1 **Evaluation of Thin Film Composite Forward Osmosis Membranes:**

2 **Effect of Polyamide Preparation Conditions**

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7 **Abstract** The forward osmosis (FO) process has been considered for desalination as a competitor option to the traditional
8 reverse osmosis process. Interfacial polymerization (IP) reaction between two monomers (i.e., m-phenylene diamine (MPD)
9 and 1, 3, 5-benzenetricarbonyl chloride (TMC)) is typically used to prepare the selective polyamide layer that prevents salts
10 and allows water molecules to pass. In this research, we investigated the effect of preparation conditions (MPD contact time,
11 TMC reaction time, and addition of an amine salt) on the FO performance in terms of water flux and salt flux. The results
12 showed that increasing MPD contact time resulted in a significant increase in the water flux and salt flux. However,
13 increasing TMC reaction time caused a decline in both the water flux and the salt flux. The optimum condition that gave the
14 highest water flux was found to be as 5 min for MPD and 1 min for TMC. The addition of an amine salt of camphorsulfonic
15 acid-triethylamine (CSA-TEA) was able to make an apparent effect on the FO process by increasing water flux.
16

17 **Keywords:** Forward Osmosis; Thin-Film Composite; Polysulfone; Interfacial Polymerization; Polyamide

18

### 1. Introduction

20 Water Purification is the process of removing pollutants from raw water to produce water for human consumption (drinking
21 water) or other beneficial purposes (irrigation, livestock, and industrial use). Membrane processes are among the most
22 effective methods that can be used for water purification especially for desalination of water.

23 At this time, the most effective technique is the reverse osmosis (RO) process, where it can be used to desalinate seawater
24 and also for wastewater reuse (Kadhom et al., 2019; Kalash et al., 2020). RO can be defined as the process that relies on
25 external force, in which the applied hydraulic pressure is responsible for transporting water through the membrane (Peñate
26 and García-Rodríguez, 2012).

27 Forward osmosis (FO) is an osmotically driven membrane process that uses the osmotic pressure gradient to drive water
28 transport across a semi-permeable membrane while rejecting most solutes (Cath et al., 2006; McCutcheon et al., 2005). In
29 the FO process, water transports from a low osmotic pressure solution (i.e., feed solution) to a higher osmotic pressure
30 solution (i.e., draw solution). Besides, FO has been considered a high water recovery and low-cost purification option
31 compared to the pressure-driven membrane processes like reverse osmosis (Linares et al., 2017). One of the most critical
32 factors affecting the development of the FO process is preparing a suitable membrane for the process. The ideal membranes
33 for FO have to be able to provide high water permeability, high rejection of solutes, substantially reducing internal
34 concentration polarization (ICP), and has high chemical stability and mechanical strength (Ren and McCutcheon, 2014;
35 Zhao et al., 2012).

36 Thin-film composite (TFC) membranes have been studied widely for FO applications (Al-Furaiji et al., 2019; Chowdhury et
37 al., 2017; Ren and McCutcheon, 2017). TFC membranes consist of two layers: a selective layer that only allows water to
38 pass and rejects salt and a support layer that gives the membrane the required mechanical properties. Most of the FO studies
39 on TFC membranes have been focusing on developing the support layer, while fewer studies have been considering
40 improving the selective layer.

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41  The preparation of the polyamide selective layer is conducted using interfacial polymerization (IP) reaction
42  (Mohammadifakhr et al., 2020). Typically, the IP reaction occurs between two reactive monomers: m-phenylene diamine
43  (MPD) in the aqueous phase with 1, 3, 5-benzenetricarbonyl chloride (TMC) in the organic phase (Raaijmakers and Benes,
44  2016). Previous studies have reported that controlling the IP reaction conditions could significantly affect the performance of
45  the formed polyamide layer (Kadhom and Deng, 2019a) however, most of these studies were dealing with reverse osmosis
46  membranes (Dong et al., 2015; Jin and Su, 2009; Zhao et al., 2013). In contrast, very few studies have investigated the effect
47  of interfacial polymerization reaction on the performance of the TFC FO membranes (Klaysom et al., 2013). Therefore,
48  studying the effect of the preparation conditions can help in preparing highly efficient FO membranes.

49  In this work, the effect of m-phenylenediamine (MPD) aqueous solution exposure time and trimesoyl chloride (TMC)
50  organic solution reaction time is studied. Besides, the effect of incorporating an amine salt to the MPD solution was reported.
51  This paper aims to study the conditions of the interfacial polymerization reaction on the efficiency of the TFC membranes in
52  the FO process. Scanning electron microscopy (SEM), atomic force microscopy (AFM), and contact angles measurements
53  were used to characterize the prepared membranes.

## 2. Materials and Methods

### 2.1. Materials

56  Polysulfone (PSU, MW= 22000) from Xian Lyphar Biotech, China, was used to fabricate membranes substrates. N,N
57  dimethylformamide (DMF, 99.8%) and 2,2,4-trimethylpentane (isooctane, 99%) were purchased from Fluka Chemie
58  AG,Buchs, Switzerland. M-phenylenediamine (MPD, >99%) and trimesoyl chloride (TMC, 98%) were ordered from Merck.
59  Triethylamine (TEA, ≥99%), and (1s)- -10-(+)camphorsulfonic acid (CSA, 99%), were purchased from Sigma Aldrich.
60  Sodium chloride (NaCl) was purchased from Thomas Baker, India. Deionized water (DI water) was used to prepare NaCl
61  and MPD aqueous solutions and for other purposes such as cleaning.

### 2.2. Preparation of PSU support layer

63  The phase inversion method was used to prepare PSU supporting sheets. The casting solution was prepared by dissolving 17
64  wt. % dry polysulfone pellets in DMF. The mixture was stirred and heated to 60ºC for 6 h until a clear solution was formed,
65  which was then degassed for more than 24 h at room temperature before use. Afterward, the solution was cast using a home-
66  made casting knife by taking an aliquot from the clear solution by a pipette to spread on a clean glass plate to the desired
67  thickness. The glass plate with the solution was then immersed into a water bath at room temperature resulting in the
68  immediate formation of the PSU support sheet that was separated from the glass plate in a moment. Then, all of the sheets
69  were collected and stored in DI water for 24 h or more at 4ºC before use.

### 2.3. Preparation of TFC membrane

71  TFC Forward osmosis membranes were fabricated on the top surface of the PSU sheet by interfacial polymerization reaction
72  between MPD aqueous solution and TMC organic solution. MPD aqueous solution was prepared by dissolving 2% MPD in
73  DI water while the TMC solution was made by dissolving 0.15% of TMC in isooctane. Firstly the MPD solution was poured
74  onto the PSU sheet at different contact times. Then, the TMC solution was poured onto the PSU sheet that is containing the
75  MPD active sites and the reaction time was also varied to study the effect of IP reaction time. At first, the MPD contact time
76  was varied from 2 to 5 min with keeping the contact time of the TMC at 1 min. Then, the best MPD contact time (i.e. 5
77  minutes) that gave the highest water flux was chosen and the TMC solution contact time was studied in the range of 1 to 4
78  minutes. In order to study the effect of adding CSA-TEA (2:1), they were added to the MPD solution with a weight percent

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79    of 1%. The IP reaction was conducted at room temperature. Finally, the obtained TFC membranes were dried in the oven at

80    60ºC for 10 min and then collected and stored in DI water for 24 h until testing.

### 2.4. Membrane characterization

82    Scanning Electron Microscope (Fesem Tescan Mira3 France) and Atomic Force Microscope (Angstrom advanced Inc.,

83    2008, U.S.A) were used to determine the morphology of the prepared membrane. The hydrophilicity of the membranes was

84    measured using contact angles (Theta Lite TL-101 Thailand).

### 2.5. FO performance test

86    The FO performance was tested in a bench-scale system, as shown in Figure 1. This system consists of two tanks: one of

87    them is used for the feed solution and the other contains the draw solution. DI water was used as a feed solution while 1 M

88    NaCl was used as a draw solution based on the standard methodology that was described by (Cath et al., 2013). These

89    solutions were pumped to the membrane cell using two pumps from Pure-water (model: 75GPD, volts: 24VDC, workflow:

90    28LPH). All experiments were conducted in FO mode (i.e., active layer faces the feed solution). The membrane was

91    installed in a custom-made cell with the chamber's dimensions of length 7.62 cm, width 2.54 cm and a depth of 0.3 cm.

92    Water flux $J_w$ can be estimated using the following equation (Al-Furaiji et al., 2018):

$$J_w = \frac{\Delta V}{At}$$

93

94    Where $J_w$ is the water flux (LMH: $Lm^{-2}\,h^{-1}$), $\Delta V$ is the change in feed solution volume (L), A is the active area of the

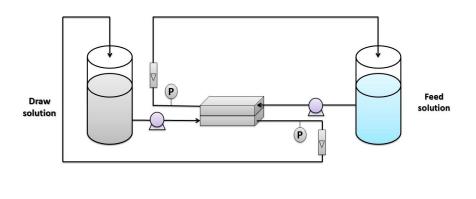95    membrane ($m^2$), and t is the experiment's time (h).

96    Salt flux through the membrane was estimated by monitoring the change in conductivity of the feed solution and using the

97    following equation (Al-Furaiji et al., 2020):

$$J_s = \frac{\Delta CV}{At}$$

98

99    Where $J_s$ is the salt flux (GMH: $gm^{-2}\,h^{-1}$), $\Delta C$ is the change in the feed solution concentration (g/L), V is the volume of

100   feedwater flow (L), A is the active area of the membrane ($m^2$), and t is the experiment's time (h).



101

102    **Figure 1. Schematic diagram of the FO bench-scale test unit.**

103

## 3. Results and discussion

### 3.1. Membrane characterization

Two dimensional (2D) and three dimensional (3D) AFM images of the top surface of the TFC membrane are presented in a scan area of 2500 x 2500 nm, as shown in Figure 2. It can be clearly seen that the surface of the polyamide layer has a ridge-and-valley structure with an average roughness of the FO membrane surface is 5.07 nm. The surface roughness of the prepared membrane was quite similar to what has been reported for typical FO (Mi and Elimelech, 2008) and Nanofiltration membranes (Li et al., 2017, 2020). The rougher surface could be more beneficial for membrane performance as it gives higher areas for mass transfer especially when dealing with low fouling feed solution.

SEM images were used to investigate the surface morphology of the TFC membranes, as shown in Figure 3. It can be seen that the polyamide selective membrane was successfully formed on the PSU support sheet. This was confirmed by the leaf-like morphology which is a typical structure for polyamide TFC membranes (Kadhom and Deng, 2019b; Zhou et al., 2014).
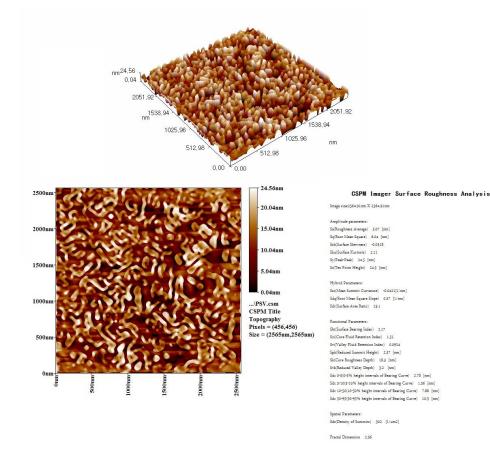
Figure. 4 shows the contact angle measurement of the PSU support membrane and the polyamide selective layer. The contact angle of the PSU sheet was about 65°, while the thin polyamide layer had a contact angle of 33°. When the contact angle is small, that means the membrane is hydrophilic, meaning that the water penetrates easily into the pores of the membrane, so that gives a better osmotic water flux performance. Nevertheless, when the contact angle is large, it means that the film is hydrophobic, so the internal surfaces of the pores get dry. That gives a membrane with lower water flux.
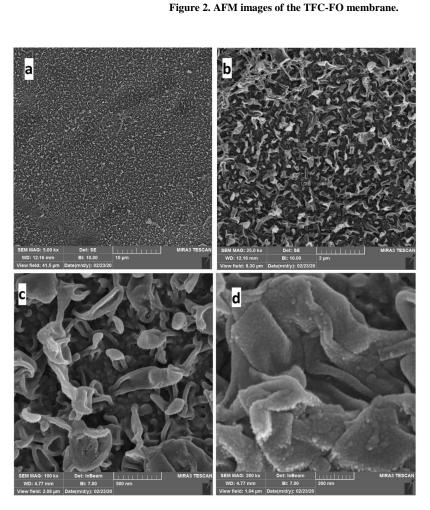
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121    **Figure 2. AFM images of the TFC-FO membrane.**

122



123

124    **Figure 3. SEM images of the TFC-FO membrane: a) 5000X, b) 25000X, c) 100000X, and d) 200000X.**
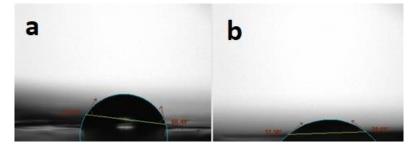


125

126    **Figure 4. The contact angle of a) PSU substrate membrane and b) polyamide thin layer.**

127

128    **3.2.  Effect of MPD exposure time**

129    After the PSU support sheet has been prepared, the active layer is prepared by pouring the MPD solution onto the PSU layer

130    after fixing it well on a glass plate. The effect of MPD exposure time on the performance of the TFC-FO membrane was

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131  studied by varying the contact time from 2 to 5 minutes while fixing the TMC reaction time at 1 minute, as shown in Figure

132  5.

133  The osmotic performance results revealed that water flux increases when the MPD exposure time increases. Also, increasing

134  the MPD contact time leads to increasing salt flux. In fact, higher MPD exposure time means more MPD molecules would

135  react with the support layer and accordingly increasing the IP reaction active sites. Besides, well-formed crosslinking would

136  be achieved at higher MPD exposure time, which gives better IP reaction conditions when reacts with the TMC later
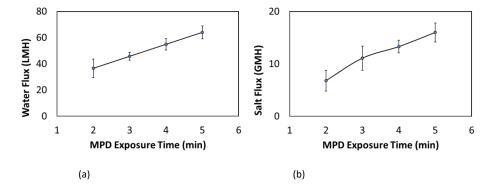
137  (Kadhom and Deng, 2019a).



138

139  (a)                                      (b)

140  **Figure 5. The effect of MPD contact time on membrane performance. (a) The water flux (LMH) changing with**
141  **different MPD exposure time (min.). (b) The salt flux (GMH) changing with different MPD exposure time (min.).**

142  **3.3.  Effect of TMC reaction time**

143  In order to study the effect of IP reaction time, TMC contact time was varied from 1 to 4 min with fixing the MPD exposure

144  time at 5 min, as shown in Figure 6. TMC organic solution was poured on the PSU substrate that contains the MPD active

145  sites to conduct the IP reaction. It can be seen that the optimum condition that gave the highest water flux was recorded at a

146  reaction time of 1 min. Interestingly, it can also be noticed that water flux and salt flux decreased sharply with increasing the

147  TMC reaction time. This is mainly attributed to that increasing the TMC contact time leads to generating a thicker polyamide

148  layer and consequently higher mass transfer resistance to permeation of water(Zhou et al., 2014). Moreover, the extent of the

149  cross-linking is increased with increasing the IP reaction time and as a result, water flux and salt flux decreased (Wang et al.,
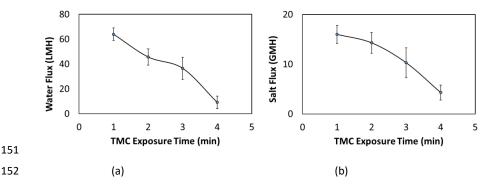
150  2017).



151

152  (a)                                      (b)

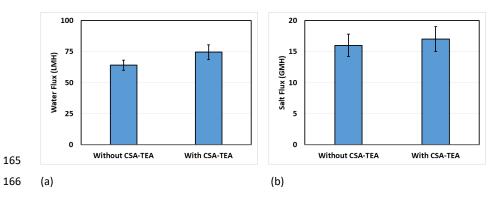153  **Figure 6. The effect of TMC contact time on membrane performance. (a) The water flux (LMH) changing with**
154  **different TMC exposure time (min.). (b) The salt flux (GMH) changing with different TMC exposure time (min.).**

155

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156 **3.4. Effect of CSA-TEA salt**

157 The effect of adding an amine salt (i.e., CSA-TEA) on the performance of the FO process was studied as shown in Figure 7.

158 It has been found that adding 1% of the CSA-TEA to the aqueous MPD solution exhibited a moderate increase in both water

159 flux and salt flux. Similar behavior was reported for reverse osmosis and Nanofiltration processes (Khorshidi et al., 2017). It

160 is known that polyamide formation during the IP reaction can result in the release of hydrogen chloride (Raaijmakers and

161 Benes, 2016). The formation of hydrogen chloride can affect the reactivity of the monomer reactant in the aqueous phase

162 (i.e., MPD). Therefore, the addition of a strong base such as TEA enhances the reactivity of the MPD and consumes the

163 produced acid (i.e. hydrogen chloride). Also, it has been reported that the TEA acts as a catalyst by accelerating the MPD–

164 TMC reaction and generating thinner and more crosslinked polyamide layer (Vatanpour et al., 2017; Wang et al., 2017).



165

166 (a)                                                      (b)

167 **Figure 7. The effect of adding CSA-TEA to the MPD-aqueous solution on a) water flux and b) salt flux.**

168

169 **4. Conclusion**

170 In this work, TFC forward osmosis membranes were prepared on PSU substrate (17wt %) as a support layer via IP reaction

171 between MPD and TMC to form a polyamide selective layer. The effect of MPD and TMC reaction times was investigated.

172 The best results were found to be at 5 min for MPD and 1 min for TMC reaction times. These results gave the best

173 performance of FO membranes in terms of water flux and salt rejection. Increasing MPD exposure time leads to increasing

174 the active sites on the PSU layer. By changing the TMC reaction time, it is possible to control how dense the polyamide

175 layer and, consequently, the amount of water and salt that passes through the membrane. Also, the effect of adding an amine

176 salt (CSA-TEA) on the performance of FO membranes was demonstrated. The result showed that moderate improvement in

177 water flux was achieved. Finally, this study can be considered as a useful guide for researchers and workers in the field of

178 preparing TFC forward osmosis. Future research can focus on investigating other additives to the MPD and TMC solutions.

179 Also, studying the effect of changing MPD and TMC concentrations in preparing TFC-FO is highly recommended for future

180 works.

181 **Declaration of competing interest**

182 The authors declare that they have no known competing financial interests or personal relationships that could have appeared

183 to influence the work reported in this paper.

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