Investigation towards salt rejection performance on thin film composite membrane prepared through single layer method and layer by layer method

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Abstract. Forward osmosis (FO) membrane has becomes a promising membrane technology due to its lower energy consumption and high salt rejection performance. However, in prolong application, FO membrane is susceptible to internal concentration polymerization (ICP) that reduce water flux through the membrane. Therefore, layer by layer (LbL) method was proposed to improve the FO performance. This study focused on the effect of fabrication method to cast thin film composite (TFC) membrane using SL method and LbL method. The membranes were prepared using interfacial polymerization technique and tested through salt rejection experiment. Theoretically, LbL method should provide high salt rejection value as it is good at controlling the structures and thickness compare to SL method. However, from the testing, the results showed that the salt rejection value of TFC membrane using SL technique is higher (97.17%) compared to LbL technique (73.33%). Thus, it is suggested, co-casting method should be used towards the TFC membrane for future studies due to its advantageous over SL and LbL method.

1. Introduction
In recent years, overpopulation had become the main factor that causes water supplies to plunge worldwide [1]. The human body use water to help regulate its temperature and maintain other body function [2]. According to S. Zhao et al., [3], they reported that more than 1.2 billion people in this world have lack of access to clean and safe drinking water. Besides, W. Xu et al., [4] verified that more than 80% illness in developing countries are caused by unsafe drinking water and insufficient water supply. Hence, a solution was found in the form of reclaimed saline water [5].
Desalination is the process of removing salt from the water and their commercial proven technologies can be categorized into two which are thermal processes and membrane processes [6]. Thermal desalination often termed as distillation and it required a large input of energy to heat the water until it reaches the evaporation state. The salt is left while the vapor is condensed to produce fresh water [6]. The second categories which is membrane desalination also plays an important role in this field as it provides high quality of water as well as it minimizes the secondary pollution. Microfiltration, nanofiltration, reverse osmosis (RO) and are the examples of membrane processes. Among them, RO had been the major option for the desalination process in order to produce high quality of water [7].

Generally, RO is a process that requires internal hydraulic pressure to flow water through semipermeable membrane from high concentration of solute to low concentration of solute [8]. However, the need for RO to have more energy in order to flow the water leads it to have high degree of membrane fouling. Therefore, forward osmosis (FO) is the alternative way of substituting the RO processing as it requires low hydraulic pressure and it produce lesser degree of fouling. RO and FO can be differed by its driving forces which RO utilize external pressure while FO optimize its driving force by the presence of osmotic pressure [9].

Among the membrane developed for FO applications, thin film composites (TFC) membranes consisting of a polyamide (PA) selective layer on a top of polysulfone (PSf) porous support have proven to be a promising choice for high performance FO membrane owing to their excellent selectivity properties [10].

Nevertheless, long term application of FO membrane has shown decreasing water flux performance due to severe internal concentration polarization (ICP) or solute build up in the membrane structure [11]. ICP generates large boundary layer within the support layer that affects membrane performance [12]. One of the approaches to minimize ICP rate in FO membrane is to improve the structural properties of the membrane substrate [13]. Previous work by Emadzadeh et al., has incorporated inorganic nanoparticles titanium dioxide (TiO$_2$) into the membrane substrate to improve the membrane substrate [9]. TiO$_2$ was chosen due to its properties of super hydrophilic surface, good chemical stability and their effect towards porosity of the membranes [14].

However, it was also reported by Emadzadeh et al., that excessive loading of the nanoparticles content into the substrate leads to increase the reversed solute flux and decrease selectivity ability of the membrane [9]. These behaviours may attribute to the changes of the substrate surface morphology that was affected by the nanoparticles content. By having a more distorted surface, the PA layer structural integrity may have been compromised [9], [15]–[17].

Previous work by Xiao Liu & Ng, reported that dual layer substrate was used to create a porous bottom layer substrate consisting of a silica nanoparticle and a top virgin substrate layer with smooth surface morphology for PA layer deposition. The dual layer membrane demonstrated increased water flux compare to the single layer membrane, without compromising on the reserve salt flux [18]. Therefore, dual layer substrate is shown to be a good approach to minimize the effect of nanoparticles loading into the membrane substrate.

A technique called layer by layer (LbL) have been introduced as a method for fabricating dual layer substrate for FO membranes [19], [20]. Instead of using single layer (SL) method, previous work has shown that LbL is better at controlling the membrane structures and thickness [19]. Over the past few years, LbL which involve cationic and anionic nanostructures become the most promising method for desalination process as it requires few simple steps to cast it and it is environmentally friendly [19]. Additionally, Husaini et al., [20] claims that LbL method has potential in improving the FO membrane performance.

Therefore, the main objective of this study is to observe the salt rejection performance between the membrane prepared through SL technique and LbL method.
2. Methodology
2.1 Materials
The materials used for the experiments were based from previous research works that related to TFC membranes in FO process [9], [21]. Polyvinylpyrrolidone (PVP), N-methyl-2-pyrrolidone (NMP) and PSf used for fabrication of the membrane substrate. 1, 3-Phenylenediamine (MPD) and trimesoyl chloride (TMC) were chemical compound for create the PA layer for the membrane. TiO$_2$ was used for modifying the membrane properties due to its features. The process flow chart of this study is shown below in Figure 1.

![Figure 1. Research flowchart.](image)

2.2 Dope Preparation
The steps to prepare the dope solutions were taken from other previous studies [9], [21]. Initially for the first dope solution, PVP, NMP and PSf was weighted where PVP 0.5 wt%, NMP 84.5 %, PSf 15.0% and mixed. Then, the second solution were mixed with TiO$_2$ nanoparticles in ratio of PVP 0.5 wt%, TiO2 0.05 wt%, PSf 8 wt% and NMP 91.45 wt% and mixed together. The solutions were left to mix for 24 hours at room temperature to ensure the PSf fully dissolved in both dope solutions [19].

2.3 Membrane Casting Single Layer (SL)
Membrane casting methods from previous work by Emadzadeh et al., was referred to cast the SL substrate [9]. At first, the 15 wt% PSf solution was poured on a glass plane and rolled downwards with a glass rod to cast the support layer. Then, the layer was submerged in a basin filled with tap water to form the substrate. The layer was left for over 24 hours to ensure full removal of all impurity in the substrates especially residual solvent.

2.4 Membrane Casting Layer by Layer (LbL)
The LbL technique to cast the membrane were referred to works by Husaini et al, and Xu et al, [19], [20]. Initially, the 8 wt% PSf solution was poured on a glass plane and rolled downwards with a glass rod to cast the substrate layer. Then, the layer was submerged in a basin filled with tap water to form the first substrate layer. The first layer that had been casted was dried using a rubber roller. The second layer of 15 wt% PSF solution was then casted on the dried first layer. Both substrates then were submerged into a water bath and were left for 24 hours to ensure complete solvent removal from the membrane.

2.5 Polyamide (PA) layer Interfacial Polymerization
The SL substrate was first dried using a rubber roller. Afterward, 50 ml of MPD and RO water solution was poured onto the PSf substrate surface and left on the surface for 1 minute to ensure the solution penetrate the substrate layer. The MPD and RO solution then was drained off and a rubber roller was used to remove the remaining residue. Then, 50 ml of TMC and n-Hexane solution was poured on the substrate layer and left to maintain for 1 minute. After 1 min, the TMC and n-Hexane solution was drained off from the substrate surface and any remaining residue. The membrane then was put in an oven for 5 min to be dried before being submerged into water bath for 24 hours until the membranes were tested [10]. The same steps were repeated for the LbL substrate.

2.6 Salt Rejection Testing
The SL membrane was cut into a circle shape and installed at the base part of the testing before RO water was filled into the testing unit. The pressure was set at 16 bar to simulate high pressure condition.
The permeate solution conductivity was taken after 30 minutes duration using conductivity meter (Mettler-Toledo) and the salt rejection value of the permeate was analysed [9]. These steps were repeated for the LbL membrane.

3. Result & Discussion

Table 1 below shows the permeate solution conductivity and salt rejection value between membranes fabricated through SL method and LbL method. The salt rejection value of membranes prepared through SL method was an average of 97.17%. Based on research review from Chen et al., [23], this result shows that SL membrane have a good salt rejection performance. The salt rejection value by the LbL membranes was recorded an average of 73.33%. Kwon et al., [24] reported that in their works, membrane prepared through the LbL method also recorded salt rejection value around 70.0 %. From their study, the low percentage of salt rejection value for LbL due to lose structure of the substrate layer. This is probably due to the structure of the substrate layer that was not properly adhere to each other when the casting of second layer on the top of the first layer and consequently leads to the failure of LbL fabricated membrane [24]. Another factor that may contributes to lower percentage of salt rejection in LbL membrane is the membrane does not form a smooth surface compare to SL membrane which can be observed in figure 1. This characteristic may affect the PA layer structure making it less selective resulting in lower salt rejection value [9]. From the previous study by Xiao Liu & Ng [18], the salt rejection was higher when the membrane dual layer substrate was produced by co-casting method. Therefore, in order to overcome this setback, it is proposed, co-casting method to be used in fabrication of dual layer membranes for future research works.

| Method                                    | Single Layer (SL) | Layer by Layer (LbL) |
|-------------------------------------------|------------------|----------------------|
| Membrane samples                          | Sample 1 | Sample 2 | Sample 3 | Sample 1 | Sample 2 | Sample 3 |
| Feed solution conductivity (µS)           | 3830.0   | 3790.0   | 3920.0   | 4030.0   | 3000.0   | 3423.1   |
| Permeate conductivity (µS)                | 113.1    | 132.65   | 78.4     | 960.0    | 900.0    | 890.0    |
| Salt rejection (%)                        | 97.0     | 96.5     | 98.0     | 76.0     | 70.0     | 74.0     |
| Average salt rejection (%)                | 97.17    |          |          |          |          | 73.33    |
Figure 2. Image of SL membrane (left) and LbL membrane (right)

4. Conclusion and recommendations
In this study, TFC membrane were successfully fabricated using two different method which are SL method and LbL method to observe their salt rejection performance. Based on previous research review made by Xu et al., [19] they showed that membrane produced by LbL will obtain higher percentage of salt rejection compare to SL. However, in this study, the salt rejection value recorded was less than expected. This can be contributed to the factor of the fabrication method whereby the substrates were not fully adhered between each other. For the future studies, it is recommended to use co-casting method to fabricate the membrane as it is a one-step non solvent technique resulting in greater adhesion between the substrate layer [18].

Acknowledgement
The authors are grateful for the technical supports and the equipment provided by UiTM Pasir Gudang and Advanced Membrane Technology Research Centre (AMTEC), University Teknologi Malaysia.

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