

POLYAMIDE FORWARD OSMOSIS MEMBRANE: SYNTHESIS, CHARACTERIZATION AND ITS PERFORMANCE FOR HUMIC ACID REMOVAL

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ABSTRACT

In this research, modification on 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 concentration 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 Field Emission Scanning Electron Microscope (FESEM) and contact angle measurement. Forward osmosis membrane performances in term of water flux (L/m^2hr) and humic acid rejection (%) were evaluated in order to obtain the best performances of FO membrane. It has been demonstrated that the result of membrane with MPD concentration of 2.0% w/v revealed a large number of fully sponge-like structure and posse a high hydrophilic properties. Moreover, experimental results clearly demonstrated that 60s reaction time of polyamide FO membrane with MPD of 2% w/v exhibited lower water flux of $1.98 L/m^2.h$ and highest humic acid rejection (99%) when 2.5M of sodium chloride (NaCl) used as draw solution. Compared to 60s reaction time of polyamide FO membrane prepared with MPD concentration of 1.0% w/v with the same concentration of feed and draw solution exhibit a higher water flux, $3.80L/m^2$ but a lower humic acid rejection with 95.4% of salt rejection was observed. It is found that the overall characterization and performances 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.

Keywords: Polyamide membrane; Forward osmosis; Water flux; Humic acid rejection

INTRODUCTION

Nowadays, the rapid growth of population and industrial development are factors of global water scarcity problems that need the source of clean water [1]. Developments of alternatives water sources has become a main discussion among researchers and engineers, and one of the alternative water sources by applying membrane filtration technologies [2]. One of the membrane filtration technology used over the past few decades for desalination and of seawater and wastewater reused is reverse osmosis (RO) technology. Reverse osmosis is one of the water treatment methods that established as the industry benchmark for membrane technologies because of its high quality water product and competitive cost. However, this type of membrane technology is operated in high pressure conditions which will leads to high utilities cost consumption (i.e. electricity) and membrane fouling [3].

Recently, forward osmosis (FO) has attracted much attention of researcher to use this type of membrane technology for seawater-desalination [4], food processing [5] and wastewater treatment [6]. Unlike RO that used pressure as a driving force, FO employs osmotic pressure naturally created by the differences of two concentration 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 use a lower energy consumption rather than RO [7]. Because of these advantages, it is believed that FO has high potential to be applied in water treatment as well. In water treatment process, natural organic matter (NOM) is one of the common compound found in the surface water. Humic acid is example of NOM which is a common molecules that presence in terrestrial and aquatic ecosystems [8]. Humic acid are extracted from the soil, river, lake sediments, coal, fresh water, waste waters and plants and coral skeletons [9].

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

MATERIALS AND METHODS

Materials

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 were 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 was 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.

Preparation of polyamide membrane

Through 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. Firstly, MPD solution was immersed on the active surface of the PES membrane for 30 minutes before draining the excess MPD and then the membrane 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 store 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.

Membrane characterizations

Morphology of 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 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 room temperature, 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.

Forward osmosis performance

Similar process reported by Widjojo et.al [10], the performances of polyamide FO membrane was evaluated via a lab-scale FO cross flow filtration system unit as shown in Fig. 1. The temperature of feed and draw solution during the experiment were maintained at room temperature of about 24°C. The flow velocities of both solution, feed and draw solution during FO system experiment were kept constant at 0.11 L min⁻¹ which flowed concurrently along the membranes.

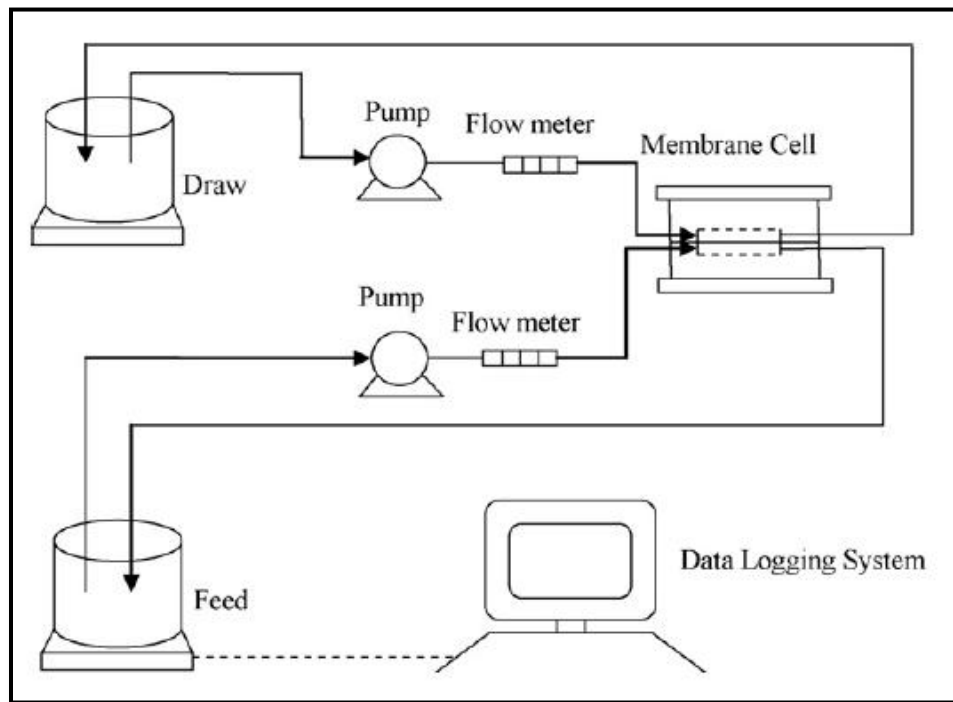


Figure 1: The schematic diagram of FO lab-scale system [11]

15 mg/L of humic acid 0.5M of sodium chloride were prepared as feed and draw solution, respectively. Both solution were diluted with ultra pure water in two different 1000mL beakers. The feed solution, humic acid solution was palced on the electronic weight balance to record the mass changes of the feed solution. The membrane was placed vertically in membrane frame which an active layer of membrane (polyamide layer side) facing feed solution and porous layer of membrane facing draw solution. This orietation of membrane (active layer facing the

feed solution) was used to increase the humic acid solute rejection and thus obtaining higher water flux [12]. The initial mass of the feed solution was recorded and within the process of forward osmosis takes place, the mass changes was measured every 5 minutes until the experiment was completed (1 hour). Duration of experiment for each concentration of draw solution was fixed within 1 hour. The FO process is kept in 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 [13].

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

Where ΔV (L) is the permeation water collected through in the FO process, Δt (h) is 1 hour, time taken by the FO process and A = effective membrane surface area (m^2). The mass changes then converted into volume to obtain the water flux value using the equation 1. For humic acid rejection, Hitachi Ratio Beam Spectrophotometer (U-1800) at wavelength of 254nm (humic acid wavelength) with Hellma 10mm cell made of Quartz SUPRASIL was used to determine initial and final concentration of humic acid while FO process conducted. In order to get concentration of humic acid in draw and feed solution in term of absorbance calculated by UV-Vis spectrophotometer, standard curve was constructed to derive the equation 2. The concentration of humic acid solute in both solutions then was inserted in equation 2 to calculate the humic acid solute rejection (%).

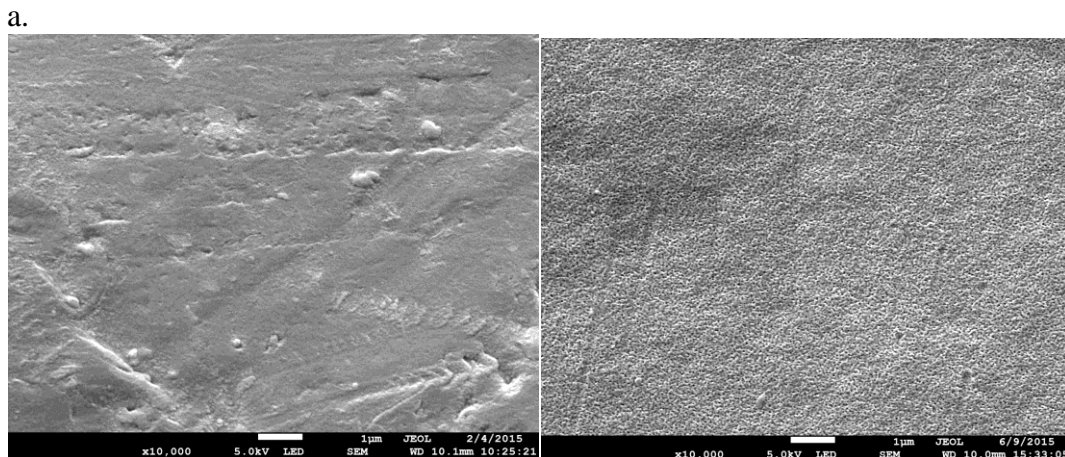
$$R = \left[1 - \left(\frac{C_p}{C_b} \right) \right] \times 100\% \quad (2)$$

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

RESULTS AND DISCUSSION

Characterization of the polyamide membrane

The morphology of the polyamide FO membrane was characterized by FESEM. Fig. 2 shows the FESEM images of the top surface of the polyamide FO membranes.



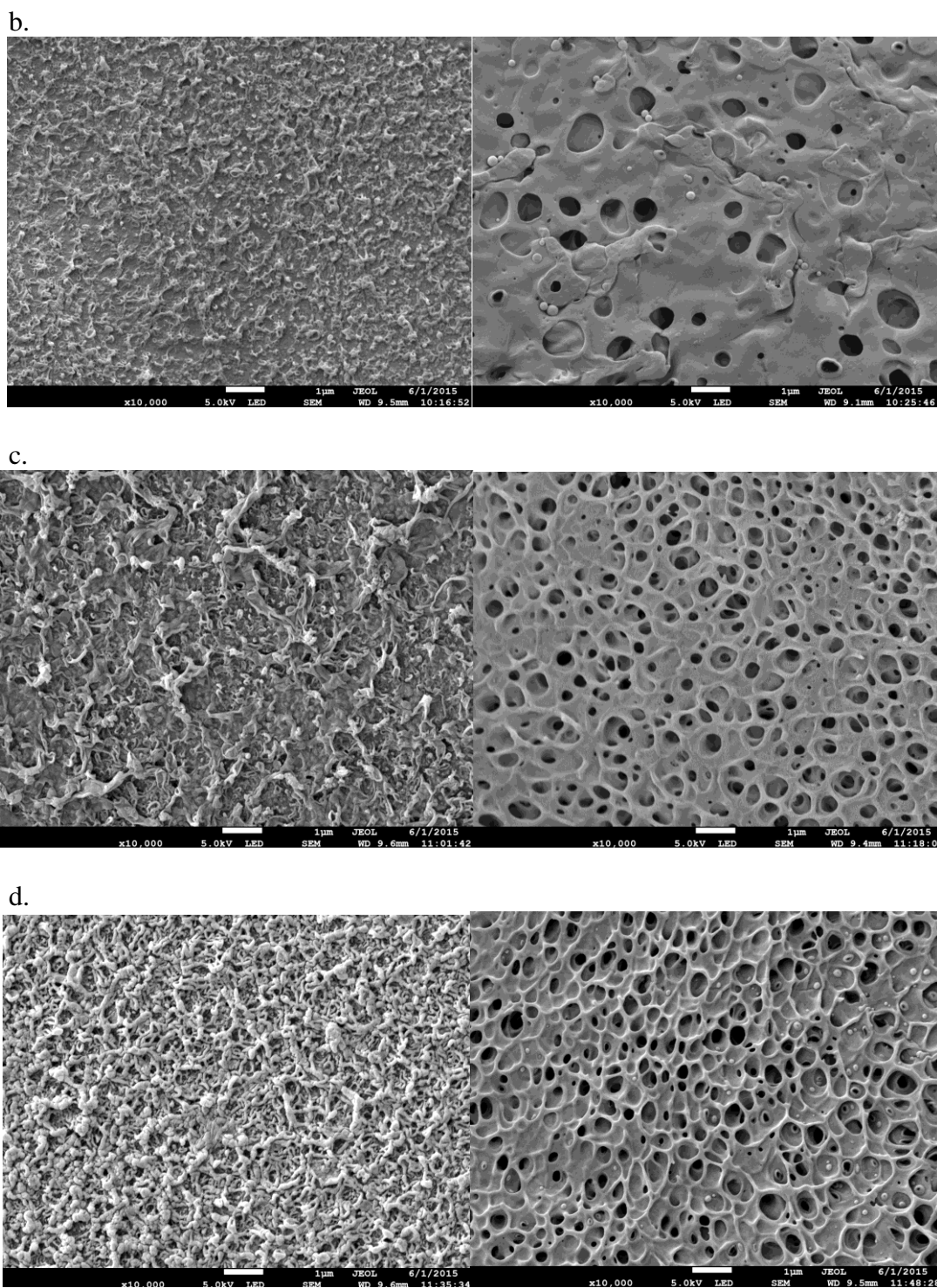


Figure 2: FESEM pictures of the top surface (right) and bottom surface (left) (a)UF PES membrane and three different polyamide membranes produced by 2% w/v of MPD at different reaction time, (b) 10s, (c) 30s, (d) 60s

Generally, by referring to the Fig. 2 above, compared to UF PES membrane which poses smooth surface, the top surface of the polyamide FO membrane had tightly packed globule and consists of “ridge-and-valley” morphology. It clearly shows that the surface of polyamide layer membrane modified at longest reaction time (60s) was much rougher compare to 10s and 30s membranes.

Contact angle measurements indicate that membrane with higher concentration of MPD has a lower contact angle. By referring to Figure 3, membrane with concentration 2% w/v of MPD has lower contact angle compare to membrane modified with 1% w/v of MPD and UF PES membrane. Other than that, membrane modified using longest time of reaction also indicates lower contact angle. Figure 3 shows that at 2% w/v of MPD, 60s membrane has lowest contact angle reading (45.9°) compare to 30s and 10s membranes with 46.2° and 51.9°, respectively. However, there are difference of contact angle between UF PES membrane compare to polyamide membrane indicates that the presence of polyamide layer increase the hydrophilicity of the membrane. Differences of contact angles degree were due to the reaction time of monomers that applied to the membrane to form polyamide layer and due to the hydrophilic characteristic of polyamide layer itself. The decreasing of contact angles because of addition more polyamide layer on top of the active surface of FO membrane.

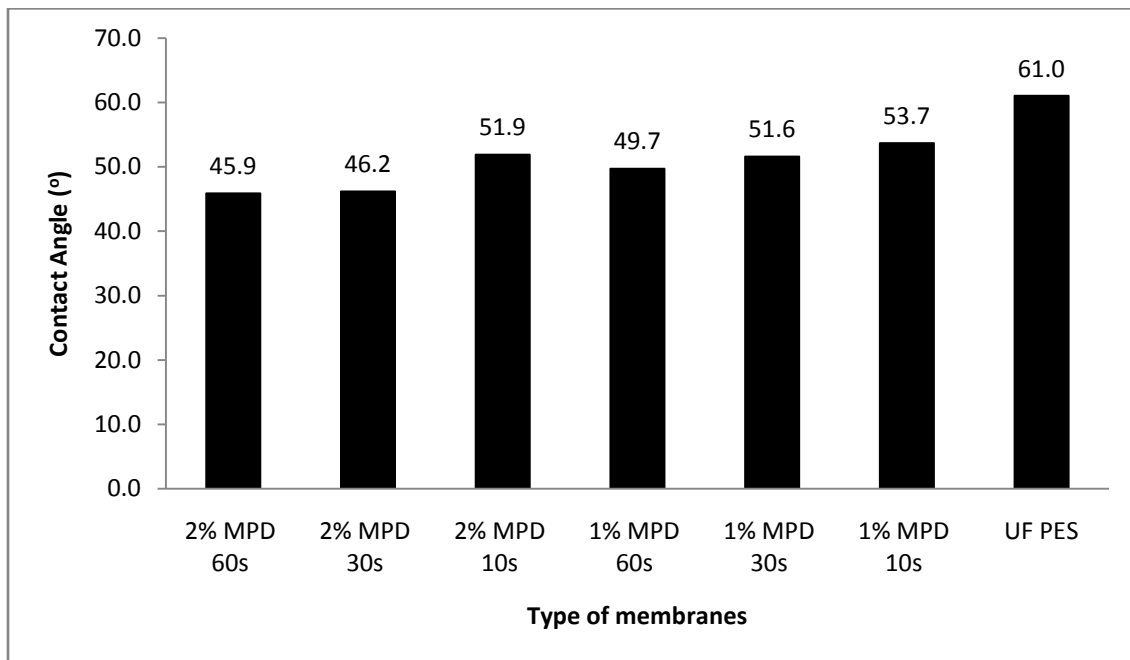


Figure 3: Summary of contact angle measurement

Performance of polyamide FO membrane

As mention previously, 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 time (10s, 30s, and 60s). For polyamide FO, performance of membrane was investigated based on water flux and humic acid rejection.

Figure 4 shows performance of polyamide FO membrane in term of water flux. The figure clearly shows that the increasing concentration of draw solution will lead to the increasing

of water flux of the membranes. The more concentrated solution, its increase the osmotic pressure and also increase the water flux. In addition, water flux for membrane produced by using 1% w/v of MPD is higher than 2% w/v of MPD membrane. The increasing of MPD concentration will lead to the more formation of a dense polyamide barrier layer due to the presence of a large number of MPD monomer reacted with TMC. On top of that, it was observed that for both MPD concentrations, 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 decrease [14]. In general, both monomer concentration and reaction time are significantly affecting the membrane performance.

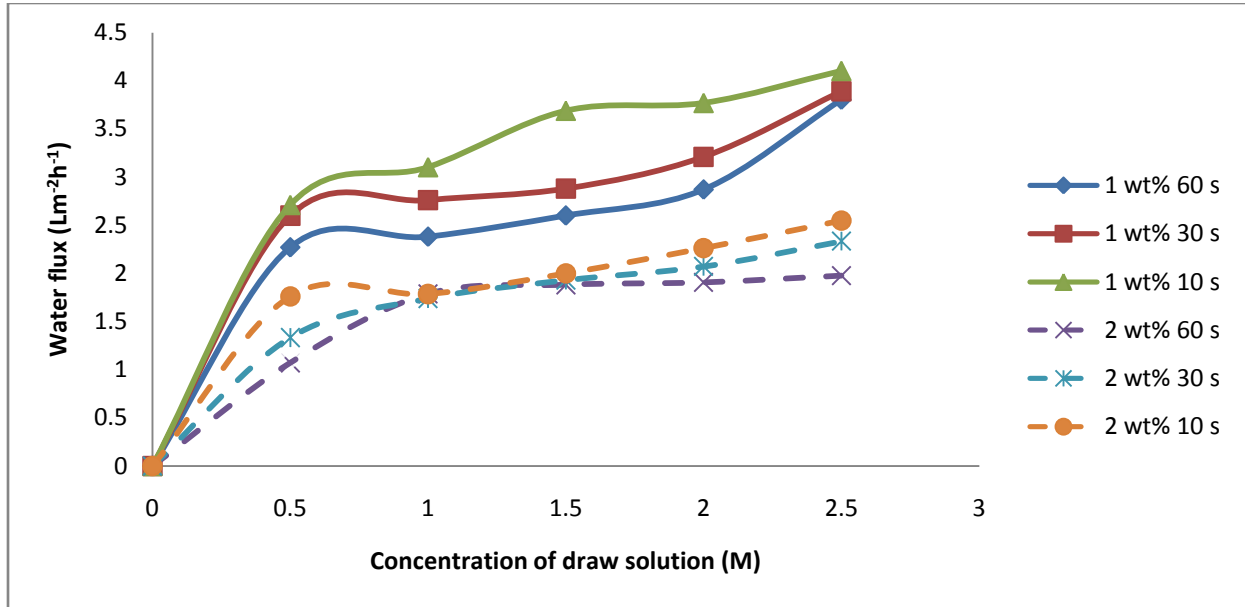


Figure 4: Effect of NaCl concentration (draw solution) on water flux for different type of membranes

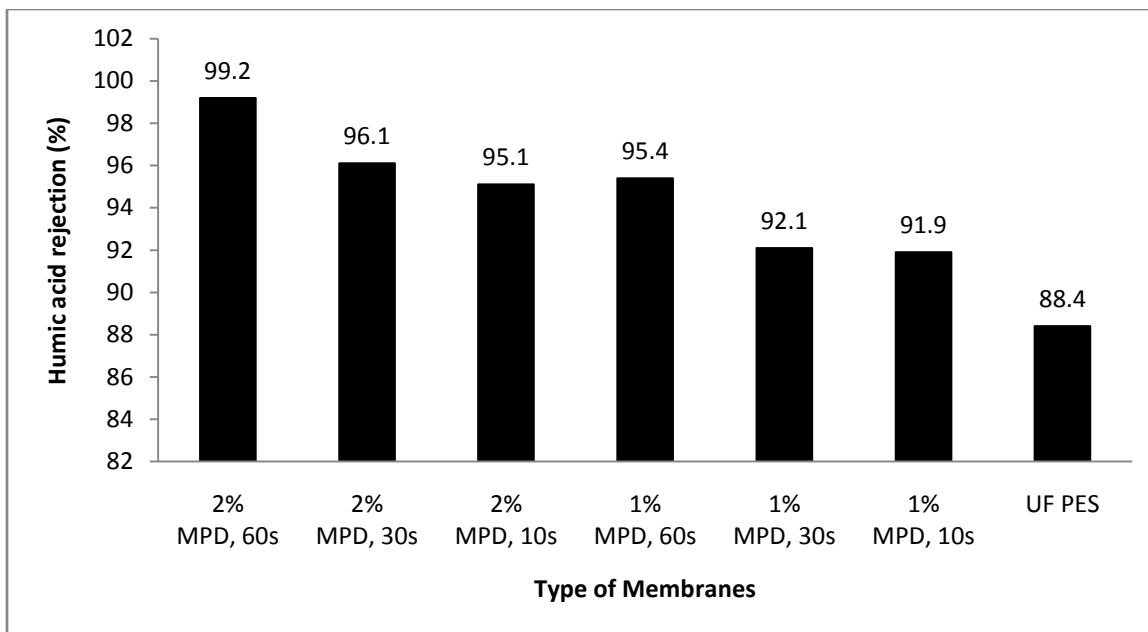


Figure 5: Humic acid rejection of membranes at 2.5M of NaCl

At 2.5M of draw solution concentration, the humic acid rejection performances are summarized in Figure 5. It obviously shows 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 polyamide FO membrane. It is postulated that membrane modified with higher monomer concentration produce a denser active layer and smaller pore size lead to higher humic acid rejection. In addition, reaction time between monomers also plays a significant role in term of rejection. For both monomer concentrations (2%w/v and 1 %w/v), it was observed that membrane modified with longest reaction time indicates higher humic acid rejection compared to the membrane reacted at shorter reaction time. Membrane at 2% w/v of MPD with 60s reaction time recorded 99.2% of humic acid rejection compared with 30s and 10s membrane with 96.1% and 95.1%, respectively. Longest reaction time between two monomers will form a denser polyamide and thicker active layer on top of the membrane surface. This was supported by previous research study done by Jalanni et al. [15], found that the variation of reaction time in interfacial polymerization improved the performance of membrane in term of water flux and humic acid rejection.

CONCLUSIONS

In this study, seven different types of the membranes have been compared based on their characterization and performances. Study findings shows that the produced polyamide FO membrane shows an excellent performance in term of water flux and humic acid rejection compared to 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 increasing of MPD concentration and the reaction time resulted in polyamide FO membrane with a lower water flux but poses a higher humic acid rejection. In addition, these monomer concentration and reaction time also affecting the morphology and surface chemistry (hydrophilicity) of the membranes. Even the polyamide FO membranes show an excellence

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 FO system which may contribute to a lower flux and feed contamination, respectively.

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