

Effect of Methacrylic Acid Monomer on The Reverse Salt Diffusion in Chemical Grafted Forward Osmosis Membrane

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Reverse salt diffusion (RSD) is a common issue in forward osmosis (FO) membrane normally contribute to substantial fouling and lead to a lower water flux. Commercial nanofiltration (NF) membrane surface was grafted using chemical grafting for controlling this RSD issue. Different concentrations of 0.3, 0.6, and 1.0 M of methacrylic acid (MA) were selected as main monomer while potassium persulfate and sodium metabisulfite ($K_2S_2O_8/Na_2S_2O_5$) with concentration of 0.01 M as pair of initiators were used for the grafting modification. Then the grafted membrane was evaluated in term water flux (J_w) and RSD using 1 M sodium chloride (NaCl) as draw solution. The result shows that, the highest J_w (0.7534 L/m².h) and the lowest RSD (4.272 g/m².h) both were recorded at the grafting of 30 min with 1.0 M concentration of MA. Both performance increase with the increasing in the MA concentration and grafting time. Therefore, modification of the commercial NF membrane using chemical grafting can therefore be used as an alternative technique for enhancing the performance of commercial membrane in the application of FO.

1. Introduction

The demand and supply of fresh water and mounting are already at a critical point in the world. In forecast, demand for water is expected to increase by 20-30 % in year 2050 due to the domestic and industrial activities. It was reported that more than half of the world's population (4 billion) experienced water shortage at least a month every year (The United Nations World Water Development Report 2019). Forward osmosis (FO) is one of the alternative technologies recently applied in water treatment industry to solve this problem since it has the potential to be energy-efficient and it has ability to reject the undesired components better than the reverse osmosis (RO) process. This FO technology also has longer lifespan, low capital as well as minimal operating expenditure. All of these advantages from FO technology brings the innovation in replacing the traditional technique from RO. However, there are still problems arise that can affect the performance of FO process. Reverse salt diffusion (RSD) is one of the problems encountered when using FO process. It can happen when the solute has diffused through the selective permeable membrane from the draw solution (higher osmotic pressure) to the membrane polymer matrix and thus, directly into the feed solution (Ryu et al., 2020). This phenomenon will lead to decline in osmotic pressure difference between the feed and the draw solution (FO driving force) because of the lower water chemical potential of feed solution compare to water chemical potential in draw solution. Thus, the water flux also will be declined in this process which also will reduce the efficiency of water recovery. Other adverse effects that occur due to RSD problem is that it is able to bring the contaminates or pollutant to the feed solutions (Xu et al., 2017).

Many alternatives and research done by researchers to reduce this problem in FO system among of them are grafting method. Chemical grafting is a process of grafting the hydrophilic layer on the membrane by permanently attached the specialized substrate activator and monomer system. Chemical grafting helps to increase the surface energy by localizing oxidized functional group on the surface of the membrane which lead

to high percentage of obtaining hydrophilicity on the membrane. The procedure is effective because of deep penetration of the solvent into the monomer matrix pores at low costs besides it has minimal side effects (Nemani et al., 2018). Redox reactions with initiator such as metabisulfite or peroxydisulfate have been previously used for initiation of free radical polymerization grafting in PES membrane (Belfer et al., 2000). This initiator is used due to having water-soluble characteristics (Lutz et al., 2012) thus, a better redox system for grafting the monomer on PES membrane which lead to higher grafting efficiency (Kochthongrasamee et al., 2006). For the monomer, sulfopropylmethacrylate (SPM), methacrylic acid (MA) and polyethyleneglycol-methacrylate (PEG-MA) are commonly use in RO and ultrafiltration (UF) (Belfer et al., 1998). Shi et al. (2010) reported that MA grafted PES showed excellent properties where its hydrophilic characteristic not only improve the PES hydrophilicity, but also offer pH-responsive property of the UF membrane.

In this work, the commercial membrane surface has been modified through this chemical grafting approach to alter the surface properties in order to improve the water flux and minimize RSD problem in FO application.

2. Methodology

2.1 Membrane modification

A commercial polyethersulfone (PES) nanofiltration membrane (NF2, Amfor Inc., China) used as the base support for grafting modification. Methacrylate acid monomer, $K_2S_2O_8$ and $Na_2S_2O_5$ as redox initiators were purchased from Sigma Aldrich. For the preparation, 0.3 M of methacrylate acid (MA) as a monomer in this process was mixed with a mixture of 0.01 M potassium persulfate ($K_2S_2O_8$) and 0.01 M of sodium metabisulfite ($Na_2S_2O_5$) of redox initiators. In a glass container, the monomer solution and the initiator mixture were stirred until they were fully dissolved. Next, polyethersulfone (PES) membrane was immersed in the mixture of monomer-initiator solution for different time interval (10, 20 and 30 min). After that, the membrane was washed it in the large volume of washing water. The procedures were then repeated with different concentration of monomer such as 0.6 and 1.0 M.

2.2 Membrane Characterization

The surface morphology of the membrane was characterized by Field Emission Scanning Electron Microscope (FESEM, JSM7800F Schottky FESEM, JEOL Ltd.) and the surface hydrophilicity was determined by contact angle measurement using goniometer telescope of Rame-Hart, Model 290.

2.3 FO Experiment setup

1 L of deionized (DI) water as a feed solution and 1 M of sodium chloride (NaCl) as a draw solution were used to evaluate the water flux, J_w and reverse solute diffusion, J_s . Next, weight of DI water was recorded using a digital balance at interval of five min until the process complete after 1 h. The flowrate of 168.7 mL/min was fixed for feed and draw solution and both solutions were circulated throughout the process. The initial and final concentration of feed side (DI water) then recorded for RSD determination.

As for the analysis of experimental data, J_w ($L/m^2.h$) was calculated as follows:

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

The RSD was evaluated and represented by the following J_s ($g/m^2.h$) in Eq (2):

$$J_s = \frac{V_t C_t - V_o C_o}{A \cdot t} \quad (2)$$

Where V_o and V_t are the initial and final volume of feed (L); C_o and C_t are the initial and final concentration of NaCl in feed solution (g/L); $t = 1$ h of operating time to complete the experiment; and A is an effective area of membrane, 0.0042 m^2 .

3. Results and discussion

3.1 Surface morphology

The surface morphology of the neat NF2 membrane and modified membrane were characterized by FESEM technique. Fig. 1(a) and Fig. 1(b) show the FESEM images of the bottom and top surface image of the unmodified NF2 membrane respectively. Fig. 1(a) show the image of the bottom layer of the unmodified NF membrane with clear visible pores. In contrast, the bottom surface of the modified membrane as shown in Fig. 1(c) show that the pores were disappeared after MA monomer has been added. This is due to after modification, the MA monomer acts as polymer grafted onto the membrane pores and blocking the pores in the porous support of the bottom layer. From the Fig. 1(b), it can be observed that the top surface of the unmodified NF2 membrane

has a uniform surface, but the modified membrane (Fig.1(d)) can be distinguished as zones with significant contrast (dark areas). Moreover, after grafting with redox initiators (potassium persulphate and sodium metabisulfite) and MA, a significant change in surface morphology was observed where the roughness increased. The rougher surface of modified membranes resulted in visible and uniformly distributed big particles as shown in Fig. 1(d).

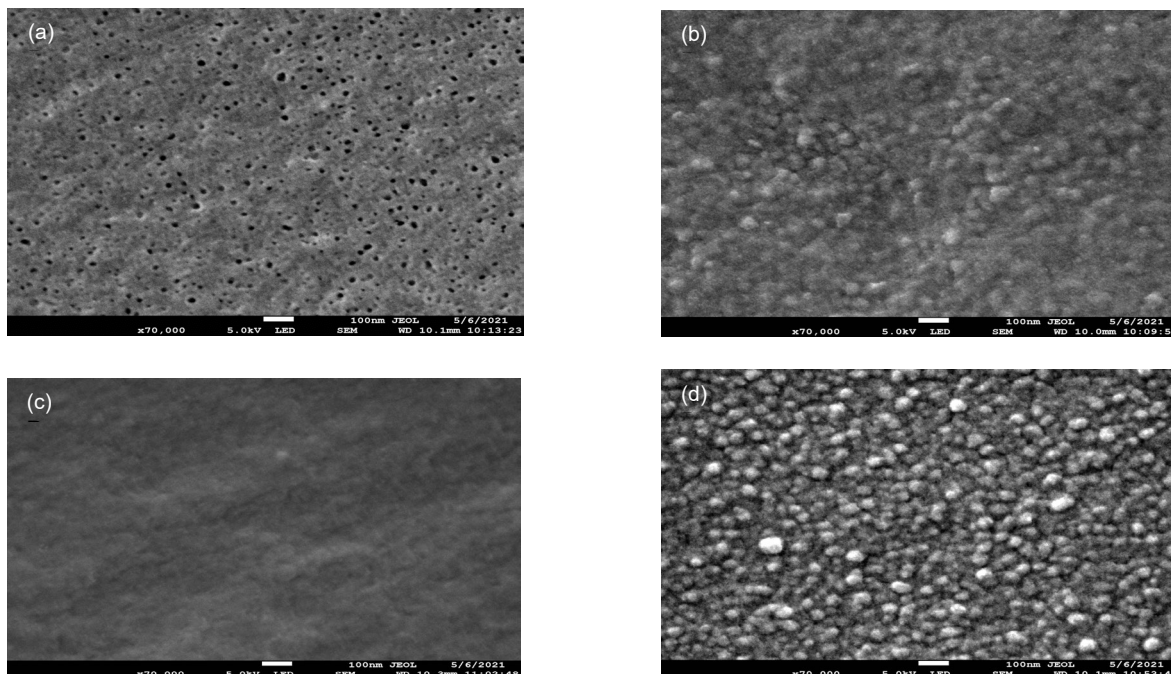


Figure 1: FESEM images of 70,000 \times magnifications of (a) bottom surface and (b) top surface of neat NF2 membrane, (c) bottom surface and (d) top surface after modification with 1M of MA

3.2 Hydrophilicity properties

Figure 2 shows the unmodified NF2 membrane recorded the largest value of contact angle among the others nine modified membranes which the average value of 53.02°. For modified membrane with grafting time of 30 minutes with 0.3M of concentration, the value of contact angle is 39.98° which lower than the modified membrane that rafted at 10 minutes (42.46°) with the same concentration. Modified membrane that having the longest grafting time and the most concentrated monomer (1.0M at 30 minutes of grafting time) seems to have the lowest value which is 31.86° compared to the others unmodified and modified membranes. The more concentrated of concentration and the longer the grafting time, the more the monomer and the initiator are being grafted onto the membrane and this improves the hydrophilicity of the membrane. Hydrophilicity cause from the formation of the carboxyl group from the monomer that has been grafted on the membrane surface (Abdul Rahman & Abu Seman, 2018). Carboxyl is a highly polar group which can make the modified membrane to have high surface energy. As a result, water can have a good adhesive toward the membrane surface. In addition, the hydroxyl group of methacrylic acid that attached/grafted to the membrane surface also increases the hydrophilic properties. The hydroxyl is polar which it can interact well with the molecules of water through Van der Waals' force and hydrogen bond (Luo et al., 2005). As the result, it will enhance the amount of water that can be permeated across membrane.

3.3 Effect of MA concentration and grafting time on water flux

Figure 3 shows the effect of MA concentrations (0.3, 0.6 and 1.0 M) modified at different grafting time on the water flux. The highest J_w (0.7534 L/m².h) was obtained at the grafting of 30 min with 1.0 M MA while, membrane grafted for 5 min with 0.3 M MA exhibited the lowest water flux (0.1177 L/m².h). The J_w increased significantly at longer grafting time for 1.0 M methacrylic acid concentration and reach the highest value at 0.7534 L/m².h when the grafting time was 30 min. Similar results also observed for membranes modified with lower MA concentration of 0.6 and 0.3 M. Thus, from this Figure 3, longer time for grafting time and high concentration of monomer leads to higher water flux for the membrane.

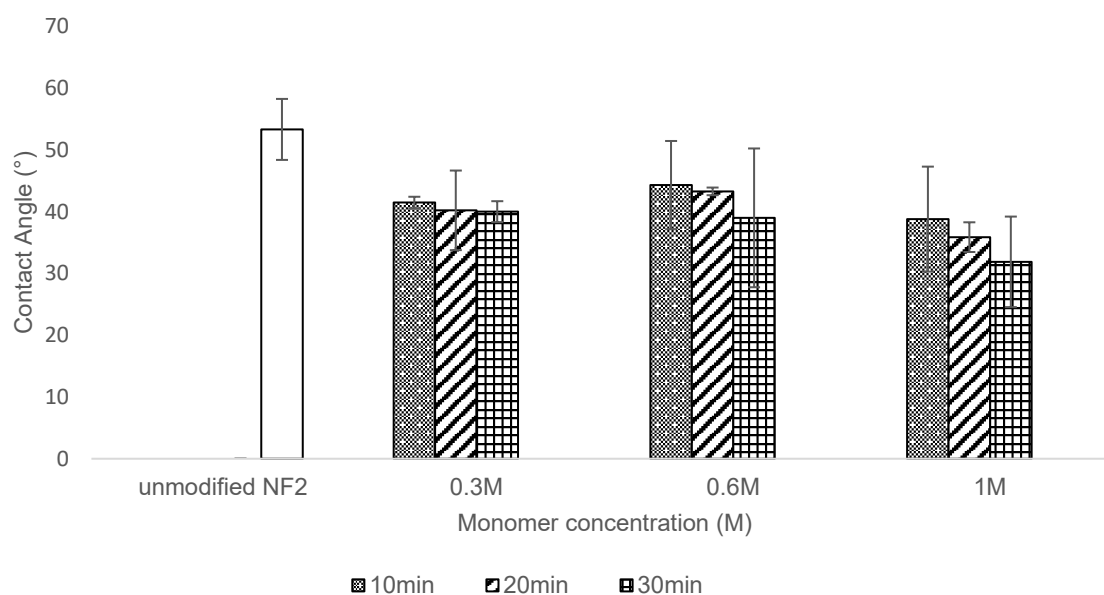


Figure 2: Contact angle value for unmodified NF2 and modified membrane at various concentrations of MA (0.3M, 0.6M, 1M) and grafting time (10min, 20min, 30 min)

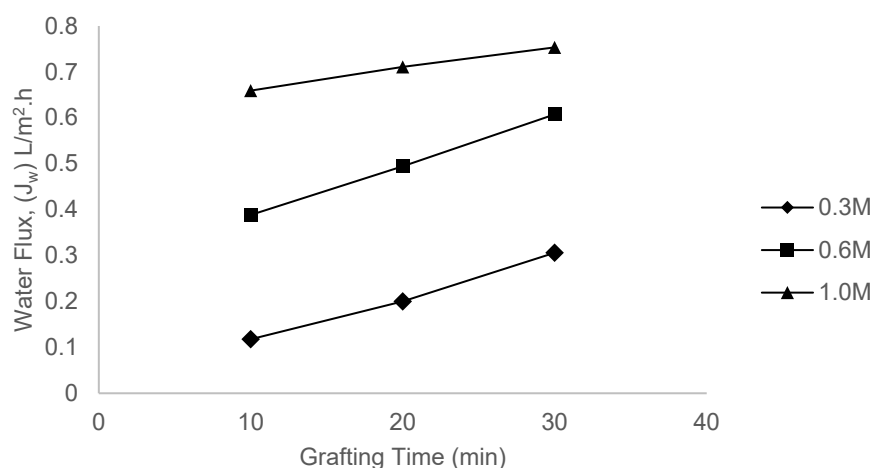


Figure 3: J_w (water flux) of membranes grafted at variation of MA concentration and grafting time

3.4 Effect of MA concentration and grafting time on RSD

Figure 4 shows the highest value of reverse solute diffusion, RSD was recorded at $10.457 \text{ g/m}^2\cdot\text{h}$ for membrane grafted at 10 min using 0.3 M of methacrylic acid meanwhile the lowest RSD reached at $6.676 \text{ g/m}^2\cdot\text{h}$ at the longest grafting time of 30 min and 1.0 M methacrylic acid. For 0.3 M of methacrylic acid concentration, the reverse solute diffusion will gradually decline as the grafting time increase from 10 to 30 min. Besides, the reverse solute diffusion for 0.6 and 1.0 M of methacrylic acid exhibited a similar trend whereby the RSD values decreased when the chemical grafting time was prolonged. As a result, the graph showed that the longer the chemical grafting time and high concentration of monomer, the lower the modified membrane's reverse solute diffusion. The longer the grafting time and higher concentration of methacrylic acid cause more amount of monomer being grafted onto the membrane. The conformation on the surface of the membrane has altered after the monomer which is methacrylic acid is began to appear and grafted on the membrane following the surface modification. Moreover, the channel and pore structure both side of membrane layer which are active layer and support layer was changed after the process of chemical grafting. Grafting of hydrophilic monomer onto the membrane surface cause the presence of thin layer that cause the size of pore on the membrane surfaces are

decrease and some of the rough surface are covers. This decline in size of porous cause the NaCl cannot perform reverse diffusion through membrane to feed solution. This is the fact that the porosity of the support layer inversely proportional to extra resistance of mass transfer coefficient of the diffusive boundary layer (Guan et al., 2019). Thus, longer the grafting time and highly concentrated monomer used in chemical grafting are important in decreasing the reverse solute diffusion because more monomer will be grafted on the surface of membrane that lead to decrease in size of the pore on support layer.

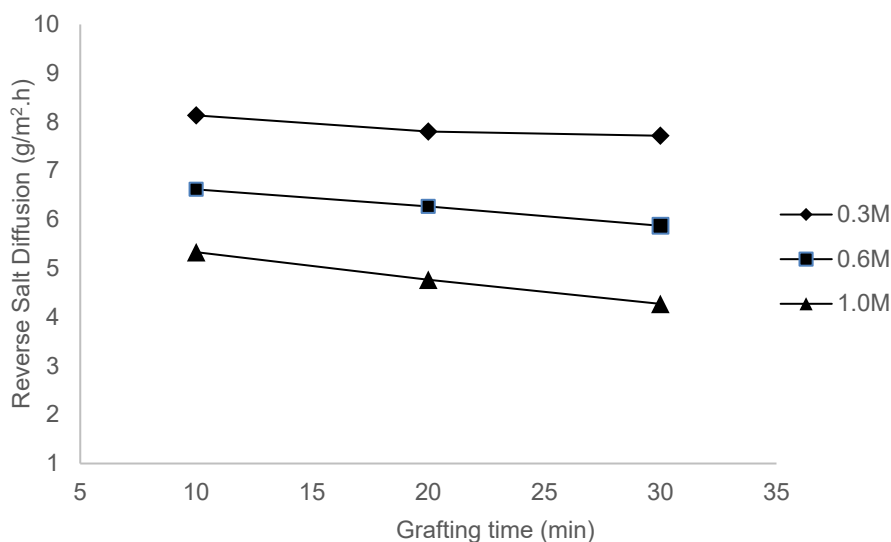


Figure 4: Reverse salt diffusion (RSD) against the grafting time for membranes modified with different concentration of MA monomer

4. Conclusions

In this work, the surface of forward osmosis membrane was successfully grafted by the methacrylic acid as the monomer and $K_2S_2O_8/Na_2S_2O_5$ as the initiators pair. The hydrophilicity of the modified membranes was improved compared to the neat NF2 membrane which is good for water flux. The highest J_w and the lower J_s (RSD) were recorded at the longest grafting time (30min) and the most concentrated (1M) of MA monomer used. Monomer concentration and grafting time plays a significant role in improvement of the FO membrane performance. However, as the MA-grafted PES may poses pH-responsive characteristic as mentioned earlier, the performance of the grafted membrane may be further investigated especially the effect of pH of the feed on the water flux and RSD.

Nomenclature

A_m – effective membrane area, m ²	DI- deionized
C_o – initial concentration of NaCl, g/L	FO- forward osmosis
C_t – final concentration of NaCl, g/L	MA - methacrylic acid
J_s – reverse solute diffusion, gm ⁻² h ⁻¹	NF- nanofiltration
J_w –water flux, Lm ⁻² h ⁻¹	PEG-MA - polyethyleneglycol-methacrylate
t – time taken for FO operation, h	RO- reverse osmosis
V_o – volume of feed solution measured at initial, L	RSD – reverse salt diffusion
V_t – volume of feed solution measured at the time of t , L	SPM- sulfopropylmethacrylate
	UF- ultrafiltration

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