Synthesis and Performance of Polyamide Forward Osmosis Membrane for Natural Organic Matter (NOM) Removal

M. N. Abu Seman, L. M. Kei, M. A. Yusoff

Abstract—Forward Osmosis (FO) polyamide thin-film composite membranes have been prepared by interfacial polymerization using commercial UF polyethersulfoneas membrane support. Different interfacial polymerization times (10s, 30s and 60s) in the organic solution containing trimesoyl chloride (TMC) at constant m-phenylenediamine (MPD) concentration (2% w/v) were studied. The synthesized polyamide membranes then tested for treatment of natural organic matter (NOM) and compared to commercial Cellulose TriAcetate (CTA) membrane. It was found that membrane prepared with higher reaction time (30s and 60s) exhibited better membrane performance (flux and humic acid removal) over commercial CTA membrane.

Keywords—Cellulose Triacetate, Forward Osmosis, Humic Acid, Polyamide.

I. INTRODUCTION

WATER is generally known as an important necessity for all activities such as living consumption, industries, agricultural washing and bathing. Clean drinking water is essential to human and other living things. For increasing population in Malaysia nowadays, drinking water is taken primarily from surface water sources like rivers, lakes, and reservoirs. However, the sources of the clean drinking water are contaminated by chemical constituents (organics, inorganics and gases) and physical contaminants (colour, odour and solid) [1]. In rivers, about 50 % of the dissolved organic materials are humic substances that affect pH and alkalinity [2]. The principal constituent of humic substances is humic acid which is a natural organic matter (NOM) that causes the colour of fresh water to turn dark brown at high concentration. As a result, the river water in Malaysia needs to be treated correctly at low cost and energy before consuming by the citizens.

Among many water treatment methods, osmosis is the most common method used in desalination of water. For this research, forward osmosis was chosen over reverse osmosis as the process to treat river water due to the fact that the process of reverse osmosis has high cost, high energy consumption and has limited recovery which is roughly about 30%-50%

M.N. Abu Seman*, L.M. Kei, and M.A. Yusoff are with the Faculty of Chemical and Natural Resources Engineering,Universiti Malaysia Pahang, LebuhrayaTunRazak, 26300 Gambang, Kuantan, Pahang, Malaysia. (Corresponding author* phone: +609-5492904; fax: +609-5492889; e-mail: mazrul@ump.edu.my).

[3], [4]. On the other hand, the process of forward osmosis can be done at lower cost, energy and also has higher recovery rate [5]. Although FO has a number of advantages, one of its challenges is the lack of optimized membrane to produce high water flux. One of the current available commercial FO membranes is developed by HTI (Hydration Technologies Inc., OR) using cellulose triacetate (CTA) as the membrane material [6]. It is suitable to be used to treat river water as it is not prone to biodegradation and hydrolysis compared to other fabricated membranes [7].

There are a lot of studies have been done related to desalination of seawater particularly by using RO techniques. However, researches based on river water treatment by using membrane processes are scarce especially by using FO membrane process. In order to produce high quality drinking water that is conforming to drinking water quality standard in Malaysia, the application of FO in river water treatment is needed to be examined. This process is believed to be able to help the citizens who live in rural areas without clean water and far away from the city's water pipes. It was reported that there are only a few companies (i.e. Hydration Technology Inc. (HTI) and Catalyx Inc. (Anaheim, California)) producing commercial FO membranes. This commercial available membrane is made of cellulose acetate and thin film composite membrane [8]. Hence, the development of FO membrane is considered still new and a crucial part in order to advance the FO field. In this study, we investigated the performance of the fabricated polyamide and commercial CTA membrane in NOM removal using FO system.

II. METHODOLOGY

A. Chemicals

The chemicals used in this experiment are including solid sodium chloride, ≥99.5% purity (Sigma-Aldrich), humic acid (Aldrich Chemical) and cellulose triacetate (CTA) membrane (HTI water). Sodium chloride is the chemical used to form draw solution while humic acid is used to form the feed solution. M-phenylenediamine (MPD), Trimesoyl Chloride (TMC), hexane and NaOH were used forpolyamide membrane preparation.

B. Preparation of Polyamide Membrane

Aqueous MPD solution with concentration of 2% w/v was prepared by dissolving 2 g MPD in 100 ml NaOHaqeous solution, (NaOH 1% w/v). On the other hand, organic Trimesoyl Chloride (TMC) solution with concentration 0.15%

World Academy of Science, Engineering and Technology
International Journal of Agricultural and Biosystems Engineering
Vol:9, No:2, 2015

w/v prepared in organic phase form by dissolving 0.15 g TMC in 100 ml n-hexane. Ultrafiltration (UF) Polyethersulfone (UF PES50, AMFOR INC) supporting membrane was fixed onto a rectangular acrylic frame and then aqueous MPD solution was poured on the surface of supporting membrane for 30 minutes. Then, the excess MPD solution on the membrane surface was drained at room temperature about 2 minutes. After that, the MPD coated membrane was immersed in TMC-hexane for 15 minutes for interfacial polymerization purpose. The resulting aromatic composite polyester membrane was dried overnight at room temperature. Three membrane samples were produced at three different reaction times (10, 30 and 60s) and summarized in Table I.

TABLE I
SUMMARY OF MEMBRANES FABRICATED

Membranes	Reaction Time (s)	MPD concentration (%w/v)
FO10	10	2
FO30	30	2
FO60	60	2

C. Forward Osmosis Experiment

The forward osmosis experiment was conducted on a lab scale unit as shown in schematic diagram (Fig. 1). The membrane is inserted between two chambers to separate the feed solution (15 mg/L of humic acid) from the draw solution (0.5 M NaCl). The membrane orientation was fixed such that its active layer will face the draw solution compartment to reduce the internal concentration polarization and thus obtaining the higher flux flow. Peristaltic pump (Longer pump, China) is used to circulate the feed and draw solution. 1L of each draw and feed solution is filled into respective compartments. The humic acid solution reservoir which is the feed solution is placed on a digital balance and weight changes was recorded for 1 hour in 5 minutes interval to calculate the permeate flux. Hitachi UV-VIS (U-1800) was used to measure the humic acid concentration in both feed and draw solution sides. The experiment was repeated with different draw solution concentrations (1M and 1.5M).

After the experiment, the volume of water permeated is calculated by using (1) as:

$$\Delta V = \frac{\Delta Mass}{Density\ of\ water} \qquad (1)$$

where ΔV is the volume of water permeated, ΔMass is the changes in mass of feed solution and density of water is 1000 kg/m^3. After that, the water flux of each draw solution at different concentration was calculated by using (2):

$$J_w = \frac{\Delta V}{A\Delta t} \qquad (2)$$

where J_w is the water flux, ΔV is volume of water which permeates through the membrane, Δt is time taken in minutes and A= effective area of the membrane which is 0042 m^2 in this experiment. Humic acid rejection was calculated by (3):

$$R = \left(1 - \frac{c_p}{c_b}\right) x\ 100\% \qquad (3)$$

where R is the humic acid rejection in percentage (%), C_p is the humic acid concentration in permeate and C_b is the bulk concentration of humic acid.
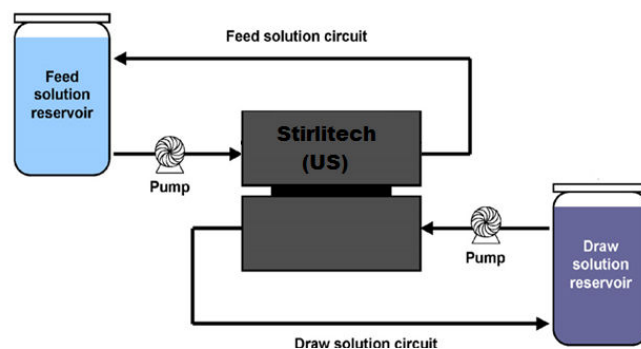

Fig. 1 Schematic diagram of Forward Osmosis system [9]

III. RESULTS AND DISCUSSION

A. Contact Angle

Fig. 2 shows the contact angle of four membranes of commercial and fabricated at different reaction time. Based on membrane performance, it is known that a rougher membrane, which larger effective surface area and more hydrophilic membrane provides a better wettability, possess a higher permeate flux on surface properties [10]. Based on results in Fig. 2, the synthesized membrane (polyamide membrane) are more hydrophilic than original UF PES50 membrane (θ= 62.6^o). The contact angle values decreased (hydrophilicity increased) when the reaction time was increased and this was obvious at longest reaction time of 60s where it is more hydrophilic than commercial CTA membrane. The increase of hydrophilicity might be due to increase of amount of amino and carboxylic functional group of the formed polyamide layer.
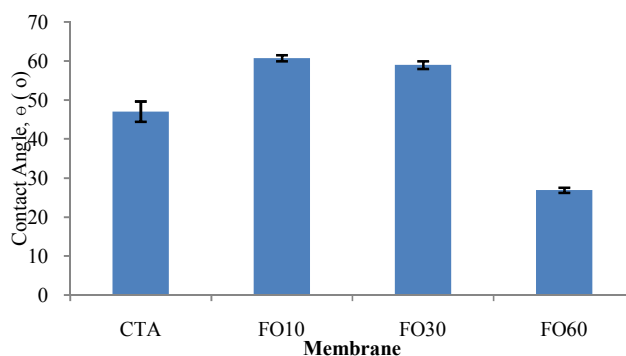

Fig. 2 Contact angle value of four different membranes

B. Membrane Morphology

Field Emission Scanning Electron Microscopy was employed to see the top surface of CTA commercial membrane, ultrafiltration (UFPES50) and polyamide membrane. Figs. 3 (b) and (c) show the surface comparison between the unmodified membrane and modified membrane surface. Fig. 3 (b) shows the top surface of the of

World Academy of Science, Engineering and Technology
International Journal of Agricultural and Biosystems Engineering
Vol:9, No:2, 2015

ultrafiltration membrane (support layer for polyamide membrane). This surface is smooth compare to the top surface of the polyamide membrane which has rougher surface. This new layer with rougher surface confirms the successful of formation of new polyamide layer on the top surface of UF membrane substrate.
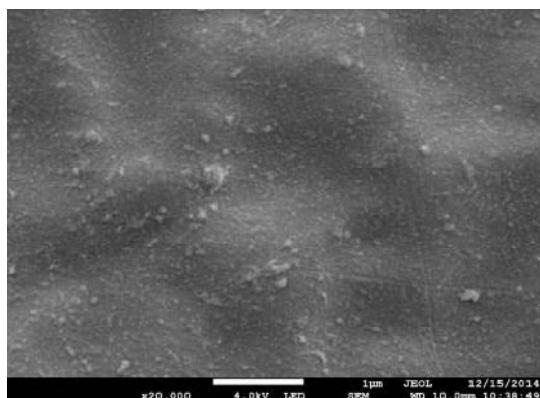
(a)
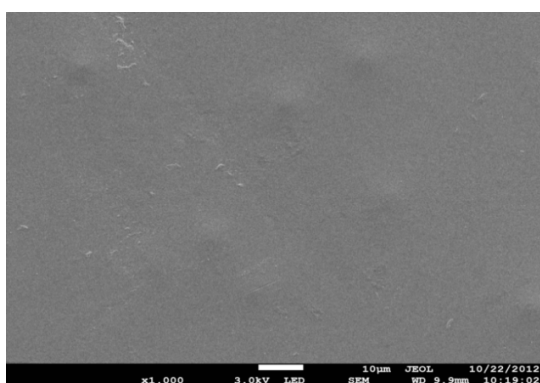
(b)
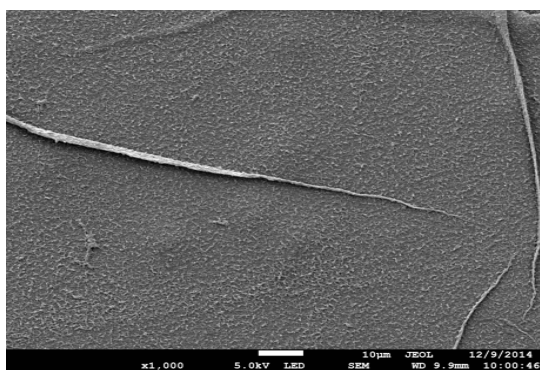
(c)

Fig. 3 FESEM top surface images for (a) commercial CTA membrane (b) unmodified UFPES50 and (c) Polyamide membrane

C. Flux

Based on the results presented in Fig. 4, it can be seen that the trend of flux increases with the increase in molarity of draw solution. For example, the water flux obtained by CTA membrane showed the highest value of 1.2L/m^2.h at 1.5 M

NaCl draw solution, whereas the lowest flux (0.31L/m^2.h) was obtained when 0.5 M NaCl draw solution applied to the system. The similar trend also observed for the synthesized membranes. This phenomenon can be explained by equation 2 which shows that the flux is inversely proportional to the time taken for the water to permeate through the membrane. In conjunction to this, due to high water potential at high concentration, the time taken for the water to permeate through membrane is relatively shorter at higher concentration which ultimately causes an increase in flux for the NaCl draw solution side. Besides that, this phenomenon is further supported by previous studies done by [11] which proved that higher water fluxes can be achieved by increasing draw solution concentration as increase in concentration will also increase the osmotic pressure thus promoting the process of forward osmosis. Interestingly, all the synthesized membranes show higher flux than commercial CTA membrane. This could be due to the synthesized membranes have bigger pores or/and more hydrophilic than CTA membrane lead to higher flux. The further investigation of solute rejection (i.e. humic acid removal) could confirm this.
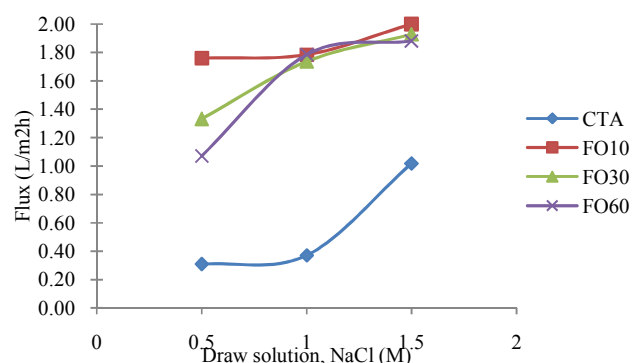

Fig. 4 Effect of draw solution concentration on membrane flux

D. Humic Acid Removal

From Fig. 5, it can be clearly seen that the increase in molarity of NaCl draw solution causes the decrease in humid acid rejection. For instance, CTA membrane shows the highest reading of humic acid rejection of 98.70 % at 0.5 M NaCl; whereas the lowest humic acid rejection is shown by 1.5 M NaCl draw solution, with the reading of 97.03 %. Similar results obtained for the synthesized membrane. This phenomenon can be explained by [12] where the increase of draw solution concentration will increase the solute flux of feed solution and decrease the solute rejection, due to the increase of solute flux that causes the feed solute to penetrate through the membrane to the draw solution side. This is further explained by [13] which claims that the increase in flux of water caused by increase of draw solution concentration will decrease solute rejection as the driving force of water flux pulls and moves along a small amount of feed solute towards the membrane and forces some to seep through the membrane.

In addition, it was observed that membrane synthesized at longer reaction time of 30s and 60s exhibited higher humic

World Academy of Science, Engineering and Technology
International Journal of Agricultural and Biosystems Engineering
Vol:9, No:2, 2015

acid removal and the values are almost similar for all draw solution concentration. This could be due to the reaction was completed at these reaction times produce a compact layer with smaller pores while at shorter reaction time of 10s, the layer formed might still loose and the pores are not enough small to retain humic acid molecules.
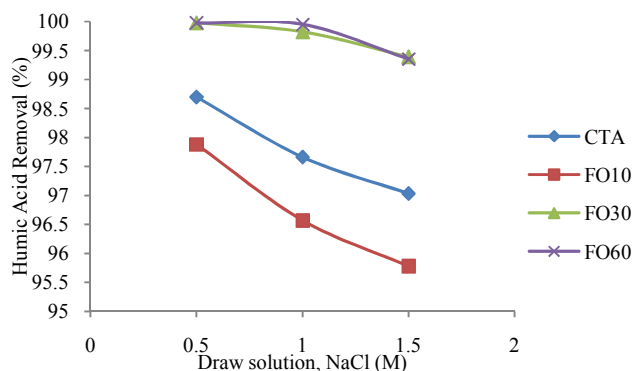

Fig. 5 Effect of draw solution concentration on humic acid removal

IV. CONCLUSION

Overall, the synthesized membranes showed excellent performance in term of both flux and humic acid removal. This was achieved by FO30 and FO60 membranes where synthesized at longer reaction time of 30s and 60s, respectively. In general reaction time play important role for membrane fabrication in interfacial polymerization approach as it could produce different membrane properties and indirectly affect overall membrane performance. Even the fabricated membranes (FO30 and FO60) shows excellent flux and solute removal over commercial CTA membrane however these two parameters only are not enough to justify the overall performance. 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.

REFERENCES

[1] P. S. Srivastava, "Characterizing Monsoonal Variation on Water Quality Index of River Mahi in India using Geographical Information System", *Water Quality, Exposure and Health, 2*(3-4), 2011, pp. 192-203.
[2] D. E. Kile and C. T. Chiou, *Aquatic Humic Substances* (Vol. 4). American Chemical Society, 1989.
[3] L. Chekli, S. Phuntsho, H. K. Shon, S. Vigneswaran, J. Kandasamy, and A. Chanan, "A review of draw solutes in forward osmosis process and their use in modern applications," *Desalination and Water Treatment, 43*, 2012, pp.167-184.
[4] L. Liu, M. Wang, D. Wang, and C. Gao, "Current Patents of Forward Osmosis Membrane Process," *Chemical Engineering, 2*, 2009, pp. 76-82.
[5] R.L. McGinnis, and M. Elimelech, "Global Challenges in Energy and Water Supply: The Promise of Engineered Osmosis," *Environmental Science and Technology, 42*, 2008, pp. 8625–8629.
[6] J. Herron, *Patent No. US 7,445,712 B2.* United States of America. 2008
[7] R.C. Ong, and T.-S. Chung, "Fabrication and positron annihilation spectroscopy (PAS) characterization of cellulose triacetate membranes for forward osmosis," *Journal of Membrane Science, 394*, 2012, pp. 230–240.
[8] R. Wang, L. Shi, C.Y. Tang, S. Chou, C. Qiu, and A.G. Fane, "Characterization of novel forward osmosis hollow fiber membranes," *Journal of Membrane Science 355*, 2010, pp. 158-167.
[9] Achilli, A., Cath, T. Y., & Childress, A. E. Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science, 364*, 2010, pp.233-241
[10] A. Schafer, L. Nghiem, and T. Waite, "Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis," *Environmental Science Technology, 37(1)*, 2003, pp.182–188.
[11] Y. Xu, X. Peng, C. Y. Tang, Q. S. Fu and S. Nie, "Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis performance in a spiral wound module," *Journal of Membrane Science, 348*(1-2), 2010, pp. 298-309.
[12] F.-x. Kong, H.-w. Yang, X.-m. Wang, and Y. F. Xie, "Rejection of nine haloacetic acids and coupled reverse draw solute permeation in forward osmosis," *Desalination, 341*, 2014, pp. 1-9.
[13] M. Xie, W.E. Price, L.D. Nghiem, and M. Elimelech, "Effects of feed and draw solution temperature and transmembrane temperature difference on the rejection of trace organic contaminants by forward osmosis," *Journal of Membrane Science, 438*, 2013, pp. 57-64.