FABRICATION OF HIGHLY PERMEABLE THIN-FILM COMPOSITE FORWARD OSMOSIS MEMBRANE USING POLY-L-LYSINE AS AN ADDITIVE IN POLYSULFONE SUBSTRATE

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Abstract. Forward osmosis (FO) has received considerable interest for water and energy-related applications in recent years. However, FO has not been commercialized yet because of a few reasons. The lack of a high-performance FO membrane is one of the important barriers. To overcome this issue, a novel high-performance thin-film composite (TFC) membrane was successfully fabricated via interfacial polymerization with poly-l-lysine incorporated polysulfone substrate (PSf). Compared to the pristine PSf substrate, the incorporation of lysine (ranging 1 - 15 wt.%) meaningfully alternates the substrates chemical structure, porosity, contact angle, and morphology leading to an enhancement of the lysine -TFC membranes performance. The results showed that the new substrates with higher porosity, more hydrophilic, and smaller in pore size after the introduction of L-lysine. The membrane achieved the highest FO water flux at 15 % concentration of lysine and the maximum FO water flux was 35 L/m^2.h (LMH) with a comparable specific salt flux (J_s/J_w) of 0.002 g/L in the active layer facing the feed side (AL-FS) when 1M NaCl was applied as draw solution. The water flux was increased with increasing concentration of lysine. The addition of poly-L-Lysine in casting solution resulted in a more porous and hydrophilic support layer.

Keywords: thin-film composite, forward osmosis, poly-L-lysine, poly sulfone

Classification numbers: 2.9.4, 2.5.2

1. INTRODUCTION

Forward osmosis (FO) is a breakthrough technology that can be potentially used for concentrating solutions [1]. However, it is a relatively new technology that still has several major challenges. It is necessary to enhance the performance of FO membranes and their commercial viability. The lower water fluxes of the FO membrane compared to the established

membrane process such as reverse osmosis (RO) could be one of the major factors affecting its commercial viability.

A commercial thin-film composite (TFC) FO membrane is composed of a thin film layer (polyamide: PA) supported by a thick, dense, and tortuous support layer casted by phase inversion on a polyethylene terephthalate (PET) nonwoven layer [2]. These support layers hinder the compensation process, resulting in a decrease of the effective osmotic pressure at the interface and a decrease in the FO performance, this phenomenon is widely described as internal concentration polarization (ICP). During the FO process, both sides (selective layer and support layer) of the TFC membrane are simultaneously contacted with feed and draw solutions. The ideal support layer should be thin, highly porous, and low tortuosity to achieve desirable performance for the FO process. Moreover, the hydrophilicity of the substrates can eliminate the ICP, as well as the pore size of the support layer, which is an important parameter to enhance the FO performance.

Recent studies have demonstrated that synthesis matrix membrane formed by embedding porous materials in a polymeric matrix may significantly enhance membrane properties such as permeability, selectivity, stability, surface area, or catalytic activities in various membrane separation processes. For example, a zeolite-polyamide thin film nanocomposite membrane prepared on a polysulfone porous substrate tailored for forwarding osmosis shows a good performance in water flux and up to 50 % improvement over the TFC membrane. However, a further increase in zeolite loading led to a reduction in water permeability, possibly as a result of the formation of a thicker polyamide layer [3]. A new type of support layer of nanocomposite substrate was developed by incorporating titanium dioxide (TiO_2)/graphene oxide (GO) into polysulfone matrix by Sirinupong *et al.* [4]. The results showed that both surface hydrophilicity and roughness of PSF-based substrates were increased upon the incorporation of nanomaterials.

However, the incorporation of other nanomaterials such as silica particles, carbon nanotubes, and metal oxides has often resulted in surface defects that compromised the smooth formation and integrity of the PA active layer due to too thin dense skin layer of the membrane substrates [5]. Herein, to eliminate this obstacles, poly-L-lysine as an excellent material was embedded in PSf substate, aiming to introduce a novel and effective TFC-FO. L-Lysine is an alpha amino acid that can form proteins through the biosynthesis process. It is a hydrophilic and biocompatible material with a flexible main chain. Furthermore, the low cost of L-Lysine indicates that it can be used as an industrial additive [6]. Xu *et al.* also used L-lysine as an additive to polyamide layer to increase the water final permeability [6]. A review of literature indicates that, there are very few published studies available using poly-L-lysine as an additive in PSf substrate. To the best knowledge, poly-L-lysine incorporation into the substrates layer has never been investigated.

In this study, a high performance TFC FO membrane was fabricated by poly-L-lysine was used as an additive into the substrates PSf. These TFC FO membranes were designed to have much improved structural properties and its hydrophilicity in order to reduce ICP effects compared to the commercial CTA and TFC. The TFC FO were thoroughly characterized, tested in an FO system and critically compared with those of a commercial FO membrane.

2. MATERIAL AND METHODS

2.1. Materials

Polysulfone (average molecular weight of 35000 g.mol^{-1}, pelleted, Sigma-Aldrich) was used as a polymer for support layers, whereas 1-2-methyl-2-pyrrolidone (NMP, As One) was selected as a solvent to dissolve the polymer. 1,2-phenylenediamine (MPD, 99 % As One) and trimesoyl chloride (TMC, 98 % As One) were used as precursors of the polyamide layer which was developed on the support via interfacial polymerization (IP). n-Hexane (98 %, As One) solvent used for TMC dissolution, and sodium chloride (NaCl, As One) was used to prepare the draw solution in FO operation and salt permeability test. Poly-L-lysine (> 98 %) was purchased from Sigma-Aldrich. Deionized water was employed as feed solution.

2.2 Preparation of support layer

A traditional phase inversion technique was used to create all membrane substrates. A suitable amount of L-lysine (0 - 15 wt% based on the weight of the polymer) was dispersed in NMP to create the lysine integrated PES solution, which was then sonicated for 120 minutes. Table 1 displays the specific casting conditions for designed substrates. As a result, 10 wt% PES pellets were dissolved in lysine/NMP solution while being stirred at 60 ℃ for 24 hours. The casting solution was applied with an applicator onto a clean glass plate with a casting knife set at a gate height of 150 um. Weaved PET fabric mesh (07-105/52) was used to create lysine membrane with backing support. The casting film was placed right away in a bath of room-temperature DI water.

Table 1. Compositions of substrate solutions

Weight (g)	PSf hand cast	PSf-PLL-1	PSf-PLL-2	PSf-PLL-5	PSf-PLL-10	PSf-PLL-15
PSf	2	2	2	2	2	2
Poly-L-lysine	0	0.02	0.04	0.1	0.2	0.3
NMP	18	18	18	18	18	18

2.3 Preparation of TFC FO membranes by interfacial polymerization

The PA active layer formed with MPD and TMC monomers on the surface of the support membrane by IP process. The polyamide TFC membranes were produced by immersing the PSf in a MPD solution (2 wt.% MPD, 4wt.% CSA, 2 wt.% TEA) for 3 min. The excess MPD solution was removed from the membrane surface. A 0.15 wt.% TMC in n-hexane solution was then poured onto the support membrane for 1 min. The reaction of MPD and TMC at the interface resulted in the formation of an ultrathin polyamide rejection layer on the PSf support membrane. TFC membrane was then cured at 80°C in 10 min. Afterward, the TFC membranes were thoroughly rinsed and stored in DI water. The TFC membranes prepared from PSf hand cast, PSf-PLL-1, PSf-PLL-2, PSf-PLL-5, PSf-PLL-10, PSf-PLL-15 substrates were then denoted as TFC hand-cast, TFC- PLL-1, TFC- PLL-2, TFC- PLL-5, TFC- PLL-10 and TFC- PLL-15 respectively.

2.4 Characterization of the membrane substrates

Substrate membrane porosity (ε) (%) was measured as presented elsewhere [7]. After soaking the membrane substrates in water for 24 h, water on the membrane surface was carefully

removed using absorbent papers (Kimwipes, Kimberly Clark), and then the membrane sample were weighed (m_1, g). the same wet membranes were then dried in an oven at 50 °C for 24 h. The dried samples were weighed again (m_2, g) and to calculate value using Eq. 1 given the density water ($\rho_l = 1.00$ g.cm^{-3}) and PSf ($\rho_p = 1.24$ g.cm^{-3}) [8].

$$\varepsilon\left(\%\right) = \frac{\dfrac{m_1 - m_2}{\rho_1}}{\dfrac{m_1 - m_2}{\rho_1} + \dfrac{m_2}{\rho_p}} \times 100 \tag{1}$$

Top surface and cross section morphologies of the PSf substrate, TFC and TFC-PLL membranes were characterized by field emission scanning electron microscope (FE-SEM, JOEL JSM-7800F). All sample were dried in vacuum at room temperature for 24h, and coating with a uniform gold layer before observation in a sputter coater. Fourier transform infrared spectra of the PSf substrate, TFC and TFC-PLL membrane were recorded with Fourier transform infrared spectroscopy (FT-IR, JASCO FT/IR-4600). Sessile drop contact angles of air-dried membrane samples were measured using a contact angle goniometer (Kruss EasyDrop Goniometer, Hamburg, Germany). The data reported are the averages of 3 measurements.

2.5. Evaluation of TF FO membrane performances

The FO membrane test cell consists of two channels on each side of the membrane with an effective membrane area of 42 cm^2. The feed solution and draw solution were supplied on each channel using a gear pump under the co-current flow mode at a cross-flow velocity of 0.25L/min. DI water was used as a feed while 1M NaCl was used as draw solution. The FO water flux (J_w) was obtained by measuring the weight change of the draw solution according to the Eq:

$$J_w = \Delta V/(A_m\Delta t) = (\Delta m/\rho)/(A_m\Delta t) \tag{2}$$

where ΔV and Δm is the volume change and weight change of the draw solution over the operation time interval Δt, ρ is the density of the feed solution, and A_m is the effective membrane area. The reverse solute flux J_s (g/m^{2}h) was determined as [1]:

$$J_s = (C_tV_t - C_0V_0)/A_m\Delta t \tag{3}$$

where C_t and V_t are the permeated salt concentration (g/L) and the volume (L) of the feed solution measured are the time t (h), respectively. C_0 and V_0 are the initial concentration and the volume of the feed solution, respectively. In addition, the specific reverse salt flux and the permeated water flux (J_s/J_w, g/L) are defined as the respective amounts in the draw solute lost per liter of water.

3. RESULT AND DISCUSSION

3.1. Characteristics and performances of membrane substrates

Figure 1 shows porosity and contact angle measurements of the fabricated membrane substrates. It can be seen that the contact angle was decreased with the increase of L-lysine concentration. With respect to hydrophilicity, the lysine embedded PSF substrates exhibited lower water contact angle compared to the pristine PSf substate. The addition of L-lysine decreases the contact angle of the substrate layer when the dosage of L-lysine is 15 % wt%,

which suggests that its hydrophilicity is increased. To explain this finding, it can be assumed that the existence of carboxyl groups in the polysulfone matrix contributes more to the hydrophilic property. Due to the hydrogen bond interaction between water molecules and the selective layer, the presence of L-lysine enhances the hydrophilicity and decrease the contact angle. Figure 1 also reveals the porosity of the pristine and lysine PSf substrates. Generally, a membrane with high porosity is more favoured in FO process [6]. In addition, as shown in the SEM images, all membranes had a fully finger-like structure with interconnection pores. The membranes containing lysine exhibited high porous cross-section morphology (Fig. 2). As the result, a high porosity of about more than 80 % was obtained. Nevertheless, the higher lysine loading resulted in a less porous structure, as obtain for PSf-PLL-10, PSf-PLL-15 membrane.
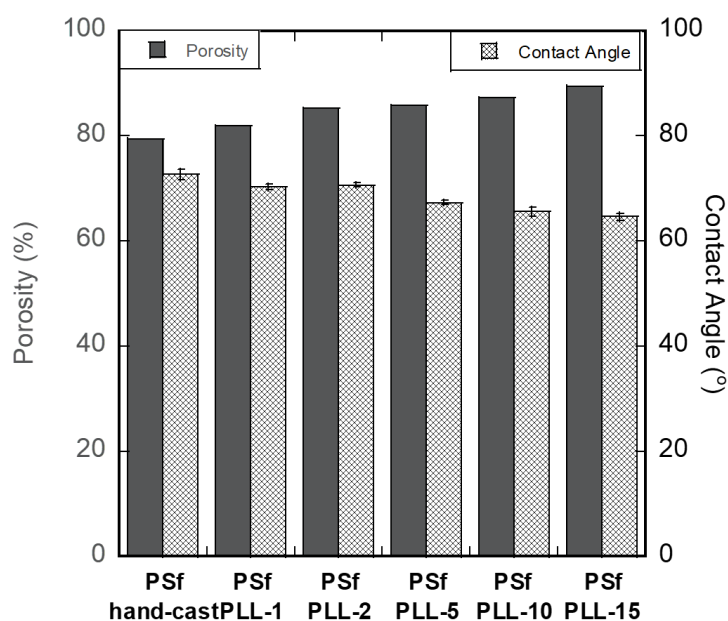

Figure 1. Porosity and contact angle of substrate membranes made of different lysine concentrations.

The SEM images (Fig. 2) show the structure of the top surface, cross-section, and bottom surface of the membrane substrates. The skin layer of all the membrane substrates is shown in Fig. 2a. It appears that the difference of pore sizes of the surface of the PSf including lysine and pristine PSf was insignificant. The pore size distribution (PSD) result presented in Fig. 3. It is observed that the pore size was ranged less than 10 nm and most of them was sized about 3 to 5 nm. As the result, the effect of concentration of lysine on the PSD on substrate was insignificant.

The finger-like cross-sectional structures with marco-voids for most Lysine membrane substrates are shown in Figs. 2a and 2b. These structures have large, opened pore diameters at the bottom of the cross-section for PSf and PSf-PLL substrates. In contrast to PSf-PLL substrates, which displayed nearly continuous finger-like voids, Psf hand-cast substrates exhibited the existence of sponge-like macro-voids coupled with finger-like voids. Lysine is probably to blame for the PSf-PLL substrates increased porosity and macro-void density. Additionally, the L-lysine that is included into the polymer solution makes it more thermodynamically incompatible with the solvent, which speeds up the phase inversion process and makes it easier to create more porous membrane substrates with finger-like structure [8].
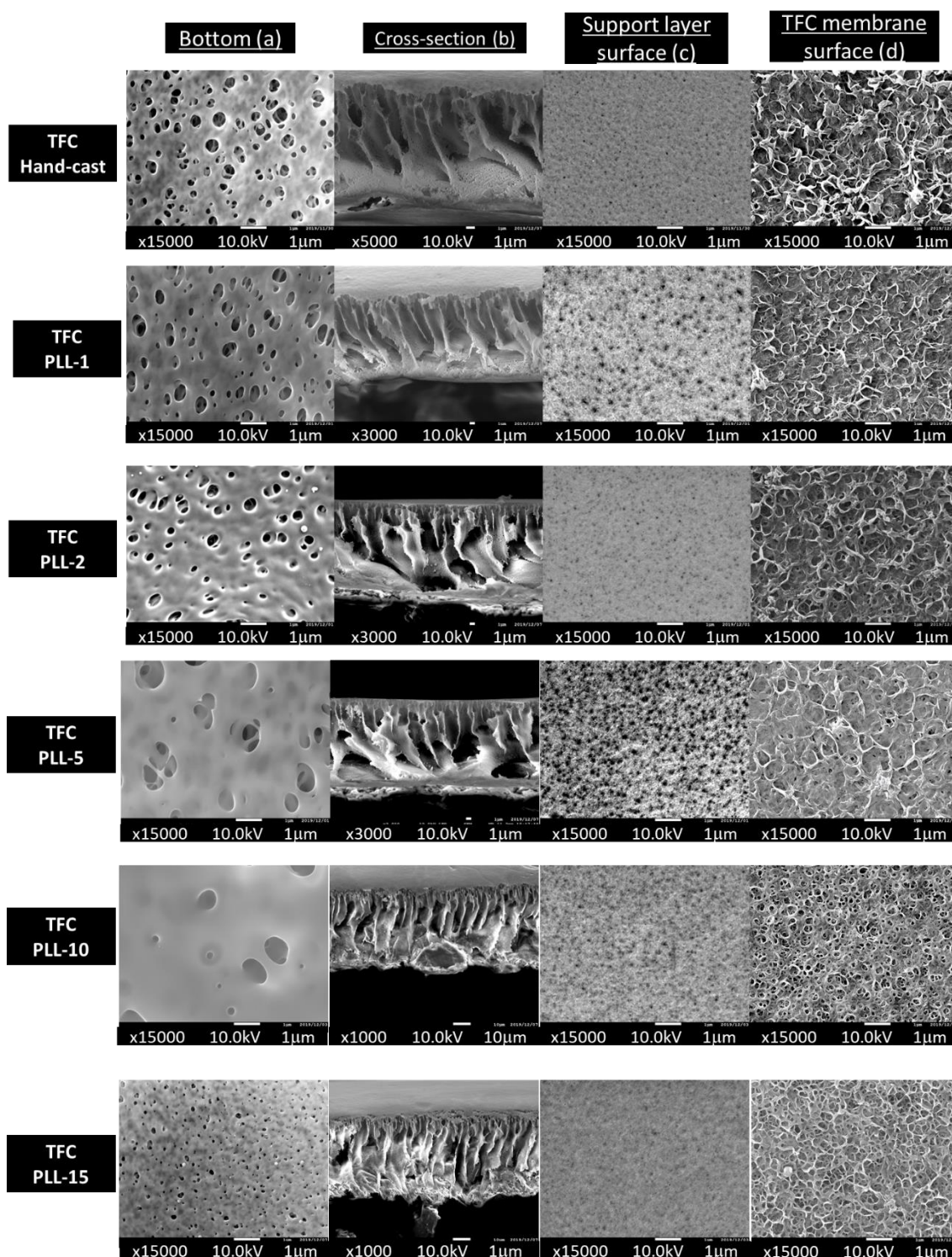
Figure 1. SEM image of top (a), cross section (b) and bottom (c) of PSf substrate and top of thin film composite membranes (d) prepared from different concentrations of poly-L-lysine.

Figure 2d displays FE-SEM images of the pristine TFC and TFC-PLL membranes-based lysine substrate. As shown, the polyamide layer (PA) was successfully formed on all the substrates and the ridge and valley of the PA can be observed. Small pore size plays an important role on the formation of the polyamide layer. A study of Li *et al.* (2012) pointed out small surface pores of the substrate facilitate simple convection at the interface during the interfacial reaction, produce nascent cross-linked films with small domain sizes, form a smoother and less dense structure, and reduce the possibility of defect formation [9]. A similar observation by Sharabati *et al.* (2019), they also explained that in small pores, where the aqueous phase is thin, migration of MPD is not expected to be governed by advection, but by diffusion causing nodular structures to be formed. The interfacial reaction produces a cross-linked film with small domain sizes, because diffusive transport processes do not favor the formation of larger polyamide structures. As a result, the TFC membrane surface is relatively smooth [10].
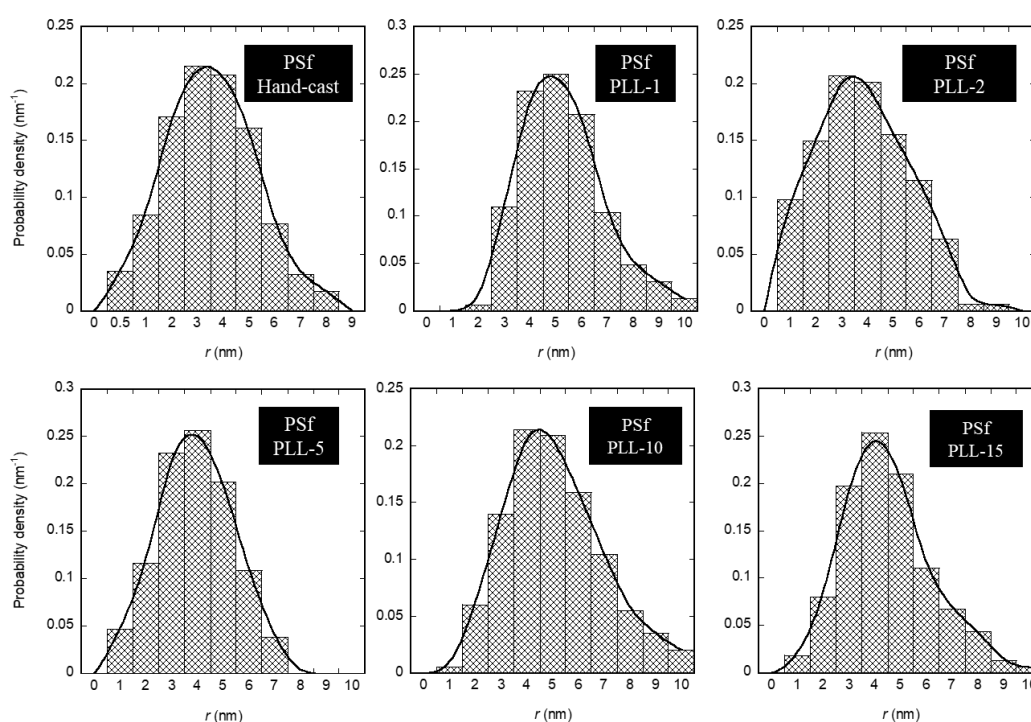

Figure 3. Pore size distribution of substrate membrane made of different concentration of poly-L-lysine.

3.2. ATR-FTIR spectra of TFC and TFC lysine membrane

The ATR-FTIR spectra of the PSf, TFC and TFC-PLL-5 membranes were presented. Figure 4 shows spectra ranged from 1800 cm^{-1} to 800 cm^{-1} for PSf substrate, TFC and TFC-PLL membrane. A comparison between the PSf spectrum and the TFC spectrum revealed the characteristic peaks of polyamide at 1663, 1609 and 1554 cm^{-1}, which can be assigned to the amide I band, the aromatic amide band and the amide II band, respectively. Obviously, the results revealed the vibrational bands of the polyamide layer at 1663, 1609 and 1541 cm^{-1} which are ascribed to amid I (C=O st., C-N st., and C-C-N deformation vibration), C=C ring st.

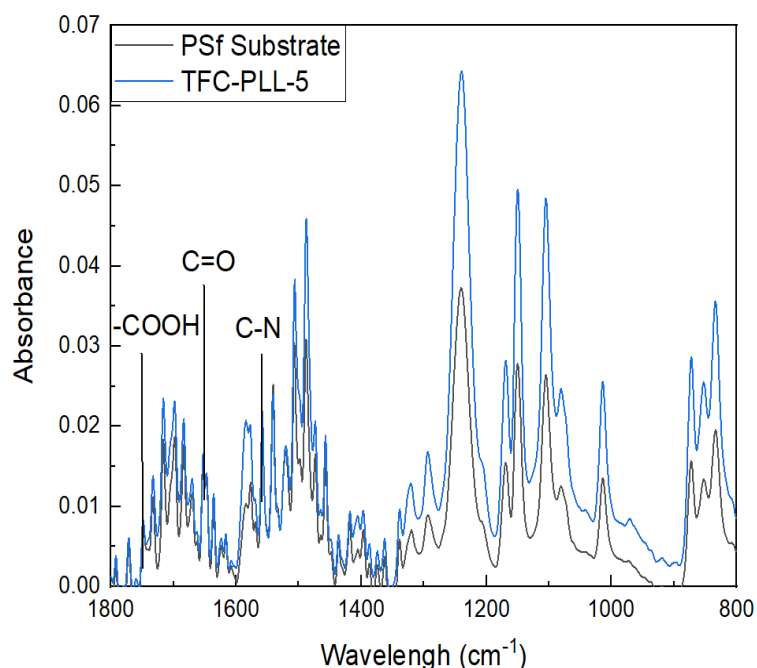vibration and amid II band, respectively. The band at 1584 cm^{-1} is the characteristic band for polysulfone.

Figure 4. FTIR spectra of PSf substrate and TFC-PLL-5.

3.3. Evaluation of TFC and TFC-lys membranes in FO system

The results of FO water flux and reverse salt flux to evaluate the fabricated membranes performance, are presented in Fig. 5.
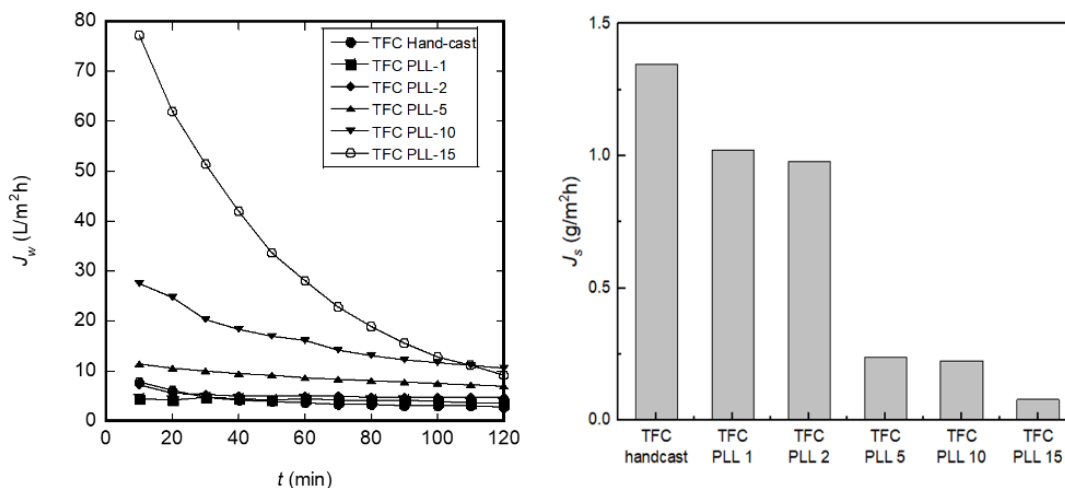

Figure 5. Water flux versus time for 2 hours experiment (a) and reverse solute flux of TFC membrane prepared from PSf substrate and PSf incorporated with different concentration of Poly-L-Lysine (1M NaCl as draw solution, DI water as Feed solution, pH 7).

Figure 5A displays the water flux of TFC and TFC-lys membranes in AL-FS mode with 1M NaCl as draw solution. It is clear to see that the control membrane TFC showed lowest water flux value. By the comparison, with increasing the loading of lysine in the substrates, the water flux increased to some extent of lysine. Interestingly, the highest water flux value of about 80 LMH was recorded for TFC-PLL-15 at first 10 minutes of experiment time. In the case of TFC-PLL-10 and TFC-PLL-15 membrane system, water flux was decreased dramatically because more diluted concentration of salt in draw solution. The water from lower osmosis pressure side always tends to pass through the membrane and dilute the more concentrated side where the osmosis pressure is higher. In the case of TFC-PLL-15, the larger amount of water was obtained in draw solution side. As the result, osmotic pressure was dramatically decreased in draw solution side.

On the other hand, the reverse salt fluxes of the TFC and TFC-lys membrane, in Figure 5b displayed that the reverse fluxes decrease with increasing the concentration of lysine. It should be noted that Na ion from draw solution was hindered by larger different osmotic pressure between two sides. Moreover, these ions found difficult to transfer from draw solution side to feed solution side because of prevention by migration of water molecule through membrane pore from feed solution side. In addition, the pore size of membrane might be smaller by increasing of concentration of lysine. As the result, the relationship between the water flux and the specific flux was observed in Fig. 6.
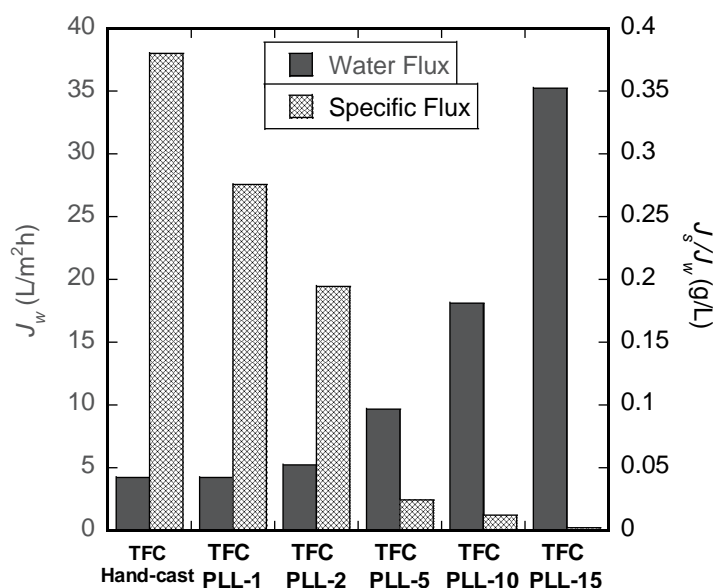

Figure 6. Water flux and specific flux of TFC hand cast and TFC membrane prepared from PSf substrate and PSf incorporated with different concentration of poly-L-lysine (1 M NaCl as draw solution, DI water as feed solution, pH 7).

The specific reverse flux showed a decreasing pattern by increasing of concentration of poly-L-lysine, and this value was strongly affected by ratio of reverse flux and water flux. It is clear that increase the hydrophilicity and decreased the substrate resistance to the draw solution flow. The water flux was increased with increase of concentration of poly-L-lysine. The addition of lysine increased the porosity of the membrane as it increases the macro-void and reduce the

thickness of the walls, thus increasing the permeability of the membrane. Canon *et al.* (2007) found that the amino acid acts both as a proton donor and a proton acceptor because of its carbonyl and hydroxyl groups [11]. It was also noted that the hydrophilic nature of acid amino helped to form larger, longer pores and macro-voids. Moreover, the presence of hydrophilic lysine in the dope solution facilitates water diffusion to the polymer cast film, causing faster solvent (NMP) and non-solvent (water) exchange rate during phase inversion process and leads to formation long finger-like voids which could be observed in morphology of much lysine concentration based substrates [4]. The similar discussion by Obaid *et al.* (2018) revealed that an increase of the hydrophilicity of the substrates and decrease of the structure parameter, prompted the passing of draw solution through the substrates to the inner side of the PA layer, to pull the water molecules of the feed through the PA layer [12]. Additionally, as substrate resistance to DS flow decreases due to an increase in hydrophilicity and a decrease in structure parameter value (improving the compensation process), there is an increase in the osmotic pressure difference across the PA layer, which lowers the ICP and improves the performance of the FO membranes [13, 14].

CRediT authorship contribution statement. Author 1: Methodology, Investigation, and Writing – original Draft. Author 2, 3: Investigation, Formal Analysis. Author 4 and Author 5: Methodology, Supervision and Writing - Review & Editing.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

4. CONCLUSIONS

In this study, TFC-PLL membrane based on the PSf-PLL substrate were successfully fabricated. The characterization results display that the Poly-L-Lysine well incorporated with PSf and the fabricated amino acid substrate showed an excellent porosity and high hydrophilicity. Moreover, the increase of lysine loading resulted in enhancing the support parameter and the selective properties of TFC-PLL substrates. The result showed that the TFC-PLL-15 membrane possesses one of the highest porosity and lowest contact angle reported in the literature. As a result, the membrane revealed the highest water permeability as well an excellent FO water flux. Compared with TFC membrane, the TFC-PLL membrane is potentially more favorable during the application of treating feed solutions with relative higher salinity water under AL-FS orientation. This study provides an additional dimension as well as new opportunities for optimizing and improving FO membrane performance, which deserves further attention from the FO research community.

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