

Article

# Dopamine Incorporated Forward Osmosis Membranes with High Structural Stability and Chlorine Resistance

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**Abstract:** The degradation and detachment of the polyamide (PA) layer in thin-film composite (TFC) membranes due to chlorine based chemical cleaning and material difference of PA layer and substrate are two major bottlenecks of forward osmosis (FO) technology. In this study, a new type of FO membranes were prepared by controlling self-polymerization of dopamine (DA) in the aqueous phase and the reaction with trimesoyl chloride (TMC) during interfacial polymerization (IP) process. These membranes were characterized by attenuated total reflection Fourier transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FESEM) and water contact angle measurements. The influence of synthesis parameters such as pH of the aqueous phase, reaction time, temperature, and monomer concentrations were systematically investigated. The optimized membrane showed enhanced structure stability in ethanol (7.1 times higher) and chlorine resistance (72.3 times higher) than the conventional Piperazine(PIP)/TMC membrane due to (poly-dopamine) PDA bio-adhesion and polyester groups in the membrane structure. In general, DA/TMC membranes could be an effective strategy to fabricate high-performance FO membranes with excellent structural stability and chlorine resistance.

**Keywords:** forward osmosis; thin-film composite; dopamine; interfacial polymerization; structural stability; chlorine resistance.

## 1. Introduction

In recent years, FO has attracted increasing interest in desalination<sup>1-3</sup>, wastewater treatment<sup>4-5</sup>, osmotic membrane bioreactors<sup>6-7</sup>, fertilizers<sup>8-9</sup> and power generation<sup>10-11</sup>, as a potential low-energy and more environmentally friendly technology<sup>12</sup>. Forward osmosis (FO) is a natural process that drives water molecules across a semi-permeable membrane from the feed solution (with a low osmotic pressure) to the draw solution (with a high osmotic pressure). Thin-film composite polyamide (TFC-PA) membranes consisting of an active PA layer and a porous substrate layer have been widely investigated for FO due to their excellent separation capability, wide range pH tolerance and independently tailorable support layer and active layer properties<sup>13-16</sup>.

Generally, the thin active polyamide (PA) layer is obtained by interfacial polymerization over the support layer by two monomers with amino groups and acid chloride groups<sup>17</sup>. In order to meet the crosslinking and mechanical properties of the PA layer, at least one selected monomer must have more than two functional groups as well as an aromatic compound<sup>18</sup>. The concentration of the monomers, the reaction time and temperature of the interfacial polymerization can all affect the separation performance of the membrane<sup>15</sup>. However, if the conventional TFC membranes are used in severe conditions containing organic solvents like ethanol, the active layer could be easily detached from the substrate, since there is no strong linkage between the PA layer and porous substrate. So the

membrane structural stability should be taken into serious consideration for more practical membrane separation applications. Apart from the membrane structural stability, membrane chlorine resistance is also a bottleneck for TFC-PA membrane applications. This is because membrane fouling is inevitable in the FO process, for example, in biological fouling it is the main cause of decreasing membrane performance<sup>5, 13, 19</sup>. Therefore, membrane cleaning with oxidizing agents to control membrane biofouling is also needed in FO applications. However, the antioxidant ability of the conventional PA layer is poor, and its polymer chain structure is easily degraded by active chlorine and consequently bring a significantly reduced membrane separation performance<sup>20-21</sup>. Hence, TFC-PA membranes with improved structural stability and chlorine resistance are highly desirable.

In recent years, mussel-inspired dopamine (DA) or polydopamine (PDA) chemistry, has shown a new route for the fabrication of high-performance membranes. PDA with adhesive proteins have been used to improve fouling resistance of ultrafiltration (UF)<sup>22</sup> and RO membranes<sup>23</sup>, by forming surface-adherent films onto either the selective layer or the support layer to increase hydrophilic property of membranes. Han *et al.*[16] first designed time-different PDA coated substrates for FO membrane synthesis and found that FO membrane based on 1 h-PDA-coated substrate showed the best FO performance. Inspired by Han's work, Huang *et al.*<sup>24</sup> prepared three kinds of substrates (PDA coated on top, bottom and dual surface substrate, respectively) with PDA for 1 h before the formation of TFC membranes, observing a reduction of reverse solute flux for the PDA coated top surface membranes. Very recently, Guo *et al.*<sup>25</sup> proved that only 0.5 h coating was enough for PDA deposition and modification on the PA active layer, which would enhance FO membrane selectivity as well as anti-fouling property.

Inspired by these works, DA was first explored as a sole monomer in aqueous phase to prepare thin film composite membranes by interfacial polymerization in FO membrane synthesis. The amine and phenol groups in DA, and the catechol groups of PDA in the aqueous phase<sup>26-27</sup> can all react with acyl chloride groups of trimesoylchloride (TMC) in the organic phase to obtain a new type of thin film active layer for separation applications, which is strongly adhered to the top of the polysulfone substrate. At the same time, the novel active layer, with ester bonds formed by DA/TMC, is much more stable than the amide bonds of the PA layer when exposed to solutions with active chloride. State-of-the-art characterization techniques including attenuated total reflection Fourier transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and field-emission scanning electron microscope (FESEM), were applied to characterize the as-prepared membranes. This study offers significant insights into developing high-performance FO membranes by exploring the relationship between the self-polymerization of dopamine in aqueous phase and FO performance.

## 2. Materials and Methods

### 2.1. Materials

Polysulfone (PSf, average molecular weight (MW) ~ 22 kDa, Sigma-Aldrich, USA), polyvinylpyrrolidone (PVP, average MW ~10 kDa, Sigma Aldrich, USA), 1-methyl-2-pyrrolidinone (ACI Labscan, Thailand), 1-methyl-2-pyrrolidinone (NMP, 99%, RCI LABSCAN LIMITED, Thailand), 1, 3, 5-Benzenetricarbonyl chloride (TMC, Alfa Aesar®, England, 98%) were dispersed in hexane (Univar, Redmond, WA) and dopamine hydrochloride (International Laboratory, USA, 99%). For membrane performance tests, Magnesium chloride (MgCl<sub>2</sub>, ACS reagent) was dissolved in deionized water (DI) obtained from a Milli-Q ultra pure water purification system (Millipore, Billerica, MA). For membrane structural stability and chlorine resistance tests, ethanol (ACS, EMSURE®, Germany) and sodium hypochlorite (NaClO) solution (Chem Supply Pty Ltd, Australia) with 8 - 12.5 % available chlorine were used, respectively.

### 2.2. Preparation of polysulfone substrates

The porous polysulfone membrane substrate was fabricated via the phase inversion method using a PSf-PVP mixed casting solution. To prepare the casting solution, a mixture containing 15 g

PSf, 8 g PVP and 77 g NMP was magnetically stirred for 24 h and then left standing for approximately 12 h at room temperature for degassing<sup>28-29</sup>. The prepared casting solution was first cast onto a clean and smooth glass plate using a membrane casting knife (RK Print Coat Instruments Ltd., UK) with controlled wet film thickness ( $195 \pm 10 \mu\text{m}$ ), and then exposed to air for approximately 10 s before it immersion in a 60 °C DI water bath for 30 min to initiate the phase inversion process. Next, the membrane was removed from the water bath, thoroughly rinsed with Milli-Q water and then transferred into a 4 °C DI water bath for storage and later use.

### 2.3. Preparation of thin film composite (TFC) membranes

The TFC composite membranes were prepared via interfacial polymerization between the mixed-amine (DA and PDA) solution and TMC on the surface of the PSf substrates prepared as below. Specifically, a series of dopamine-containing solutions were prepared by mixing phosphate buffered solution (PBS) with different concentrations of dopamine (0.10, 0.30, 0.50 wt%). The PSf substrate was first immersed in the prepared solution for 30 min to ensure complete soaking and appropriate self-polymerization of DA<sup>30</sup>. The excess solution was removed with an air-knife (Cincinnati, Ohio USA) within 30 s. The substrate was then dipped into TMC solution (0.15 wt% in hexane) for 60 s, to initiate interfacial polymerization. Next, the substrate was removed from the hexane organic phase and set vertically for 2 min to evaporate excess organic solution. Afterwards, a dry curing process was performed by placing the as-prepared TFC membrane into an oven at 90 °C for 5 min. Finally, the obtained composite membranes were washed and stored in 4 °C DI water until testing. The resultant membranes were denoted as M-1, M-2 and M-3, containing 0.10, 0.30 and 0.50 wt% of DA in the aqueous phase, respectively. For comparison, a conventional TFC-PA membrane formed by piperazine/TMC (denoted as M-0) was also prepared as the control membrane.

### 2.4. Membrane characterizations

The morphology of the membrane surfaces was observed by FESEM (Merlin ZEISS GEMINI2) operating at 5 kV and a working distance of 6.5-7.0 mm. Surface chemistry of the active layers was determined by XPS (ESCALab220IXL, VG Scientific Company Ltd., England) with an Al/K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) anode mono X-ray source. Water contact angles were measured using a static sessile drop contact angle system (DataphysicsOCA20) by placing a 2  $\mu\text{L}$  droplet on a dried membrane surface. For each membrane, 10 measurements were performed. The functional groups of the membranes were analysed using ATR-FTIR spectroscopy instrument (Thermo Scientific Nicolet 6700).

### 2.5. FO performance tests

FO performance experiments were conducted using a lab-scale filtration unit with an effective membrane area of about 42.0 cm<sup>2</sup>. A commercial PTFE cell (CF042-FO, Sterlitech Co.) was used to hold the membrane, having two rectangular channels with dimensions of 92.1 mm in length, 45.7 mm in width and 2.3 mm in depth. Co-current cross-flow mode was selected and the flow velocities were 4.9 cm s<sup>-1</sup> for both the feed and draw solutions. The temperatures of the feed and draw solutions were controlled at  $20 \pm 0.5 \text{ }^\circ\text{C}$ . 1 M of MgCl<sub>2</sub> solution was used as the draw solution and a digital balance was connected a computer to monitor weight change of the permeated water at 30 s intervals (ML4002, METTLER TOLEDO). DI water was used as the feed solution and a conductivity meter (Con 110, Oakton Instruments) was used to monitor the conductivity change at 60 s intervals for calculating the reverse solute flux of the membrane. Membranes were tested under two different modes: active layer facing draw solution (AL-DS) mode, and active layer facing feed solution (AL-FS) mode. Each test was conducted for 60 min in triplicate.

The water permeation flux ( $J_w$ ) (L m<sup>-2</sup> h<sup>-1</sup>, LMH) was calculated by the following equation:

$$J_w = \frac{\Delta w}{\rho_m e t} \quad (1)$$

where  $\Delta w$  (kg) is the mass change of the draw solution over a period time  $t$  (h),  $\rho$  is the density of water (kg L<sup>-1</sup>) and  $m_e$  is the effective membrane area (m<sup>2</sup>).

The reverse solute flux, ( $J_s$ ) ( $\text{g m}^{-2} \text{h}^{-1}$ ), salt leakage or reverse diffusion from the draw solution to the feed solution, is an important parameter in FO determined by the increase of the feed solution conductivity.

$$J_s = \frac{\Delta C_f V_f}{m_{ef}}$$

where  $\Delta C_f$  and  $V_f$  are the change of concentration and volume of the feed solution at the end of FO experiment, respectively.

The specific reverse solute flux ( $\text{g/L}$ ), which means the ratio of reverse solute flux/water flux ( $J_s/J_w$ ) ratio, is also calculated to measure the selectivity of the resultant TFC membranes.

## 2.6. Evaluation of structural stability and chlorine resistance

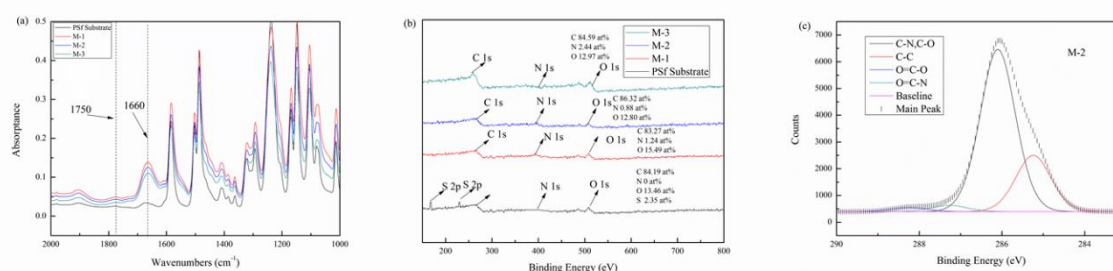
The structural stability of membranes was studied by immersing the prepared TFC membranes in ethanol for a fixed period. Chlorine resistance of the as-prepared membranes was evaluated by exposing the membrane surfaces to 1000 ppm NaClO solution over different periods at room temperature. To maintain the constant concentration of NaClO during the experiment, the container of NaClO solution was kept in darkness and NaClO solution was replaced every 24 h. Before the membrane testing, the FO membranes were removed from ethanol or NaClO and washed thoroughly with DI water for 3 times to avoid the residual chlorine and ethanol swelling during performance tests.

## 3. Results and discussion

### 3.1. Membrane Surface Characterization

#### 3.1.1. Membrane Surface Chemistry

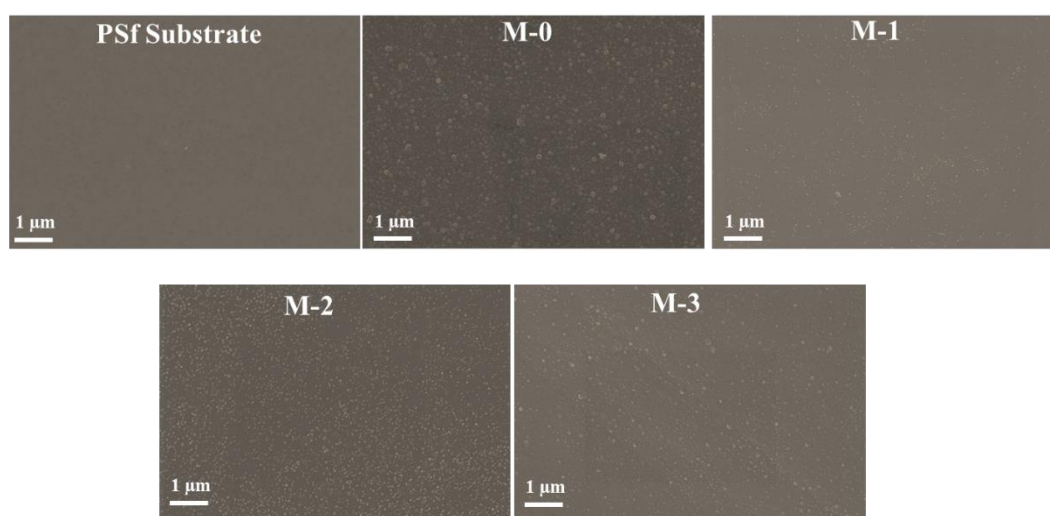
It is well known that TFC membrane possesses a dense and thin layer on top of the substrate, which is critical for high membrane water flux and salt rejection<sup>31</sup>. In this study, ATR-FTIR and XPS analysis were utilised to confirm the reaction between DA/PDA and TMC, and the formation of these thin layers. The ATR-FTIR spectra for PSf-substrate, M-1, M-2 and M-3 are presented **Figure 1a**. It is clear that, apart from the bands of the PSf substrates, the DA/TMC TFC series membranes showed enhanced peaks at  $1660 \text{ cm}^{-1}$  and additional peaks at  $1750 \text{ cm}^{-1}$ , which are attributed to the C=O stretching in amide bonds and C=O breathing in ester bonds, respectively. These characteristic bands indicated that the DA/TMC thin film active layers were obtained successfully onto the top of the PSf substrates. Moreover, nitrogen was detected by XPS on the DA/TMC membrane surfaces (**Figure 1b**), which further confirmed the existence of the DA/PDA on the top of substrates since amine groups were the exclusive N source<sup>16</sup>. High-Resolution XPS spectrum C 1s spectra of the M-2 surface is also shown in **Figure 1c**, the peaks at bonding energies of 285.2, 286.1, 287.4 and 288.2 eV can be attributed to the C-C, C-N and C-O, O=C-N and O=C-N functional groups, respectively. presence of 287.4 and 288.2 eV peaks further confirmed the formation of ester and amide groups which are resulted from the reaction between the catechol of PDA (or phenolic hydroxyl and amine groups in DA) and acyl chloride in TMC monomers. Based on ATR-FTIR and XPS analysis results, the formation of additional PA layers on the top of PSf substrates has been successful.



**Figure 1.** (a) ATR-FTIR spectra of PSf substrate, M-1, M-2 and M-3; (b) XPS spectra of the M-1, M-2 and M-3 membrane surface and (c) High-Resolution XPS spectrum C 1s spectra of M-2 surface.

### 3.1.2. Membrane Surface Morphology

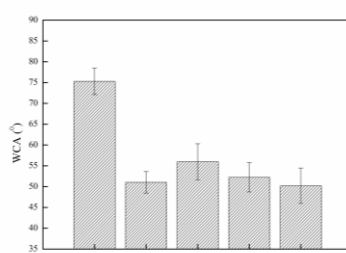
**Figure 2** shows the SEM images of the as-prepared membranes. It is clear that the surface of the PSf substrate was smooth. As for the PIP/TMC conventional TFC-PA (M-0), a typical “valley and peak” structure was found, confirming the formation of polyamide, which is similar to Dong et al.’s work<sup>28</sup>. As for the DA/TMC membrane surface (M-1, M-2, and M-3), nodular structures on membrane surfaces were found in the SEM images. When the DA concentration was low (0.1 wt %) in the aqueous phase, a relatively smooth surface with small and random specks could be found. As the DA concentration increased to 0.3 wt% (M-2), the appearance of these specks became more uniform and frequent, resulting in a rougher surface these imperfections/pass ways could be beneficial for enhancing water molecules transfer. However, when the DA concentration was increased to 0.5 wt% (M-3), agglomeration was clearly observed, which may reduce the membrane rejection.



**Figure 2.** SEM images of PSf substrate, M-0, M-1, M-2 and M-3 membrane surface.

### 3.1.3. Membrane Surface Hydrophilicity

It is expected that the introduction of DA and PDA with abundant amine and hydroxyl groups would result in an increased surface hydrophilicity, which has been confirmed by the water contact angle analysis (**Figure 3**). Water contact angle is a classical measurement to test the wettability of membrane surfaces: the lower the water contact angle, the easier for water to wet the membrane surface and the higher the hydrophilicity. The water contact angle of the PSf substrate was relatively high at 75.3°. The water contact angle of the conventional membrane (M-0) was 51.0°, which is similar to Mohsen et al.’s work<sup>32</sup>. For the DA/TMC membranes with different DA concentrations, the water contact angles slightly decreased from 55.9° to 50.2° when the DA concentration in aqueous phase was increased from 0.1 wt% to 0.5 wt%. These results indicate that the DA concentrations in the aqueous phase had slight positive influence on the membrane surface hydrophilicity.



**Figure 3.** Water contact angles of PSf substrate, M-0, M-1, M-2 and M-3.

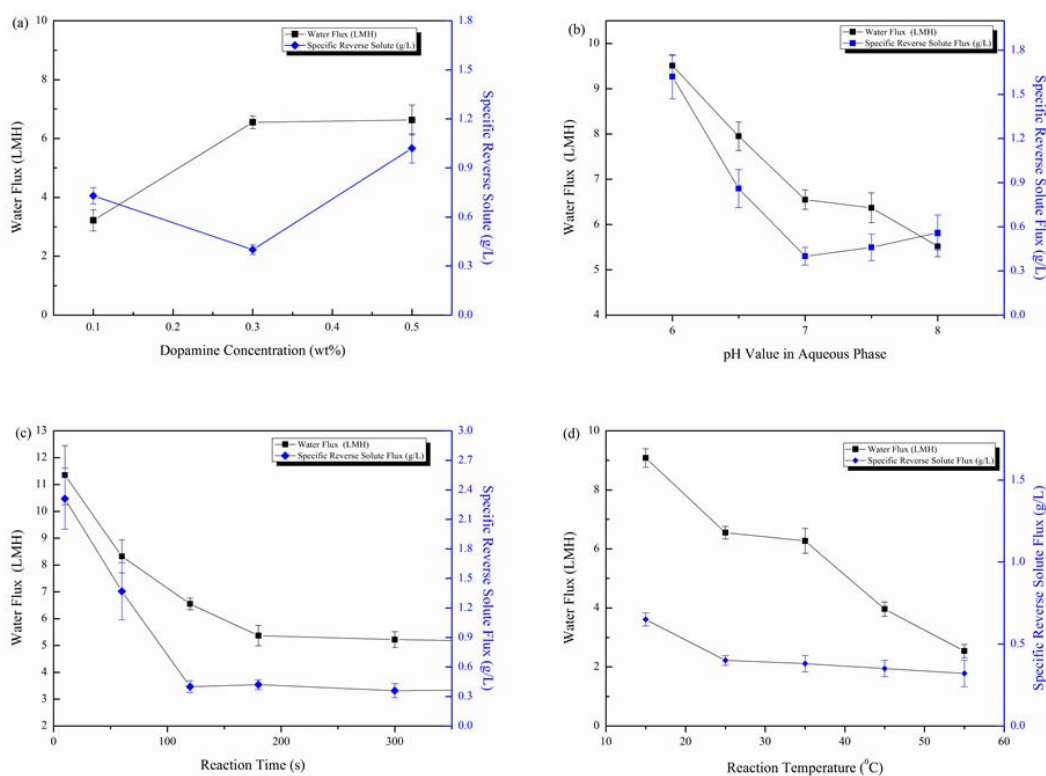
### 3.2. Membrane FO Performance and Preparation Parameter Optimization

**Figure 4a** shows the influence of DA concentration in the aqueous phase on FO performance of the DA/TMC TFC membranes. The concentration of DA was fixed at 0.1, 0.3 and 0.5 wt% in the aqueous phase, respectively. The FO water flux increased from 3.22 to 6.55 LMH. Further increasing the DA concentration to 0.5% had little influence on the water flux. However, the specific reverse flux was almost doubled with high error bars. This is because high DA concentration would easily aggregate on the top of the membrane and thus some PDA pinnacles (see **Figure 2**) might randomly increase the FO water flux but at the price of salt rejection. Based on the above experimental results, the reaction temperature and reaction time of DA/TMC for interfacial polymerization were fixed at 25 °C and 120 s, 0.3 wt% DA and pH value 7 in the aqueous phase, respectively as the optimized parameters. The formation DA/TMC of active layer was determined by not only the interfacial polymerization process, but also the self-polymerization of DA monomers. The pH value of the aqueous phase, IP reaction time, temperature and DA concentrations would directly affect these two processes, thus overall affecting membrane FO process. The influence of pH value in the aqueous phase on membrane FO performance was first studied for two reasons. First, according to Zhu's study, self-polymerization activity would be highly enhanced in alkaline solutions and reached the highest level at pH 8.5<sup>33</sup>. Another reason is that hydrochloric acid would be produced as a result of the IP reaction between amine and phenol groups in DA monomer and acyl chloride groups in TMC monomer. Thus pH value would certainly affect the processing of the positive reaction of the chemical equilibrium<sup>34</sup>.

**Figure 4b** shows the influence of pH value in aqueous phase on the FO performance of the DA/TMC TFC membranes. At the pH of 6.0, the FO water flux was relatively high (9.51 LMH) as well as the specific reverse solute flux (1.62 g/L), which indicated that acidic environment had a negative impact on both self-polymerization and IP process. When the pH value was increased to 7, the water flux sharply decreased to 6.55 LMH, and the specific reverse solute flux decreased even further to 0.4 g/L. When the pH value was further increased to 7.5 and 8.0, the FO water flux continuously decreased while the specific reverse solute flux slightly increased. This could be due to the process of DA self-polymerization was greatly enhanced at alkali solution environment<sup>35</sup>, thus, less amine and phenolic hydroxyl groups of DA could react with TMC in IP process. As a result, a low salt rejection and loose active layer was thus formed. From this, pH 7 was chosen in the following experiments.

**Figure 4c** shows the influence of reaction time on the FO performance of the DA/TMC TFC membranes. When the IP reaction time was 10 s, only a little amount of amine and phenol groups in DA monomer could react with TMC, as a result, the main component of the active layer was loose PDA, which is attributed to the high FO water flux and low salt rejection. When the reaction time increased from 60 s to 120 s, FO water flux decreased from 8.32 to 6.55 LMH and the specific reverse solute fluxes decreased from 1.37 to 0.4 g/L. However, further increase in the reaction time did not decrease the specific reverse solute flux obviously, but reduced the FO water flux. This might be attributed to the fact that too long IP reaction time increased the active layer cross-linking degree thus a relatively dense active layer was formed.

**Figure 4d** shows the influence of reaction temperature on the FO performance of the DA/TMC TFC membranes. When the IP reaction temperature was 15 °C, a very high FO water flux (9.08 LMH) and low salt selectivity (0.65g/L) was obtained. When the reaction temperature was increased from 25 to 55 °C, FO water flux decreased from 6.55 to 2.54 LMH and the specific reverse solute fluxes gradually decreased from 0.40 to 0.32 g/L, respectively. This might be attributed to the fact that higher IP reaction temperature increased the reaction between DA and TMC. The obtained dense active layer lowered the FO water flux but maintained membrane selectivity. Based on the above experimental results, the reaction temperature and reaction time of DA/TMC for interfacial polymerization were fixed at 25 °C and 120 s, 0.3 wt% DA and pH value 7 in the aqueous phase, respectively as the optimized parameters.



**Figure 4.** (a) The influence of DA concentration (0.1 wt%, 0.3 wt% and 0.5wt%) in aqueous phase on the FO performance of the DA/TMC TFC membranes; (b) The influence of pH value (6, 6.5, 7, 7.5 and 8) in aqueous phase on the FO performance of the DA/TMC TFC membranes; (c) The influence of reaction time (10 - 300 s) on the FO performance of the DA/TMC TFC membranes and (d) The influence of temperature (15, 25, 35, 45 and 55 °C) in aqueous phase on the FO performance of the DA/TMC TFC membranes.

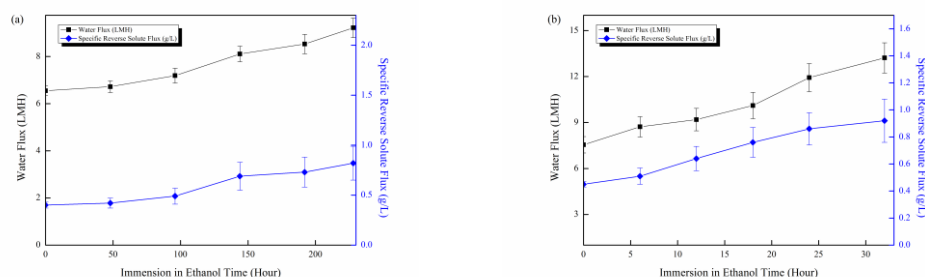
### 3.3. Membrane Structural Stability and Chloride Resistance

In practical applications, membrane characteristics such as structural stability and chloride resistance are important for the lifespan of FO TFC membranes. In the first scenario, some feed solutions may contain organic solvents like ethanol which could massively swell the substrates and separation layers, which are generally comprised of two different materials, causing the detachment of active layers from the substrates, thus shortening membrane lifespan. In the second scenario, in order to control the bio-fouling in FO process, disinfectants with free chloride are widely used, which can inevitably cause the conformational changes of the PA chains, leading to drastic damage in FO membrane separation performance. In order to evaluate the structural stability and chloride resistance of the as-prepared membranes quantitatively, in our study, a doubled value increase in specific reverse solute flux was chosen as an upper limit, resembling when the PA layers were detached or degraded too dramatically to be acceptable in practical applications.

#### 3.3.1 Membrane Structural Stability

The optimized DA/TMC membrane (M-2) and the conventional PIP/TMC membrane (M-0) were separately immersed in ethanol to examine the structural stability, their FO performances are shown in **Figure 5**. For M-2, its FO water flux increased from 6.55 LMH to 9.22 LMH after 228-hour ethanol immersion, and the specific reverse solute flux also increased to 0.515 g/L, it took 228 hours to double the initial specific reverse solute flux value. On the other hand, it only took 32 h for M-0 to double its specific reverse solute flux. This enhancement of structural stability of M-2 (~7.1 times stronger) might be ascribed to the strengthened bond formation between the active layer and the substrate under the selected optimal conditions. Namely, when the pH value of the

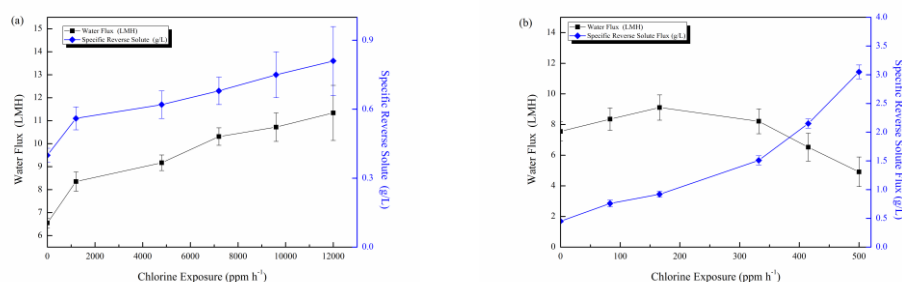
aqueous phase was fixed at 7.0, small amounts of DA monomers were readily able to self-polymerize<sup>33</sup> to form tightly adhesive PDA particles with plenty of  $\pi$ - $\pi$  and hydrogen-bonding interactions in between active layer and substrate<sup>36</sup>.



**Figure 5.** (a) The influence of ethanol immersion on the FO performance of M-2 membrane; (b) The influence of ethanol immersion on the FO performance of PIP/TMC conventional membrane. The FO performance was tested in active layer-feed solution (AL-FS) mode with 1.0 M  $\text{MgCl}_2$  as draw solution and DI water as the feed solution.

### 3.3.2 Membrane Chlorine Resistance

Chlorine-resistance studies were conducted for both DA/TMC (M-2) and PIP/TMC membranes (M-0) as shown in Figure 6. For M-2, a gradual increase of water flux and specific reverse solute were observed during the course of chlorine exposure, which lasted up to  $12000 \text{ ppm h}^{-1}$ , before the specific reverse solute value was doubled. The ester bonds of M-2 were much more stable than amide bonds of PA membranes when exposed to chlorine. Therefore, a gradual increase of water flux due to the slow destruction of the surface inadequate cross-linking structure was observed. Meanwhile, due to a relatively complete active layer structure, the rise in reverse solute flux on top of the membrane was avoided. The water flux of the M-0 membrane was firstly increased like the trend for M-2 but eventually decreased to approximately 65% of the initial flux in  $500 \text{ ppm h}^{-1}$ , while the specific reverse solute flux was finally increased from 0.45 to  $3.05 \text{ g/L}$ . This is because the amide bonds of the PA layers were vulnerable to free chlorine owing to their high electron density. At the beginning of the degradation of PA layer, the water molecules can easily pass through the membrane, however, because of the drastic degradation of the PA layer a highly increased reverse solute flux was observed, which caused an RO-like concentration polarization on top of the active layer thus decreasing water permeability and selectivity. Such significant failure of membrane separation performance may hinder the application of PIP/TMC TFC-PA membranes in wastewater treatment, which usually involves high bio-foulant components. The much slower destruction of the surface inadequate cross-linking structure as portrayed by M-2 was due to its more stable ester bonds, which are much stronger than amide bonds of PA membranes when exposed to chlorine, therefore showing far superior chlorine resistance characteristics (72.3 times enhancement). Additionally, due to its more complete active layer structure, the surging reverse solute flux on the top of membrane was avoided.





**Figure 6.** (a) The influence of chlorine immersion on the FO performance of M-2 membrane; (b) The influence of chlorine immersion on the FO performance of PIP/TMC conventional membrane. The FO performance was tested in active layer-feed solution (AL-FS) mode with 1.0 M MgCl<sub>2</sub> as draw solution and DI water as the feed solution.

#### 4. Conclusions

A new type of DA/TMC TFC membranes was prepared through the self-polymerization process of DA monomers and interfacial polymerization of DA and TMC monomers on PSf substrates. Uniform nodular structures were generated on the membrane surfaces of the novel membranes at a moderate DA concentration. The optimized parameters for this novel membrane synthesis process were obtained, including DA concentration (0.3 wt%), reaction temperature (25 °C), reaction time 2 min and aqueous phase pH value 7, respectively. The optimized membrane showed enhancement of 7.1 times more structurally stable and 72.3 times more chloride-resistant characteristics than the conventional PIP/TMC membrane due the PDA bio-adhesion and polyester groups in this novel membrane structure. The excellent structural stability and chloride resistance shown by this new type of membrane could facilitate wider applications of FO membranes in wastewater treatment.

**Author Contributions:** Conceptualization, Yi Wang and Zongli Xie; Methodology, Yi Wang;; Investigation, Yi Wang and Derrick Ng; Resources, Chaoxin, Xie; Writing-Original Draft Preparation, Yi Wang; Writing-Review & Editing, Yi Wang, Derrick Ng, Shuaifei Zhao and Zongli Xie; Supervision, Zongli Xie, Zhendong Fang and Chaoxin Xie; Funding Acquisition, Yi Wang, Chaoxin Xie and Zongli Xie.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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