# Enhanced Hydrophilicity of Integral Membrane

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***Abstract*—A novel blend membrane from polysulfone (PSf), polyvinyl alcohol (PVA) and chitosan (CS) was fabricated by phase inversion method. The integral membranes with different compositions of PVA (1 wt% and 2 wt%) were characterized in terms of thermal stability, water uptake, pure water flux, antifouling properties, and mercury removal. Prior to performance testing, the blending of the integral membranes were confirmed via FTIR analysis. Results show that the integral membranes exhibit higher thermal stability, water uptake and pure water flux compared to pure PSf membrane. PSf/CS/PVA 2 wt% has the highest water uptake and pure water flux which are 233% and 57.96 L/m$^2$h respectively. This enhanced hydrophilicity is attributed to the presence of OH groups in PVA. Meanwhile, PSf/CS/PVA 1 wt% exhibited constant and total mercury removal (100%) during a filtration period of 1 hour. In terms of antifouling properties, both membranes undergo irreversible fouling. This may be due to the high concentration of humic acid used during filtration. Hence, further studies are required on the antifouling performance of the membranes.**

***Keywords*— Polysulfone membrane, Mercury Removal, Polyvinyl Alcohol, Blend Membrane, Hydrophilicity**

## I. INTRODUCTION

Rapid industrialization and urbanization have resulted in a large emission of heavy metals into the environment, particularly into water sources. One of the most toxic element is mercury, Hg, which is carcinogenic, toxic, non-biodegradable, and highly soluble in water [1][2]. In industrial wastewaters, Hg is present at levels of parts per billion (ppb) and industries are required to adhere to strict discharge regulations [3]. Many of these industries are facing challenges in meeting the limits set by respective governing bodies.

Thus, in order to minimize the amount of mercury in wastewater, various removal techniques can be implemented. These include adsorption, absorption, filtration, coagulation, reverse osmosis, and chemical precipitation [4][5]. One of the methods that is explored widely is membrane separation. Currently, many applications utilize polymers such as polysulfone, polyvinyl alcohol, and polyethylene glycol in the synthesis of the membranes [6]. Furthermore, blending of two different compounds are often carried out to further enhance the membrane's properties [7][8].

The works of various researchers have found that integral membranes have better adsorption/absorption capabilities, chemical stability, tensile strength, thermal properties, and anti-fouling properties compared to pure membranes [9][10][11]. However, most of the available researches available fabricate membranes from only two compounds. Hence, this research aims to fabricate a novel blend membrane from three compounds which are polysulfone (PSf), chitosan (CS), and polyvinyl alcohol (PVA) and characterize the improvements in terms of pure water uptake, water flux, thermal stability, antifouling properties, and percentage removal of mercury.

## II. METHODOLOGY

### A. Materials

Polysulfone (avg mn~22000 by mo, beads) and Polyvinyl Alcohol, 87-89% hydrolyzed (MW 85 000 – 124 000) were purchased from Sigma Aldrich USA. Chitosan, (medium molecular weight) deacylated chitin, Poly(O-glucosamine) was purchased from Sigma Aldrich Germany. N-Methyl-2-Pyrrolidone, Acetic Acid (100% purity) and DMSO were purchased from Merck. Baker applicator 80 mm Art No VF1500 (15/30/60/90 µm) was purchased from TQC Eu.

### B. Methodology

#### 1) Preparation of Blend Membrane

*a) Preparation of CS*

0.02 wt% CS solution was prepared by dissolving 0.02 g of the powder into 99.98 g of 2 wt% aqueous acetic acid solution at 80˚C with stirring at 450 RPM for 2 h.

*b) Preparation of PSf*

13 wt% PSf solution was prepared by dissolving 13 g of PSf pellets into 87 g NMP at 80˚C for 9 hours while stirring at 500 RPM.

*c) Preparation of PVA*

1 wt% and 2 wt% PVA solution were prepared by dissolving 1 g and 2 g of PVA into 99 g and 98 g DMSO respectively. The solutions were mixed at 80˚C for 2 hours while stirring at 300 RPM.

*d) Preparation of Blend Membrane Solution*

Table 1 shows the summary of the blend membrane solutions. Preparation of PSf/CS/PVA 1 wt% was done by mixing PSf with 1 wt% PVA at 80˚C. The solution was stirred at 400 RPM for 30 minutes to ensure homogeneity. Then, CS was added and the precipitation of CS took place. The solution was stirred at 600 to 1000 RPM for one hour. The ratio (v/v) of PSf:PVA:CS is 1:0.005:0.005. PSf/CS/PVA 2 wt% solution was prepared similarly.

**Table 1. Summary of blend membrane solutions**

| Membrane | Composition | PSf | PVA | CS |
|---|---|---|---|---|
| PSf | PSf | 20 ml | - | - |
| M1 | PSf/CS/PVA 1 wt% | 20 ml | 0.1 ml PVA 1 wt% | 0.1 ml |
| M2 | PSf/CS/PVA 2 wt% | 20 ml | 0.1 ml PVA 2 wt% | 0.1 ml |

*e) Membrane Casting*

The blend membrane solution was allowed to cool before it was casted on a glass plate using a Baker Film Applicator with thickness set at 90 µm. It was immersed in deionized water for 24 hours. Then, the membrane was rinsed with deionized water and dried at room temperature for 24 hours. The dried membrane was then cured for 1 hour at 45˚C

## C. Membrane Characterization & Performance Testing

*a) FTIR*

The samples were evaluated at wavelength range of 400 $cm^{-1}$ – 4000 $cm^{-1}$.

*b) TGA*

Thermogravimetric analysis was carried out using a thermogravimetric analyser under nitrogen atmosphere. The gas flow rate was set at 50 mL/min and the heating rate was 10˚C/min. The starting temperature was from 30˚C to a final temperature of 900˚C with and initial sample weight of 10 mg.

*c) Water Uptake*

First, the membranes were cut into 1 $cm^2$ and immersed in deionized water. After 24 hours, the wet samples were removed and weighed immediately. Next, the samples were oven dried at 50˚C for 24 hours. The dry weight of the membranes were then recorded. Based on the average obtained from 3 samples, the gravimetric water uptake was calculated [12]. The % water uptake was calculated using Eq. (1)

$$\boldsymbol{Water\ uptake} = \frac{\boldsymbol{m_{wet} - m_{dry}}}{\boldsymbol{m_{wet}}} \times \mathbf{100} \quad (1)$$

Where
$m_{wet}$ is the wet mass
$m_{dry}$ is the dry mass

*d) Pure Water Flux*

The dead end mode of membrane filtration rig was used for the pure water flux experiment. The rig comprises of 300 mL bench stainless steel tangential flow stirred cell connected to a pressurized nitrogen system set at 3.5 bar. The amount of permeate was recorded at an interval of 15 minutes for an hour filtration [13]. Water flux was determined using Eq. (2)

$$\boldsymbol{J_W} = \frac{\boldsymbol{Q}}{\boldsymbol{A\Delta t}} \quad (2)$$

Where
Q is the volume of permeate (L)
A is membrane area, $m^2$
Δt is the sampling time (h)

*e) Antifouling Properties*

The antifouling experiment was carried out in 3 stages at a pressure of 6 bars. In the first stage, the membrane was filtered with deionized water for 30 minutes and the stabilized flux was recorded as $J_{w1}$. Then, permeation using humic acid solution (10 g in 1 L of 1000 ppm sodium hydroxide) was carried out for 2 hours. The volume of the permeate stream was recorded every 20 minutes, where the final flux was recorded as $J_{HA}$. Prior to the final stage, the membrane was backwashed for 30 minutes. It was conducted by immersing it in a beaker containing deionized water and the solution was stirred at 150 rpm. Then the procedures in the first stage were repeated, and the pure water flux was recorded as $J_{w2}$. Finally, the FRR (flux recovery ratio), RFR (reversible), IFR (irreversible) and TFR (total fouling ratio) were calculated using Eq. (3), (4), (5) and (6) respectively.

$$\boldsymbol{FRR}\ (\%) = \frac{\boldsymbol{J_{w2}}}{\boldsymbol{J_{w1}}} \times \mathbf{100} \quad (3)$$

$$\mathbf{RFR}(\%) = \frac{\mathbf{J_{w2} - J_{HA}}}{\mathbf{J_{w1}}} \times \mathbf{100} \quad (4)$$

$$\mathbf{IFR}(\%) = \frac{\mathbf{J_{w1} - J_{w2}}}{\mathbf{J_{w1}}} \times \mathbf{100} \quad (5)$$

$$\mathbf{TFR}(\%) = \mathbf{RFR}(\%) + \mathbf{IFR}(\%) \quad (6)$$

*f) Removal of Mercury*

The performance of the composite membrane on the removal of Mercury was tested using the same rig as described in Section C (d). 3 ppm mercury solution was prepared. The pressure for nitrogen system was set at 6 bar. The concentration of mercury in the permeate ($C_p$) and feed ($C_f$) streams were determined using ICP-OES. The percentage of mercury ion rejection/removal is calculated using Eq. (7)

$$\%\boldsymbol{R} = \left(\mathbf{1} - \frac{\boldsymbol{C_p}}{\boldsymbol{C_f}}\right) \times \mathbf{100} \quad (7)$$

# III. RESULTS AND DISCUSSION

## A. Membrane Characterization

### 1) Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fig. 1 compares the IR spectra of PSf with that of integral membranes. The peaks observed at 1240 and 1488 $cm^{-1}$ in PSf spectra correspond to the stretching vibration of C–O–C and $CH_3$–C–$CH_3$ [14]. Sulfone group S=O symmetric can also be seen at 1150 $cm^{-1}$[15]. These peaks that represent PSf can clearly be seen in M1 and M2. Hence, PSf is clearly present in all membranes.

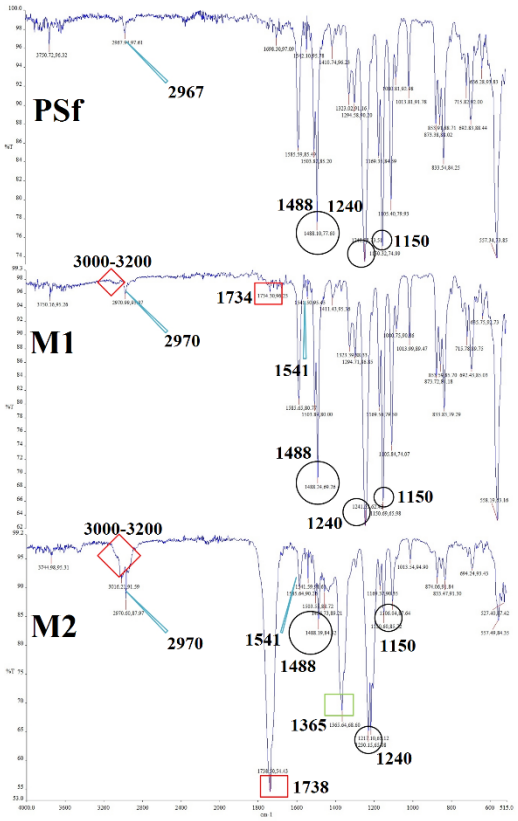


**Fig. 1. FTIR Spectra of PSF, M1 and M2.**

In M2 spectra, the distinct broad absorption band at 3000–3200 $cm^{-1}$ occurs due to the stretching vibration of O–H groups of PVA. The broad absorption is only barely seen in M1 due to the low wt% of PVA in the membrane. In addition, there is a strong peak at 1738 $cm^{-1}$ in M2 which is due to the stretching C=O and C-O from acetate group remaining from PVA [16]. In M1, the peak occurs at 1734 $cm^{-1}$. In PSf, both these peaks are absent.

Lastly, since there is low CS (wt%) content in the blend, presence of $-NH_2$ group can be verified only by the weak absorption peak around 1541 $cm^{-1}$ for both M1 and M2 [11]. There is an additional strong peak at 1365 $cm^{-1}$ in M2 which is due to the bending vibration of $CH_3$ and $CH_2$ [17]. In all three spectra, C-H stretch can be seen at 2967 $cm^{-1}$ for PSf and at 2970 $cm^{-1}$ for M1 an M2. The presence of all these peaks in the IR spectra of M1 and M2 confirms the blending of CS, PVA, and PSf.

### 2) *Thermogravimetric Analysis (TGA)*

Thermogravimetric analysis was carried out to measure the thermal stability and weight loss of the integral membrane at a heating rate of 10°C $min^{-1}$ in nitrogen atmosphere. The weight losses at different stages were analyzed and the data collected was plotted with weight on they y-axis and temperature on the x-axis. The thermal stability of the membranes is shown in Fig. 2. Pure PSf is also shown for the comparative analysis.

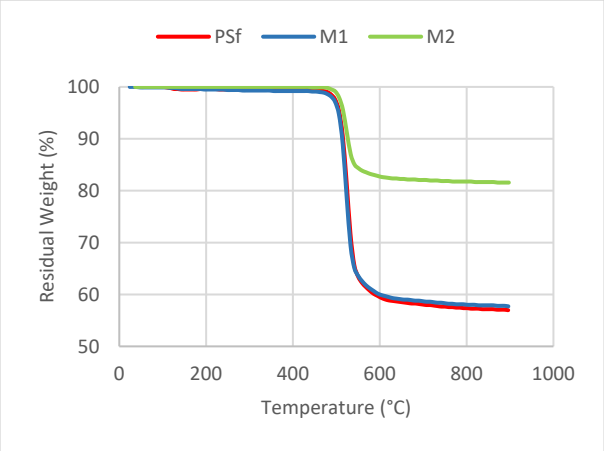


**Fig. 2. Thermal stability of the membranes.**

For the PSf membrane, the initial weight loss in the temperature range of 109.18 to 514.61°C corresponded to the removal of moisture and solvent from the sample [18]. The degradation of the membrane started at 523.46°C and continued to 869.78°C.

The weight loss of M1 and M2 at temperature range 117.63 to 514.73°C, and 444.65 and 515.28°C respectively are associated with the loss of adsorbed and bound water [12]. When the temperature reached the range of 523.61 to 585.64°C, the weight loss of M1 happened rapidly which indicated that PSf and PVA have decomposed into $CO_2$ and $H_2O$ [19]. As shown in Fig. 2, M2 also decomposed rapidly but at a slightly higher temperature which is from 524.15 to 586°C.

Overall, M2 exhibit the highest thermal stability compared to M1 and PSf. Disregarding water loss, M2 started decomposing at 524.15°C which is higher than M1 at 523.61°C and PSf at 523.46°C. The final degradation temperature of the membranes are 871.31, 870.16 and 869.78°C respectively.

In addition, M2 also maintains the highest residual weight which is 8.23 mg of the initial 10 mg. M1 and PSf degraded from 10 mg to 5.81 and 5.73 mg respectively. M1 undergo 42% weight degradation while PSf lost 43% of the initial weight. The membrane with the higher PVA content, M2, maintained 80% of the initial weight.

Hence, it can be said that the blend membranes show better thermal stability compared to pure PSf membrane due to improved packing and H-bonding between the components of the membranes [20].

### 3) *Water Uptake*

Water uptake or swelling behavior of polymers depend on the nature of the polymer, the polymer solvent compatibility and the degree of cross linking [21]. Fig. 3 and Table 2 show the water uptake of the membranes. The percentage of water uptake is lowest in PSf membrane, at 34%, and highest in M2, at 233%. Meanwhile, the water uptake of M1 is 72%. The increment of water uptake in the blend membranes is due to the increase in number of –OH group of PVA in the membranes. Similar results was also obtained in a study by Casey et al. [20]. As shown in Fig. 3, the increment of water uptake of M1 and M2 compared to PSf, reflect the higher hydrophilicity of the blended membranes.

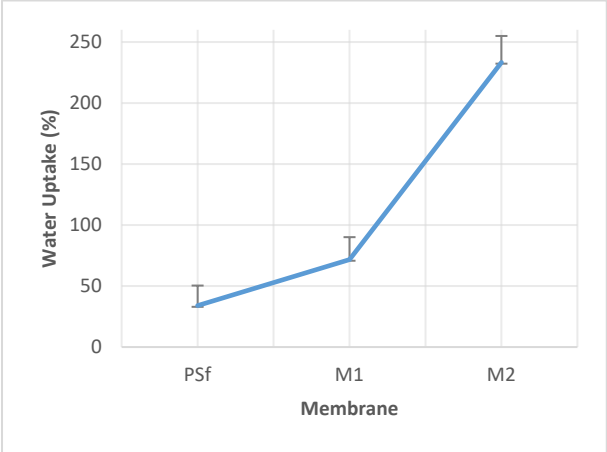


**Fig. 3. Water uptake of membranes.**

**Table 2. Percentage of water uptake of membranes.**

| Membrane | Water uptake (%) |
|---|---|
| PSf | 34 |
| M1 | 72 |
| M2 | 233 |

### 4) *Pure Water Flux*

Pure water flux has a direct relationship with hydrophilicity. The total permeation flux for a duration of 1 hour at 3.5 bar of PSf, M1, and M2 membranes are 13.09, 17.98 and 57.96 $L/m^2h$ respectively. The pure water flux of the membranes at intervals of 15 minutes for a period of 1 hour are shown in Fig. 4.

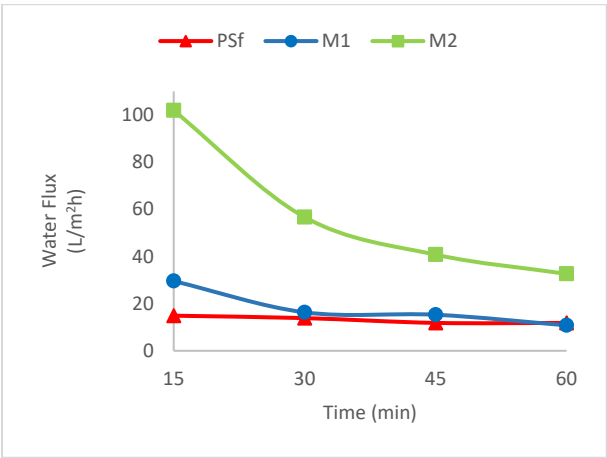


**Fig. 4. Pure water flux of the membranes.**

At 15 minutes, both blend membranes, M1 and M2, showed improved water flux of 29.54 and 101.86 $L/m^2h$ compared to 14.87 $L/m^2h$ exhibited by pure PSf membrane. The significant increase in water permeability of the blend membranes is attributed to the presence of PVA that increases the hydrophilicity of the membranes [22]. PVA's hydrophilic nature also give rise to higher porosity of both blend membranes [23]. As the experiment continues, the flux of all 3 membranes continue to decrease but both blend membranes continue to have a higher pure water flux compared to the pure PSf membrane.

### B. *Performance Testing*

#### 1) *Antifouling Properties*

In flux and antifouling properties, porosity and hydrophilicity are key factors that determine the membranes' performance [24]. The permeate flux for the integral membranes are shown in Fig. 5. The initial flux for M1 and M2 during the first 20 minutes are 18.33 and 5.50 L/m$^2$h respectively. Both membranes demonstrate a similar pattern of flux decline until the 120$^{th}$ minute.

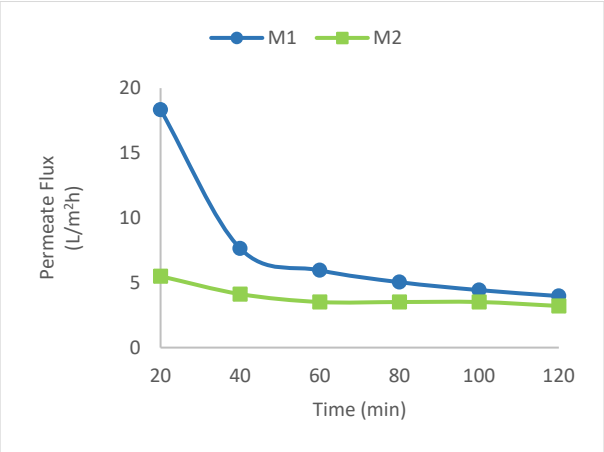


**Fig. 5. Permeate flux during humic acid filtration.**

The steep and sudden decrease in flux for M1 and gradual decrease for M2, as seen in Fig. 5, is an indicator of membrane fouling. It is attributed to concentration polarization which occurs when there is high concentration of solute at the membrane interface [25]. In this case, high deposition of humic acid on the surface of the membrane had blocked the pores and constricted the flow of the solute.

A more detailed information on the flux change of the antifouling experiment is shown in Table 3. From the high values of the irreversible fouling ratio (IFR) in Table 3, it can be said that both membranes undergo irreversible fouling. Theoretically, a higher permeate flux has a higher possibility of fouling [26]. This explains why the TFR for M1 is higher since it has a higher permeate flux (as seen in Fig. 5) compared to M2. Moreover, the negative charges of the hydroxylated groups in M2 are able to prevent fouling and flux decline [24]. This steric stabilization effect forms a strong hydrogen bonding of water molecules to the oxygen atoms in PVA [27]. Thus, since M2 has more OH groups, there is more accumulation of water molecules around the membrane which prevents hydrophobic foulants from approaching the surface.

**Table 3. Performance of the membranes in term of antifouling behaviour.**

| | L/m$^2$h | | | |
|---|---|---|---|---|
| **Membrane** | **$J_{w1}$** | **$J_{HA}$** | **$J_{w2}$** | |
| **M1** | 122.23 | 7.56 | 22.41 | |
| **M2** | 61.12 | 3.90 | 6.11 | |
| | (%) | | | |
| **Membrane** | **FRR** | **RFR** | **IFR** | **TFR** |
| **M1** | 18.33 | 12.15 | 81.67 | 93.81 |
| **M2** | 10 | 3.63 | 90 | 93.63 |

An initial observation concluded that the increment of hydrophilicity of the membranes is not sufficient to increase the antifouling properties of the membranes. However, upon further literature readings, it was found that the concentration of humic acid used in this experiment (10 g/L) may be too high since a similar study [28] using polysulfone membrane used a much lower concentration of 0.2 g/L. The study found that blending and hydrophilicity do indeed increase the antifouling properties of polysulfone membranes. Another study [27] also used a low concentration of humic acid which is 1 g/L[27]. Hence, it can be concluded that irreversible fouling of the integral membranes in this study is inevitable due to the high concentration of humic acid prepared.

#### 2) *Removal of Mercury*

The integral membranes were tested for the removal of mercury to investigate the effects of hydrophilicity on mercury removal. Fig. 6 shows the permeate flux and percentage of mercury removed by the membranes. M1 was able to consistently remove 100% of the mercury throughout 60 minutes of filtration while M2 achieved removal of 70.57% during the first 15 minutes. Then, the value decreased to 69.21% before falling to 0%.

Theoretically, hydrophilicity increases the interaction between the metal and the membrane surface since hydroxyl groups in PVA can serve as chelating sites [29]. The hydrophilicity of M2 membrane may have a relationship with the membrane's ability to retain mercury.

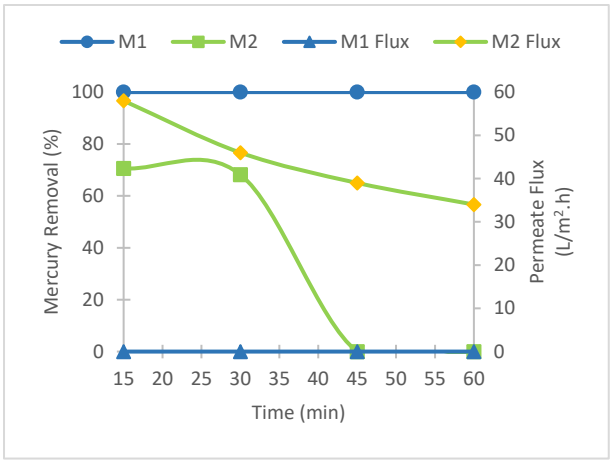


**Fig. 6. Permeate flux and percentage of mercury removed by the integral membranes.**

As seen in Fig. 6, M1 has a consistently low permeate flux of 0.0001 L/m$^2$h. This low and consistent flux enables the solute to be filtered and retained by the membrane during the whole 60 minutes. In comparison, the high permeation flux of M2 may have contributed to the escape of captured mercury by diffusion through the membrane pores.

## IV. CONCLUSION

Integral membranes consisting of PSf, PVA, and CS were successfully fabricated based on a v/v ratio. In addition, increment in wt% of PVA greatly enhanced the hydrophilicity of the integral membranes. This is evident from the water uptake and pure water fluxes of M1 and M2. M2, which contained more OH groups than M1, showed the highest water uptake and pure water flux which are 233% and 57.96 L/m$^2$h respectively. Aside from that, the integral membranes have increased thermal stabilities compared to pure PSf membrane. The weight loss of M2 during thermal analysis is the lowest compared to M1 and PSf. However, in terms of mercury removal, M1 showed superior ability than M2 due to the lower permeate flux which increased the retention ability of the membrane. Both integral membranes undergo irreversible fouling but this requires further study as the concentration of humic acid used in this research may be too high for performance testing. In short, the integral membranes exhibit better thermal stability and hydrophilicity compared to pure PSf membrane.

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