FO development (Song et al., 2021). Herein by, the deep exploration of FO membrane system is urgently needed prior to advance this highly potential technology to commercial viability. TFC FO membrane comprises of thin polyamide (PA) layer and porous substrate/support layer. Further amplification of the porous substrate layer results in distinct bulk and surface substrate characteristics and functionalities. Substrate bulk properties like pore structure, tortuosity and porosity, responsible in evaluating structural parameter, S value, in which, S value will be determining the ICP effect and membrane performances (Wang et al., 2018a). In the present work, polyethersulfone (PES) membrane was fabricated with the addition of pore former agent, polyvinylpyrrolidone (PVP). PVP is one of the most extensively utilized additive, including in FO membranes, due to its non-toxicity and miscibility in water and range of organic solvent (Amin et al., 2018). In previous work, it was demonstrated that the inclusion of PVP in PES polymer with the presence of calcium chloride,  $\text{CaCl}_2$  has increased membrane porosity and water flux effectively (Rambabu and Velu, 2016). Incorporation of PVP in another type of polymer, polysulfone (PSF) via electrospinning of hollow fibre also exhibited the outstanding result in increasing the water flux, thus, improving membrane permeability and performances (Othman et al., 2018). Wang et al. (2018b) studied performance of FO membrane prepared by PSf/PVP substrate followed by the dopamine (DA) self-polymerization, and the result showed the membrane had less flux decline and antifouling properties (Wang et al., 2018b). Based on the previous study, this clearly shown that the performances of membranes could be improve significantly by the addition PVP additive in parent polymer during blending. However, the effect of PVP properties such as molecular weight, especially for FO system were rarely investigated. In the present work, the study of effect PVP with different molecular weight (MW) on FO membrane performances were carried out.

## 2. Methodology

### 2.1 Materials

Polyethersulfone (PES) as a parent polymer, polyvinylpyrrolidone (PVP, Molecular weight~10 kDa, 40 kDa, 360 kDa, Sigma Aldrich) additive and 1-methyl-2-pyrrolidinone (NMP, 99 %, Sigma Aldrich) as solvent were used for preparation of dope solution in fabrication of porous substrate layer. For active layer formation, M-Phenylenediamine (MPD, flakes, 99 %, Sigma Aldrich) in deionized (DI) water and 1,3,5-Benzenetricarbonyl chloride (TMC, Sigma Aldrich) in hexane (Emsure®, Supelco) were utilized.

### 2.2 Fabrication of porous substrate membrane

Dope solutions were prepared by mixing the 15 wt% of PES and 3 wt% of PVP in NMP solvent. The mixture was then stirred at 300 rpm in room temperature until the homogenous solution with honey-like texture was obtained. The dope solution was left for 1 day for bubbles removal. Fabrication of membrane was done at room temperature using a semi-automated casting machine via non-solvent induced phase separation technique.

### 2.3 Preparation of TFC forward osmosis membrane

Initially, the PES membrane substrate was placed horizontally on the acrylic plate and the top surface of the substrate was poured with 2.0 wt% MPD solution for 10 min. The excess MPD solution was removed using rubber roller and 0.15 wt% TMC-hexane was then added on the MPD-coated surface for 2 min to allow interfacial polymerization process forming PA active layer. The TFC membrane formed was dried at 60 °C to remove the excess solvent.

### 2.4 Characterization of porous substrate and TFC membrane

The substrate membrane's porosity, pore size and wettability were measured using gravimetric analysis, filtration velocity method, and contact angle measurements, respectively. Meanwhile, the morphology and surface roughness of TFC FO membrane was analyzed using Field Emission Scanning Electron Microscope (FESEM; Model MERLIN, Zeiss) and Atomic Force Microscopy (AFM; Model NX-10, Park Systems), respectively.

### 2.5 FO performance test

FO performances parameter such as water flux ( $J_w$ ) and reverse salt diffusion (RSD) were determined via FO laboratory scale unit system. The system was equipped with crossflow FO cells, peristaltic pump with two heads, two of 1000 mL tanks, weighing scale and magnetic stirrer. Four silicone tubes were used to circulate the draw solution (DS) and feed solution (FS) continuously at flowrate of 167.1 mL/min crossing the membrane, which located within the FO cell. The mass changes of DS were recorded after 1 h of steady state continuous circulation. The water flux ( $J_w$ ) was calculated using Eq (1) as follow: (Abdullah et al., 2022):

$$J_w = \frac{\Delta V}{A_m \times \Delta t} \quad (1)$$

where  $\Delta V$  is the volume change of DS (L),  $A_m$  is membrane active area ( $m^2$ ) and  $\Delta t$  is time taken (h). Throughout the test, the initial and final conductivity of FS were recorded using conductivity meter (Eutech PC 2700) for RSD estimation. The NaCl calibration curves were used for conductivity and concentration correlation. RSD was estimated using Eq(2) (Abdullah et al., 2022):

$$J_s = \frac{C_t V_t - C_0 V_0}{A_m t} \quad (2)$$

where  $C_0$  and  $C_t$  are the initial and final concentration (g/L) of NaCl in feed solution, while  $V_0$  and  $V_t$  are the volume (L) of feed solution measured at initial and the time of  $t$ .

### 3. Results and discussion

#### 3.1 Effect of PVP molecular weight on pore size, porosity of PES substrate and wettability of TFC FO membrane

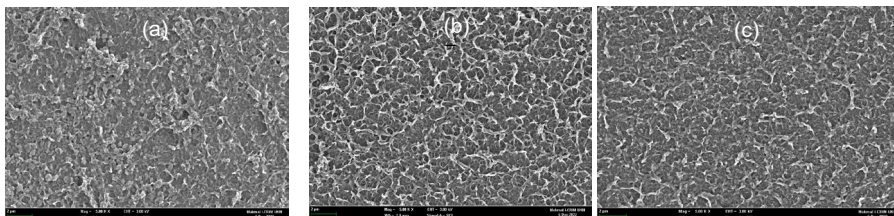
Table 1 shows the pore size, porosity and wettability values obtained via filtration velocity method, gravimetric method and contact angle, respectively. The overall substrate characteristic analysis exhibits the forecasted trend where PES/PVP40k was the highest with the porosity of  $86.00 \% \pm 0.55$  and  $41.87^\circ \pm 3.43$  of wettability followed by PES/PVP10k (porosity of  $82.44 \% \pm 0.59$  and wettability of  $46.55^\circ \pm 5.09$ ) and PES/PVP360k (porosity of  $80.22 \% \pm 0.26$  and wettability of  $53.28^\circ \pm 5.09$ ). The result demonstrates that increasing the MW of PVP from 10 kDa to 40 kDa to the parent polymer can affect membrane morphology by generating microporous structures, resulting in increased membrane porosity and wettability. However, substantial differences in pore size, porosity and wettability were identified when higher MW of 360 kDa was used resulting a lowest porosity, smallest pore size and more hydrophobic substrate compared to the other two MWs. This is owing to the distinct properties that low MW PVP and high MW PVP possess. Theoretically, low MW PVP is more water-soluble than high MW PVP, resulting in the formation of a greater number of pores during the phase inversion process. Meanwhile, high MW of PVP is typically entrapped within the polymer structure, thus decreasing membrane porosity with a denser structure (Ismail and Hassan, 2007).

*Table 1: Pore size and porosity of PES membrane substrate with different PVP molecular weight and wettability of TFC FO membranes*

| Membrane    | PVP molecular weight (kDa) | Pore size, $r_m$ (nm) | Porosity, $\varepsilon$ (%) | Wettability ( $^\circ$ ) |
|-------------|----------------------------|-----------------------|-----------------------------|--------------------------|
| PES/PVP10k  | 10                         | $18.0 \pm 0.4$        | $82.44 \pm 0.59$            | $46.55 \pm 5.09$         |
| PES/PVP40k  | 40                         | $20.1 \pm 0.3$        | $86.00 \pm 0.55$            | $41.87 \pm 3.43$         |
| PES/PVP360k | 360                        | $7.8 \pm 0.1$         | $80.22 \pm 0.22$            | $53.28 \pm 2.49$         |

#### 3.2 Morphology of FO membrane

The top surfaces of FO membranes for substrate of PES/PVP10k, PES/PVP40k, and PES/PVP360k were presented in FESEM and 3D AFM images through Figure 1 and Figure 2, respectively. Ra values of 58.494 nm for PES/PVP360k, 90.818 nm for PES/PVP40k, and 128.883 nm for PES/PVP10k indicate decrease in surface roughness as the molecular weight of PVP increases.



*Figure 1: The FESEM images of TFC FO membranes using PES substrate fabricated with different PVP molecular weight (a) PES/PVP10k (b) PES/PVP40k and (c) PES/PVP360k*

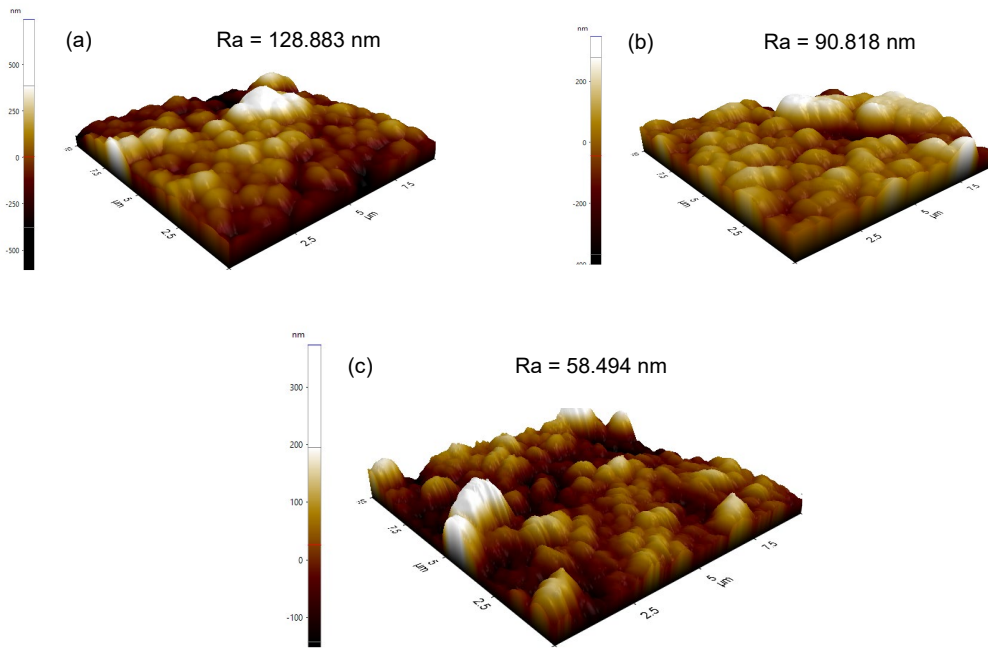


Figure 2: The 3D AFM images of TFC FO membranes using PES substrate fabricated with different PVP molecular weight (a) PES/PVP10k (b) PES/PVP40k and (c) PES/PVP360k

### 3.3 Water flux ( $J_w$ ) and reverse salt diffusion ( $J_s$ )

The results of the FO performance tests are represented in Figure 3. When the concentration of DS was increased from 0.5 to 1.25 M, the water flux,  $J_w$ , of TFC membranes constructed from different PVP molecular weights followed the expected trend. As the concentration of DS increases, the concentration difference across the membrane skyrockets, resulting in the rapid migration of water passing through the membrane to equilibrate the solute concentrations of draw solution and feed water. PES/PVP40k membrane had the maximum water flux with values of 2.2786, 2.8512, 3.0583 and 3.9310  $L m^{-2} h^{-1}$  for 0.5, 0.75, 1.0 and 1.25 M of DS. This was followed by PES/PVP10k membrane (1.8452, 2.4940, 2.6274 and 3.3738  $L m^{-2} h^{-1}$  for 0.5, 0.75, 1.0 and 1.25 M of DS) and PES/PVP360k (0.8786, 0.9798, 1.6583, 2.1952  $L m^{-2} h^{-1}$  for 0.5, 0.75, 1.0 and 1.25 M of DS).

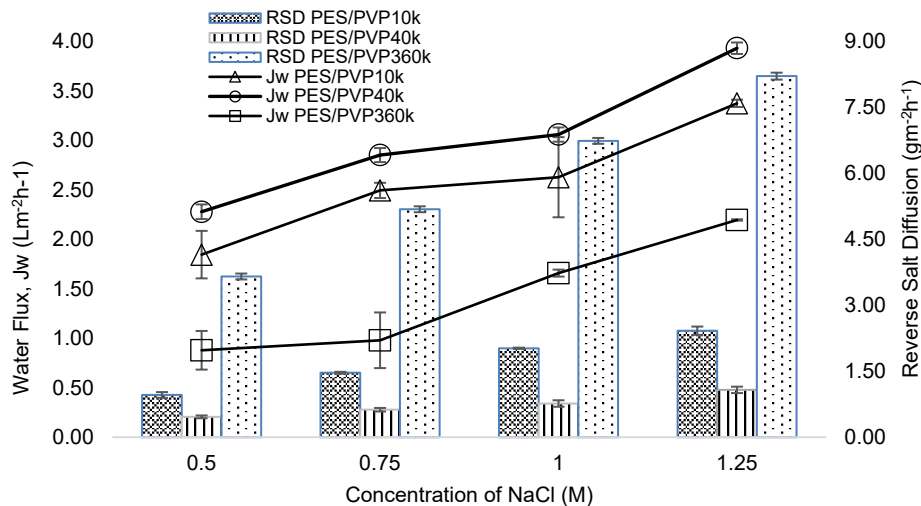


Figure 3: Water flux and RSD of TFC FO membranes using PES substrate fabricated with different of PVP molecular weight

There was a notable change between the water flux values of membranes with low MW PVP and those with high MW PVP. The low molecular weight PVP acts as a hydrophilicity enhancer that can increase the membrane's water penetration degree and the number of micropores, allowing transportation of more water molecules cross the membrane matrix (Jung et al., 2004). However, a modest difference in water flux was seen for membranes with low MW PVP; PES/PVP10k and PES/PVP40k, with a similar trend to the porosity and wettability results. In addition, it was observed that the reverse salt diffusion (RSD) was increased with increasing of draw solution concentration. For instance, PES substrate fabricated with 10 kDa PVP exhibited reverse salt diffusion ( $J_s$ ) increased from  $0.96 \text{ gm}^{-2}\text{h}^{-1}$  to  $2.42 \text{ gm}^{-2}\text{h}^{-1}$  when 0.5M and 1.25M of NaCl were applied as draw solution. Similar trend was also observed by Bai and Kruczek, (2022) when using 1M to 4M of NaCl as draw solution for FO process. At the higher draw solution concentration, it is expected an increase in driving force of water molecules together with the salt in the opposite direction thus contribute to the higher RSD value. Meanwhile, the highest  $J_s$  value was obtained for PES/PVP360k membrane with less hydrophilic characteristic may contribute to a loose PA layer formation and this will allow more NaCl solute to pass through the membrane during FO process lead to severe RSD. Interestingly, membrane prepared with 40 kDa shows the lowest RSD value while maintaining the highest water flux for the all draw solution concentrations.

### 3.4 Mathematical modelling of intrinsic parameters

Table 2 summarized the intrinsic parameters (A, B and S) of each type of membrane, were predicted using mathematical model proposed by Tiraferri et al., (2013). For both water and solute permeability coefficient, the values were dependent of the water flux and RSD. In FO membrane, A and B are responsible in predicting and describing the mass transport across the membrane quantitatively (Tiraferri et al., 2013). Based on Table 2, PES/PVP40k had the highest water permeability coefficient at  $0.0896 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , followed by PES/PVP10k at  $0.0896 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and PES/PVP360k at  $0.0454 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . This data corresponds to the value of the water flux; as the water flux increases, so will the A value. Regarding the solute permeability coefficient, the trend is as follows: PES/PVP360k ( $0.159 \text{ L m}^{-2} \text{ h}^{-1}$ ) > PES/PVP10k ( $0.0438 \text{ L m}^{-2} \text{ h}^{-1}$ ) > PES/PVP40k ( $0.0208 \text{ L m}^{-2} \text{ h}^{-1}$ ). The expected results matched the RSD values because the higher the MW of the PVP employed, the greater the solute permeability, resulting in a greater RSD value. S, the structural parameter, is another essential intrinsic property of FO membrane that is controlled by the substrate's porosity, tortuosity, and pore structure (Kahrizi et al., 2022). According to Table 2, the structural parameter of membranes climbs as the MW PVP used increases from 482 m for PES/PVP10k to 595 m for PES/PVP40k to 950 m for PES/PVP360k. The minimal structural parameter value is essential since it denotes the degree of the internal concentration polarization effect (ICP). According to the data, membranes with a high molecular weight PVP have higher structural parameter values than those with a low molecular weight PVP, resulting in a decrease in water flux and an increase in reverse salt diffusion. A substantial difference was noticed between the water flux and structural parameters of PES/PVP10k and PES/PVP40k. The structural parameter and water flux are inversely proportional for both membranes. Assuming that the bulk substrate's low structural parameter will result in the highest water flux, the membrane can be stated to have such optimal performance. The structural parameter values of both low molecular weight PVP membranes were supplemented by their porosity, but the values were also influenced by the membrane substrate's structure and tortuosity (Kahrizi et al., 2022).

Table 2: Predicted intrinsic parameters using mathematical model for different types of FO membranes

| Membrane    | Water Permeability Coefficient,<br>A ( $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) | Solute Permeability Coefficient,<br>B ( $\text{L m}^{-2} \text{ h}^{-1}$ ) | Structural Parameter,<br>S ( $\mu\text{m}$ ) |
|-------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------|
| PES/PVP10k  | 0.0755                                                                                     | 0.0438                                                                     | 482                                          |
| PES/PVP40k  | 0.0896                                                                                     | 0.0208                                                                     | 595                                          |
| PES/PVP360k | 0.0454                                                                                     | 0.1590                                                                     | 950                                          |

## 4. Conclusions

The influence of PES blending with low and high molecular weight PVP on the membrane performances and morphologies were examined. Molecular weight PVP of 40 kDa was found to be the best additive for PES membrane substrate which displayed the highest porosity of  $86.00 \% \pm 0.55$  and wettability of  $41.87^\circ \pm 3.43$ . The water flux of PES/PVP40k demonstrated the highest flux ( $3.9310 \text{ Lm}^{-2}\text{h}^{-1}$ ) with the lowest RSD value. These results indicate the dominance of molecular weight PVP of 40 kDa on the formation of TFC FO membrane with microporous structure for outstanding performances, thus can minimizing the ICP effect. However further investigation is required especially the effect of this PVP (MW:40 kDa) concentration on the physical properties and overall performance.

## Nomenclature

|                                                                                  |                                                              |
|----------------------------------------------------------------------------------|--------------------------------------------------------------|
| A – Water permeability coefficient, $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ | $J_w$ – Water flux, $\text{Lm}^{-2}\text{h}^{-1}$            |
| $A_m$ – Effective membrane area, $\text{m}^2$                                    | $r_m$ – Pore size, nm                                        |
| B – Solute Permeability Coefficient, $\text{Lm}^{-2}\text{h}^{-1}$               | S – Structural parameter, $\mu\text{m}$                      |
| $C_o$ – Initial concentration of NaCl, g/L                                       | t – Time taken for FO operation, h                           |
| $C_t$ – Final concentration of NaCl, g/L                                         | $V_o$ – Volume of feed solution measured at initial, L       |
| $J_s$ – Reverse solute diffusion, $\text{gm}^{-2}\text{h}^{-1}$                  | $V_t$ – Volume of feed solution measured at the time of t, L |

## Acknowledgements

The authors would like to thank Ministry of Higher Education Malaysia for funding this research project under Fundamental Research Grant FRGS/1/2021/TK0/UMP/02/12 (RDU210114) and Universiti Malaysia Pahang for the lab facilities and graciously acknowledge those who were directly or indirectly involved in this research.

## References

- Abdullah M.A.M., Seman M.N.A., Chik S.M.S.T., Abdullah S.B., 2022, Factorial design in optimizing parameters for thermoresponsive ionic liquids as draw solution, *Process Safety and Environmental Protection*, 161, 34–49.
- Amin P.D., Bhanushali V., Joshi S., 2018, Role of polyvinylpyrrolidone in membrane technologies, *International Journal of ChemTech Research*, 11(9), 247–259.
- Bai D., Kruczek B., 2022, Effect of membrane orientation and concentration of draw solution on the behavior of commercial osmotic membrane in a novel dynamic forward osmosis tests, *Membranes*, 12(4), 385
- Elimelech M., Phillip W.A., 2011, The future of seawater desalination: Energy, technology, and the environment, *Science*, 333(6043), 712–717.
- Goh P.S., Wong K.C., Ismail A.F., 2022, Membrane technology: A versatile tool for saline wastewater treatment and resource recovery, *Desalination*, 521, 115377.
- Gray G.T., McCutcheon J.R., Elimelech M., 2006, Internal concentration polarization in forward osmosis: Role of membrane orientation, *Desalination*, 197(1), 1–8.
- Ismail A.F., Hassan A.R., 2007, Effect of additive contents on the performances and structural properties of asymmetric polyethersulfone (PES) nanofiltration membranes, *Separation and Purification Technology*, 55(1), 98–109.
- Jung, B., Yoon, J. K., Kim, B., Rhee, H.-W., 2004. Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes, *Journal of Membrane Science*, 243(1), 45-57.
- Kahrizi M., Gonzales R.R., Kong L., Matsuyama H., Lu P., Lin J., Zhao S., 2022, Significant roles of substrate properties in forward osmosis membrane performance: A review, *Desalination*, 528, 115615.
- Nazir A., Khan K., Maan A., Zia R., Giorno L., Schroën K., 2019, Membrane separation technology for the recovery of nutraceuticals from food industrial streams, *Trends in Food Science & Technology*, 86, 426–438.
- Othman H.D., Fauzi Ismail M., Said A., Mansur N., Nidzhom Zainol Abidin S., Goh, M.S., Hasbullah P., Abdul Kadir H.S., Kamal F., 2018, Study on the effect of PVP additive on the performance of PSf/PVP ultrafiltration hollow fiber membrane, *Malaysian Journal of Fundamental and Applied Sciences*, 14(3), 343–347.
- Rambabu, K., Velu, S., 2016, Improved performance of  $\text{CaCl}_2$  incorporated polyethersulfone ultrafiltration membranes, *Periodica Polytechnica Chemical Engineering*, 60(3), 181–191.
- Song X., Zhang Y., Abdel-Ghafar H.M., Abdel-Aal E.S.A., Huang M., Gul S., Jiang H., 2021, Polyamide membrane with an ultrathin GO interlayer on macroporous substrate for minimizing internal concentration polarization in forward osmosis, *Chemical Engineering Journal*, 412, 128607.
- Tiraferrri A., Yip N.Y., Straub A.P., Romero-Vargas Castrillon S., Elimelech M., 2013, A method for the simultaneous determination of transport and structural parameters of forward osmosis membranes. *Journal of Membrane Science*, 444, 523–538.
- Unfried K., Kis-Katos K., Poser T., 2022, Water scarcity and social conflict, *Journal of Environmental Economics and Management*, 113, 102633.
- Wang Y., Fang Z., Zhao S., Ng D., Zhang J., Xie Z., 2018b, Dopamine incorporating forward osmosis membranes with enhanced selectivity and antifouling properties, *RSC Advances*, 8(40), 22469–22481.
- Wang Y., Guo H., Xie C., Zhou N., Fang Z., 2018a, Novel thin film nano-composite forward osmosis membranes prepared on a support with in situ embedded titanium dioxide to reduce internal concentration polarization, *Chemical Engineering Transactions*, 66, 289–294.