



## Research Paper

## Polyamide Forward Osmosis Membrane: Synthesis, Characterization and Its Performance for Humic Acid Removal

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## HIGHLIGHTS

- Formation of polyamide thin layer on top of PES membrane using interfacial polyamerization with different concentration of monomer, MPD (2% and 1% w/v of MPD) reacted with 0.15% w/v of TMC at different reaction time (10s, 30s and 60s).
- Monomer concentration and reaction time significantly affecting FO membrane (morphology, FESEM and contact angle) and performances (water flux and humic acid rejection) of polyamide FO membrane.
- Higher concentration of monomer produced membrane with lower flux but higher humic acid rejection.

## ABSTRACT

In this research, modification on the ultrafiltration (UF) membrane by synthesis of a thin layer of polyamide selective layer was designed for high performances of forward osmosis (FO) water treatment. Two monomers, m-Phenylenediamine (MPD) and Trimesoyl chloride (TMC) with different concentrations of MPD (2.0% w/v and 1.0% w/v) were reacted with TMC (0.15% w/v) for interfacial polymerization (IP) reaction to form a thin polyamide selective layer. The polyamide FO membrane prepared was characterized by using the Field Emission Scanning Electron Microscope (FESEM) and contact angle measurement. Forward osmosis membrane performances in terms of water flux ( $L/m^2hr$ ) and humic acid rejection (%) were evaluated in order to obtain the best performances of the FO membrane. It has been demonstrated that the result of membranes with a MPD concentration of 2.0% w/v revealed a large number of fully sponge-like structures and possess high hydrophilic properties. Moreover, experimental results clearly demonstrated that the 60s reaction time of the polyamide FO membrane with MPD of 2% w/v exhibited a lower water flux of  $1.98 L/m^2.h$  and the highest humic acid rejection (99.2%) when 2.5M of sodium chloride (NaCl) was used as draw solution. Compared to the 60s reaction time of the polyamide FO membrane prepared with a MPD concentration of 1.0% w/v with the same concentration of feed and draw solution exhibiting a higher water flux of  $3.80L/m^2$ , a lower humic acid rejection with 95.4% of salt rejection was observed. It is found that the overall characterization and performance of the polyamide FO membrane is mainly due to the formation and thickness of the thin polyamide layer that plays an important role in facilitating a high water flux in forward osmosis for humic acid removal.

## 1. Introduction

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Nowadays, an increase of the human population and industrial

development needs are factors of global water scarcity problems that require a source of clean water [1]. Developments of alternative water sources have

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become a main discussion among researchers and engineers, and are one of the alternative water sources by applying membrane filtration technologies [2]. One of the membrane filtration technologies used over the past few decades for desalination and reuse of seawater and wastewater is reverse osmosis (RO) technology. In many membrane technology methods, reverse osmosis is one of the water treatment methods that have become a viable water treatment method for industry because of their high performance in terms of quality water products and competitive operational cost. However, this type of membrane technology is operated in high pressure conditions which will lead to high utilities cost consumption (i.e. electricity) [3] and membrane fouling [4].

In the last few years, forward osmosis (FO) has gained huge attention from researchers and engineers to use this type of membrane technology for seawater-desalination [5], food processing [6] and wastewater treatment [7]. Unlike RO that used pressure as a driving force, FO employs osmotic pressure naturally created by the differences of two concentrations of solution. Osmotic pressure will ensure the transportation of water from a higher concentration of solution (draw water) to the lower concentration of solution (feed water). This operation principle shows that FO uses lower energy consumption rather than RO [8]. Due to these advantages, it is believed that FO has a high potential to be applied in water treatment as well. In the water treatment process, natural organic matter (NOM) is one of the common compounds found in surface water. Humic acid is an example of NOM which is a common molecule that is present in terrestrial and aquatic ecosystems [9]. Humic acid is extracted from the soil, river, lake sediments, coal, fresh water, waste waters and plants and coral skeletons [10].

Since the properties of humic acid must also be considered such as in natural water, humic acid tends to be hydrophobic/hydrophilic at different pH environments, so primary attention must be taken by researchers and engineers in how to develop the membrane with excellent properties that give it better performances. In this paper, the polyamide membrane produced by the interfacial polymerization (IP) technique with different monomer concentration and reaction times were investigated. The membrane performances were evaluated by the water flux and humic acid rejection.

As mentioned earlier, FO is one an alternative that has gained huge attention by researchers and engineers and is a viable technology for water treatment. In conjunction to that, nowadays, there are two types of commercial FO membranes used, the cellulose triacetate (CTA) membrane and the thin film composite (TFC) polyamide membrane. Previous studies indicate that the performance of the CTA membrane was limited by low water permeability and low salt rejection [11, 12]. In conjunction to that, many researchers and engineers are focusing on the development of a high performance FO membrane. Compared to the CTA membrane, the TFC polyamide has a good performance in terms of higher water flux and lower solute rejection that has been proven by Yip et al.'s research where deionized water was used as feed solution and NaCl as draw solution [13]. However, most of the current researches on the FO and TFC polyamide FO membrane are mostly used deionized water or NaCl as feed solution. For example, research from Emadzadeh et al. and Han et al. used NaCl and deionized water as feed solution during the FO lab-scale experiment, respectively [14, 15]. Until now, there is only one study that uses humic acid solution as a feed solution but this study used the CTA membrane as their FO membrane [16].

Therefore, the main objective of this research is to synthesize a polyamide layer on the commercial (PES) membrane and further study how the modified polyamide membrane properties would affect the performance of the polyamide FO membrane in the FO process. To the best knowledge of the authors, this is the first research on the polyamide FO membrane to humic acid removal and the FO system.

## 2. Materials and methods

### 2.1. Materials

The commercial flat sheet polyethersulfone (UF PES50) membrane purchased from AMFOR INC (China) was used as a base support membrane for surface modification. m-Phenylenediamine (MPD) with > 99.0% purity and trimesoyl chloride (TMC) with >98.0% purity where both supplied by Acros Organics and used as the monomers for the interfacial polymerization reaction. N-hexane from Merck with > 99.0% purity was utilized as the solvent for the TMC monomer. For forward osmosis system analysis, five different concentrations of sodium chloride (NaCl) solutions (0.5M, 1.0M, 1.5M, 2.0M and 2.5M) from Merck were used as draw solution in this research. For the feed solution, a diluted humic acid (HA) solution of 15 mg/L was used as feed water. Humic acid was from Fluka.

### 2.2. Preparation of polyamide membrane

Through the interfacial polymerization method, 2% w/v aqueous m-Phenylenediamine (MPD) solution and 0.15% w/v trimesoyl chloride (TMC) in hexane solution was reacted to prepare the polyamide forward osmosis membrane. Initially, MPD solution was immersed on the active surface of the PES membrane for 30 minutes before draining the excess MPD and then the membrane was reacted with TMC solution at three different reaction times of 10s, 30s and 60s. The membrane was then dried overnight in the fume hood and then stored in pure water at cool temperature to prevent bacteria growth on the surface of the polyamide FO membrane. All these steps were repeated by changing the concentration of MPD to 1%w/v aqueous MPD.

### 2.3. Membrane characterizations

Morphology of the polyamide forward osmosis membrane was observed via a field emission scanning electron microscope, FESEM (JSM-7800F). The membranes samples were fractured in liquid nitrogen before the test in the FESEM.

The hydrophilicity of the membrane was measured by a Contact Angle Geniometer using Milli-Q ultra-pure water as the probe liquid at a room temperature of about 23°C. The contact angle was measured randomly at 15 different locations for each sample to minimize the experimental error and average value of contact angle reading reported.

### 2.4. Forward osmosis performance

A similar process was reported by Widjojo et al. [17], and the performances of the polyamide FO membrane were evaluated via a lab-scale FO cross flow filtration system unit as shown in Figure 1. The temperature of feed and draw solution during the experiment were kept constant at room temperature (24 °C). The flow velocities of both solutions (feed and draw solution) during the FO system experiment were kept constant at 0.11 L min<sup>-1</sup> which flow concurrently along the membranes.

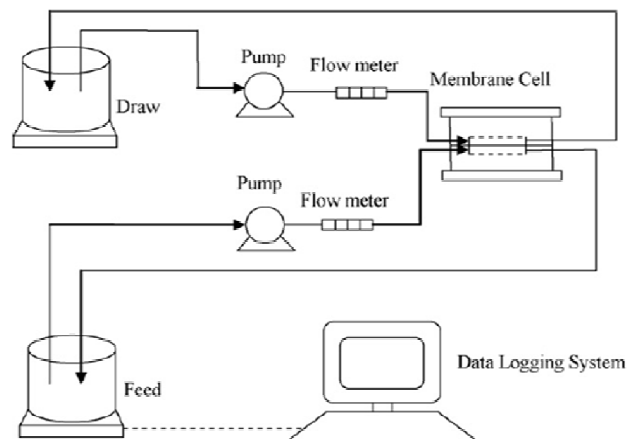


Fig.1. The schematic diagram of FO lab-scale system [18].

15 mg/L of humic acid and 0.5M of sodium chloride were prepared as feed and draw solution, respectively. Both solutions were diluted with ultra-pure water in two different 1000mL beakers. The feed solution and humic acid solution were placed on the electronic weight balance to record the mass changes of the feed solution. The membrane was placed vertically in the membrane frame with an active layer of membrane (polyamide layer side) facing feed solution while the other side of the membrane was facing a draw solution. This orientation of the membrane (polyamide layer facing the feed solution) was used to increase the humic acid solute rejection, thus obtaining higher water flux [19]. The initial mass of the feed solution was recorded and within the process of forward osmosis that takes place, the mass changes were measured every 5 minutes until the experiment was completed (1 hour). The duration of the experiment for each concentration of draw solution was fixed within 1 hour. The FO process is kept at the constant room temperature and maintained at atmospheric pressure. After 1 hour experiment, the mass changes of the feed solution is measured and the water flux is calculated using equation 1 [20].

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

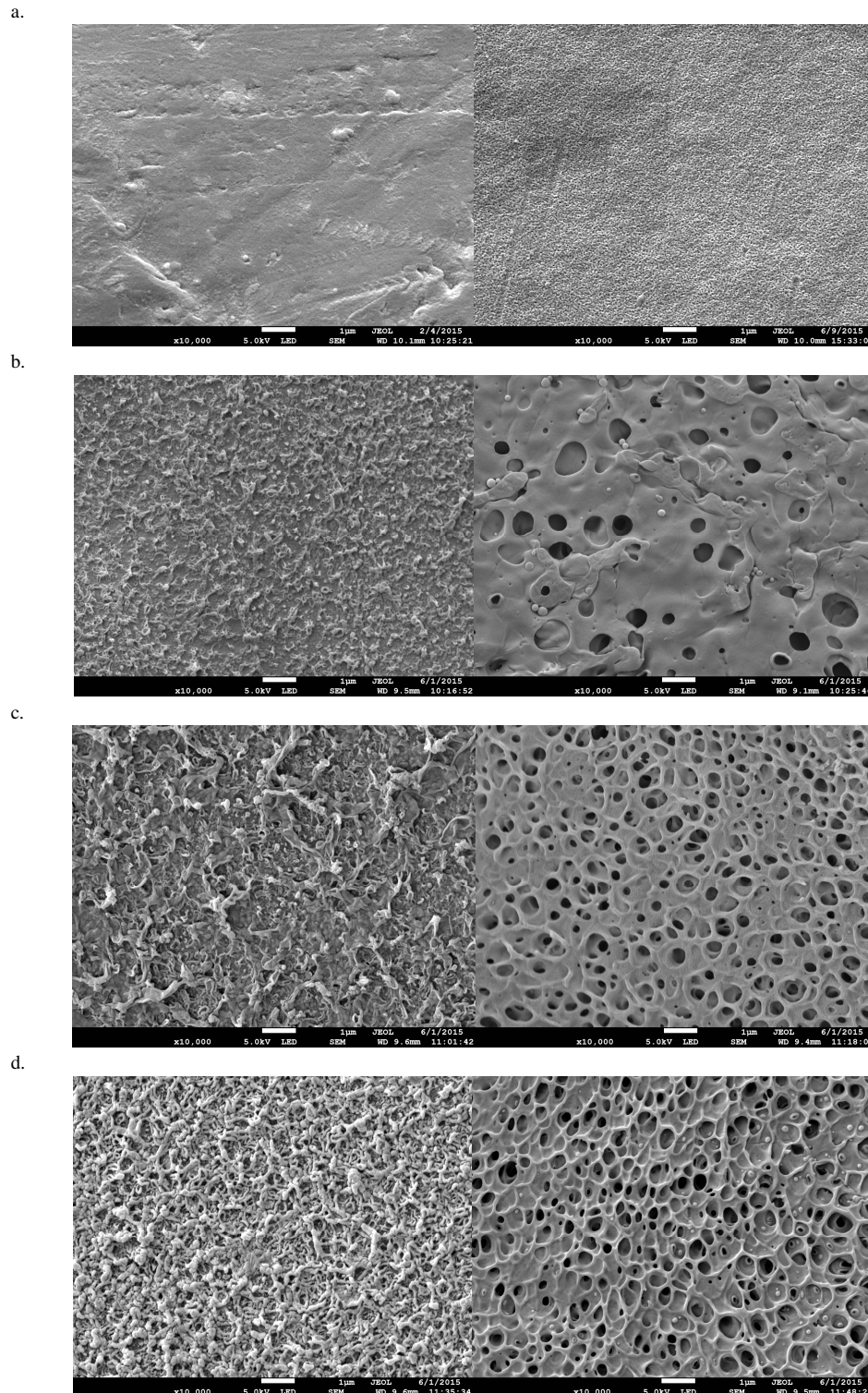
where  $\Delta V$  (L) is the permeation water collected through the FO process,  $\Delta t$  (h) is 1 hour, time taken by the FO process and  $A$  = effective membrane

surface area ( $m^2$ ). The mass changes are then converted into volume to obtain the water flux value using equation 1. For humic acid rejection, the Hitachi Ratio Beam Spectrophotometer (U-1800) at a wavelength of 254nm (humic acid wavelength) with a Hellma 10mm cell made of Quartz SUPRASIL was used to determine the initial and final concentration of humic acid while the FO process was conducted. In order to get a concentration of humic acid in the draw and feed solution in terms of absorbance calculated by the UV-Vis spectrophotometer, the standard curve was constructed to derive equation 2. The concentration of humic acid solute in both solutions was then inserted in

equation 2 to calculate the humic acid solute rejection (%).

$$R = \left[ 1 - \left( \frac{C_p}{C_b} \right) \right] \times 100\% \quad (2)$$

Where the  $C_p$  and  $C_b$  are the permeate and bulk concentration, respectively. The permeate is a concentration of humic acid solute in the draw solution and bulk is a concentration of humic acid in the feed solution.



**Fig.2.** FESEM pictures of the top surface (left) and bottom surface (right) (a) UF PES membrane and three different polyamide membranes produced by 2% w/v of MPD at different reaction time, (b) 10s, (c) 30s, (d) 60s.

### 3. Results and discussion

#### 3.1. Characterization of the polyamide membrane

The morphology of the polyamide FO membrane was characterized by FESEM. Figure 2 shows the FESEM images of the top surface of the polyamide FO membranes. Generally, by referring to Figure 2 above, compared to the UF PES membrane which poses a smooth surface, the top surface of the polyamide FO membrane had a tightly packed globule and consists of "ridge-and-valley" morphology. This clearly shows that the surface of the polyamide layer membrane modified at the longest reaction time (60s) was much rougher compared to 10s and 30s membranes. As referred to in Figure 2 (d), the morphology of the 60s membrane had tightly packed globules with a "ridge-and-valley" as presented on the top of the membrane surface compared to other membranes.

Contact angle measurements indicate that the membrane with a higher concentration of MPD has a lower contact angle. By referring to Figure 3, the membrane with a concentration of 2% w/v of MPD has a lower contact angle compared to the membrane modified with 1% w/v of MPD and UF PES membrane. Other than that, the membrane modified using the longest time of reaction also indicates a lower contact angle. Figure 3 shows that at 2% w/v of MPD, the 60s membrane has the lowest contact angle reading (45.9°) compared to 30s and 10s membranes with 46.2° and 51.9°, respectively. However, there is a difference of contact angle between the UF PES membrane compared to the polyamide membrane indicating that the presence of the polyamide layer increases the hydrophilicity of the membrane. Differences of contact angle degrees were due to the reaction time of monomers that were applied to the membrane to form the polyamide layer where more amino and carboxylic functional groups were presented due to the formation of the polyamide layer.

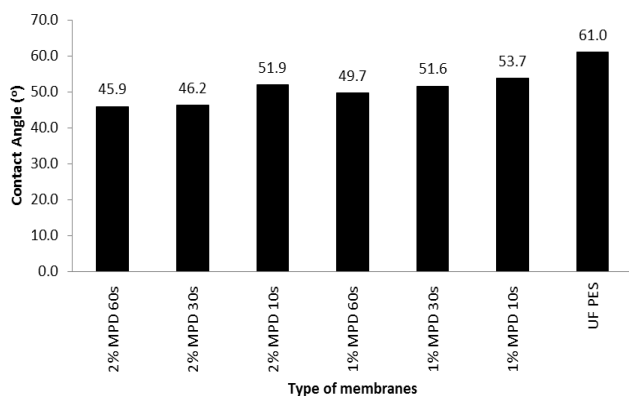


Fig.3. Summary of contact angle measurement.

#### 3.2. Performance of polyamide FO membrane

As previously mentioned, there are six types of polyamide membranes produced by using two different monomers (2% w/v of MPD and 1% w/v of MPD) where both were reacted with 0.15% w/v of TMC at three different reaction times (10s, 30s, and 60s). For polyamide FO, performance of the membrane was investigated based on water flux and humic acid rejection.

Figure 4 shows performance of the polyamide FO membrane in terms of water flux. The figure clearly shows that the increasing concentration of draw solution will lead to an increase of water flux of the membranes. The more concentrated solution will lead to an increase of osmotic pressure. An increase of NaCl concentration will lead to an increase of osmotic pressure. The increase of osmotic pressure will promote more water to pass through the membrane from higher (draw solution) to lower concentration (feed solution) of the solution. In addition, water flux for the membrane produced by using 1% w/v of the MPD is higher than 2% w/v of the MPD membrane. An increase of MPD concentration will lead to more formation of a dense polyamide barrier layer due to the presence of a large number of MPD monomer reacted with TMC. In addition, it was observed that for both MPD concentrations, the membrane produced with longer reaction time exhibited a lower water flux. The active surface of the modified membrane is expected to be thicker and denser, so the water flux decreases [21]. In general, both monomer concentration and reaction time significantly affect the membrane performance.

At 2.5M of draw solution concentration, the humic acid rejection performances are summarized in Figure 5. It is obviously shown that 2% w/v

of polyamide FO membranes exhibited the higher humic acid rejection in the range between 95% - 99% compared to 1% w/v of MPD of the polyamide FO membrane. It is postulated that the membrane modified with higher monomer concentration produces a denser active layer and a smaller pore size leads to higher humic acid rejection. In addition, reaction time between the monomers also plays a significant role in terms of rejection. For both monomer concentrations (2%w/v and 1 %w/v), it was observed that the membrane modified with the longest reaction time indicates higher humic acid rejection compared to the membrane reacted at a shorter reaction time. The membrane at 2% w/v of MPD with 60s reaction time was recorded at 99.2% of humic acid rejection compared with 30s and 10s membrane with 96.1% and 95.1%, respectively. The longest reaction time between the two monomers will form a denser polyamide and thicker active layer on top of the membrane surface. Similar results were also observed by Jalanni et al. [22] where the variation in monomer reaction time during the interfacial polymerization have improved the membrane flux and humic acid rejection in the nanofiltration (NF) system.

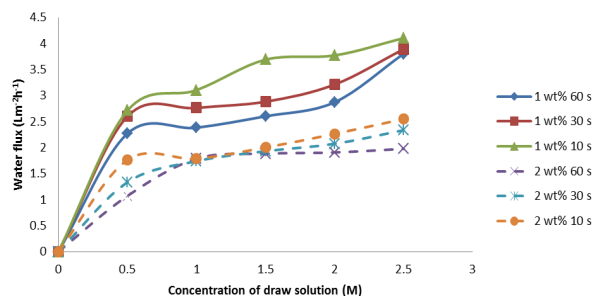


Fig.4. Effect of NaCl concentration (draw solution) on water flux for different type of membranes.

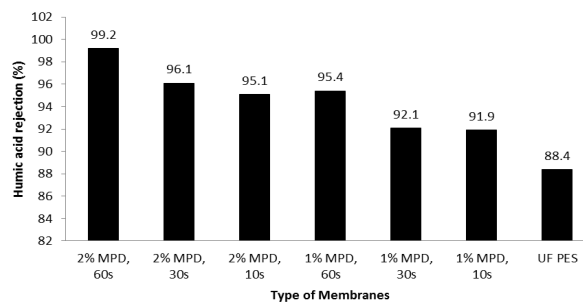


Fig.5. Humic acid rejection of membranes at 2.5M of NaCl.

### 4. Conclusions

In this study, seven different types of membranes have been compared based on their characterization and performances. The study findings show that the produced polyamide FO membrane shows an excellent performance in terms of water flux and humic acid rejection compared to the ordinary UF PES membrane. Besides that, the variation of concentration and reaction time of MPD used to react with TMC improved the filtration of the FO membrane. The increase of MPD concentration and the reaction time resulted in the polyamide FO membrane with a lower water flux, but posed a higher humic acid rejection. In addition, these monomer concentration and reaction times also affect the morphology and surface chemistry (hydrophilicity) of the membranes. Even the polyamide FO membranes show an excellent performance (water flux and humic acid rejection), however further investigation is required especially on the internal concentration polarization (ICP) and reverse salt mechanisms as these two are common problems for the FO system which may contribute to a lower flux and feed contamination, respectively.

### 5. Acknowledgments

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