

Article

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

Yi Wang ^{1,2}, Zhendong Fang ¹, Chaoxin Xie ^{1,*}, Shuaifei Zhao ³ , Derrick Ng ² and Zongli Xie ^{2,*}

¹ Water Industry and Environment Engineering Technology Research Centre, Chongqing 401311, China; Y.Wang@CSIRO.au (Y.W.); Zhendongfang1962@gmail.com (Z.F.)

² CSIRO Manufacturing, Clayton, VIC 3168, Australia; Derrick.Ng@CSIRO.au

³ Department of Environmental Sciences, Macquarie University, Sydney, NSW 2109, Australia; shuaifei.zhao@mq.edu.au

* Correspondence: a86909304@163.com (C.X.); zongli.xie@csiro.au (Z.X.); Tel.: +86-023-731001 (C.X.); +61-3-95452938 (Z.X.)

Received: 3 August 2018; Accepted: 22 August 2018; Published: 1 September 2018



Abstract: The degradation and detachment of the polyamide (PA) layer for the conventional thin-film composite (TFC) membranes due to chemical disinfectants cleaning with chlorine 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 was first prepared by controlling dopamine (DA) as the sole amine in the aqueous phase and the reaction with trimesoyl chloride (TMC) as the acyl chloride during interfacial polymerization (IP) process. The influence of membrane synthesis parameters such as monomer concentration, pH of the aqueous phase, IP reaction time and IP temperature were systematically investigated. The optimized membrane showed both improved structure stability and chlorine resistance, more so than the conventional TFC membrane. In general, novel DA/TMC TFC membranes could be an effective strategy to synthesize 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

Recently, FO has attracted increasing interest in seawater desalination [1–3], municipal sewage treatment [4,5], membrane bioreactors [6,7], agriculture fertilizers [8,9] and power generation [10,11], as a potential energy-saving and promising technology [12]. Forward osmosis (FO) is a self-driven process that drives pure water molecules across a semi-permeable membrane from the feed solution (with a low osmotic pressure or high chemical potential) to the draw solution (with a high osmotic pressure or low chemical potential). Thin-film composite polyamide (TFC-PA) membranes, which consist of ultra-thin and dense polyamide (PA) layers and porous and thick substrate layers, have been studied for their applications in FO process due to their high salt rejection capability, wide range pH stability and independently modifiable support layer and active layer ability [13–16].

Conventionally, the thin and dense polyamide (PA) layer is synthesized by a interfacial polymerization process onto the substrate layer by two different monomers with amine and acyl chloride [17]. In order to obtain PA layers with good mechanical properties, at least one selected monomer must have more than two functional groups as well as an aromatic material [18]. However, if the conventional TFC-PA membranes are used in some wastewater containing ethanol, the active PA layer could easily be detached from the top of the substrate layer, because there is no strong linkage

between these layers. So the membrane structural stability should be taken into careful consideration for more practical membrane separation applications. Apart from the membrane structural stability, membrane chlorine resistance is also another 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 [5,13,19]. 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 would be degraded by the active chlorine in the oxidizing agents easily and consequently bring a significantly reduced membrane separation performance [20,21]. Hence, TFC-PA membranes with both improved structural stability and chlorine resistance are highly desirable.

Recently, dopamine (DA) or polydopamine (PDA) inspired chemistry has shown a new route for the synthesis of high-performance membranes. PDA with adhesive proteins has been used to enhance the anti-fouling property of ultra-filtration (UF) [22] and Reverse Osmosis (RO) membranes [23], by forming surface-adherent films onto either the active PA layer or the substrate layer to increase hydrophilic property of membranes. Han et al. 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 [16]. Inspired by Han's work, Ping Yu's group [24] prepared three different kinds of UF substrates (PDA coated for 1 h on the topside, on the bottom and on both sides of the substrate before the interfacial polymerization (IP) process, respectively) for TFC-PA membranes fabrication, observing a reduction of reverse solute flux for the PDA topside-coated substrate based TFC-PA membranes. Very recently, Guo et al. [25] 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 investigated as a sole amine in aqueous phase in IP process to prepare TFC membranes for FO process. The DA monomers with amine and phenol groups, as the PDA formed by DA self-polymerization with the catechol groups [26,27] can all react with trimesoyl chloride (TMC) with acyl chloride groups to obtain a new type of thin film active layer for separation applications, which is strongly adhered to the top of the 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 conventional PA layer when exposed to solutions with active chloride. This study sheds light on developing high-performance FO membranes by improving the membrane structure stability as well as the membrane chlorine resistance.

2. Materials and Methods

2.1. Materials

Polysulfone beads (PSf, average molecular weight (MW) ~22 kDa, Sigma-Aldrich, St. Louis, MO, USA), polyvinylpyrrolidone (PVP, average MW ~10 kDa, Sigma Aldrich, St. Louis, MO, USA) and 1-methyl-2-pyrrolidinone (99%, NMP, RCI LABSCAN LIMITED, Samutsakorn, Thailand) were used to fabricate the substrates in this work. Trimesic acid trichloride (98%, TMC, Sigma-Aldrich, St. Louis, MO, USA) monomers were dissolved in n-hexane (Anhydrous, 95%, Sigma-Aldrich, St. Louis, MO, USA) as the organic phase and dopamine hydrochloride (Reagent grade, for research purpose, Sigma-Aldrich, St. Louis, MO, USA) and piperazine (PIP, ReagentPlus[®], 99%, Sigma-Aldrich, St. Louis, MO, USA) were dissolved in phosphate buffer saline (PBS) solution as the aqueous phase for IP process. For membrane performance tests, magnesium chloride (MgCl₂, 98%, Sigma-Aldrich, St. Louis, MO, USA) was dissolved in deionized water (DI). For membrane structural stability and chlorine resistance tests, ethanol (ACS, ISO, Reag. Ph EMSURE[®], Darmstadt, Germany) and sodium hypochlorite (NaClO) solution (Chem Supply Pty Ltd, Adelaide, Australia) with 8–12.5% available chlorine were used, respectively.

2.2. Preparation of Polysulfone Substrates

The porous substrate was synthesized by the classical phase inversion process [28]. To prepare the casting dope for substrate, a mixture containing PSf beads, PVP powders and NMP solvent was kept stirring till the homogenous yellow solution was obtained (this process normally needs 8 h) and then left the solution degassing for at least 12 h. Detail of the procedure can be found in our previous work [28].

2.3. Preparation of Thin Film Composite (TFC) Membranes

The TFC membranes were prepared by interfacial polymerization reaction between the DA monomers and TMC monomers. To be more specific, a series of DA-containing solutions were prepared by mixing PBS and 0.10, 0.30, 0.50 wt% DA, respectively, as shown in Table 1. The PSf substrate was first immersed into DA solution for 0.5 h [29] (0.5 wt% DA saturated PSf substrate, named M-DA, was prepared to verify if DA has become part of this membrane or not). Afterwards, the rest of the DA solution was dried by an air-knife. Then the saturated substrate was followed by immersing into 0.15 wt% TMC solution for 1 min. TMC solution was drain and the substrate was held vertically 120 s to evaporate n-hexane thoroughly. Afterwards, a heating post-treatment process was conducted by putting these as-prepared membranes into an oven at 90 °C for 300 s. After that, the as-prepared TFC membranes were washed 3 times with DI water to remove the unreacted residues and stored in 4 °C DI water in fridge until further testing. The obtained 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 in IP process, respectively. For comparison, conventional TFC-PA membranes formed by PIP/TMC (denoted as M-0) were also prepared as the control membranes.

Table 1. Reagents for thin-film composite (TFC) Membranes Preparation.

Membranes	DA (wt%) in Aqueous Phase	PIP (wt%) in Aqueous Phase	TMC (wt%) in Organic Phase
M-0	0	1.0	0.15
M-DA	0.50	0	0
M-1	0.10	0	0.15
M-2	0.30	0	0.15
M-3	0.50	0	0.15

2.4. Membrane Characterizations

The morphology of the obtained membrane surfaces was observed by field emission scanning electron microscopy (FESEM, Merlin ZEISS GEMINI2, Oberkochen, Germany). Membrane surface chemistry of the active layer was determined by X-ray photoelectron spectroscopy (XPS, ESCALab220IXL, Abingdon, UK). Water contact angles (WCA) were tested by a static sessile drop contact angle system (Dataphysics OCA20, Filderstadt, Germany). The functional groups of the membranes were analysed by Attenuated Total Reflection-Fourier Transform Infra-Red, (ATR-FTIR, Thermo Scientific Nicolet 6700, Midland, ON, Canada).

2.5. FO Performance Tests

FO performance tests were conducted by using a commercial PTFE cell (CF042-FO, Sterlitech Company, Kent, WA, USA). The flow velocities for the feed solution side and draw solution side were maintained at 4.9 cm·s^{−1}. The temperatures of both sides were controlled at 20 ± 0.5 °C to reduce the water flux variations caused by temperature changes. 1 M of MgCl₂ solution was used as the draw solution and DI water was used as the feed solution. The obtained TFC membranes were tested under only one mode, namely, active layer facing feed solution mode. Each experiment was tested for 1 h in triplicate from two independent batches.

The water permeation flux (J_w) ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, LMH) and the reverse solute flux, (J_s) ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) were calculated by the same methods detailed in our previous work [28]. The specific reverse solute flux ($\text{g}\cdot\text{L}^{-1}$) [30,31], which means the ratio of J_s/J_w , was calculated to measure the FO selectivity of the resultant TFC membranes.

2.6. Evaluation of Membrane Structural Stability and Chlorine Resistance

The structural stability of the as-prepared TFC membranes was studied by immersing them in pure ethanol for a fixed period. And the chlorine resistance of these membranes was evaluated by exposing their surfaces into a 1000 ppm NaClO solution over different periods at ambient temperature. The NaClO solution was kept in dark and replaced every 2 h during the chlorine resistance test to keep the constant concentration. Before the membrane FO testing, these TFC membranes were removed from ethanol or NaClO solution and then washed 3 times with DI water to avoid the residual chlorine attacking and ethanol swelling during performance tests.

3. Results and Discussion

3.1. Membrane Surface Characterization

3.1.1. Membrane Surface Chemistry

In this study, DA/TMC TFC membranes possesses novel dense and thin active layers on top of the substrates, which are critical for high FO water flux and membrane selectivity [32]. ATR-FTIR and XPS tests were utilised to confirm the formation of these 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 cm^{-1} at the same time additional peaks at 1750 cm^{-1} , which are attributed to the C=O breathing in the obtained amide bonds and the C=O stretching in ester bonds, respectively. The increase in the peak intensity of hydroxyl groups at about 1660 cm^{-1} was also found in all the DA/TMC TFC membranes, which are attributed to amide II band stretching vibration in the new-formed active layers. These newly formed bands indicated that the active layers were successfully formed onto the top of the PSf substrates. Moreover, nitrogen was detected by XPS on the DA/TMC membrane surfaces (Figure 1b), which confirmed the existence of the DA or PDA on the top of PSf substrates because the amine groups were the exclusive N source while no N sources can be detected in the PSf substrate [16]. As the concentration of DA increased from 0.10 wt% to 0.50 wt% in the aqueous phase, the nitrogen percent increased from 1.24% to 2.44%, accordingly. 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 ascribed to the C-C, C-N and C-O, O=C-N and O=C-N groups, respectively. The presence of 287.4 and 288.2 eV peaks further confirmed the successful formation of amide and ester groups in this novel active layer which is synthesised by 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 novel active layers on the top of PSf substrates has been successful. Moreover, these chemical changes indicated that more DA monomers were incorporated in the as-prepared membranes with the monomer concentrations.

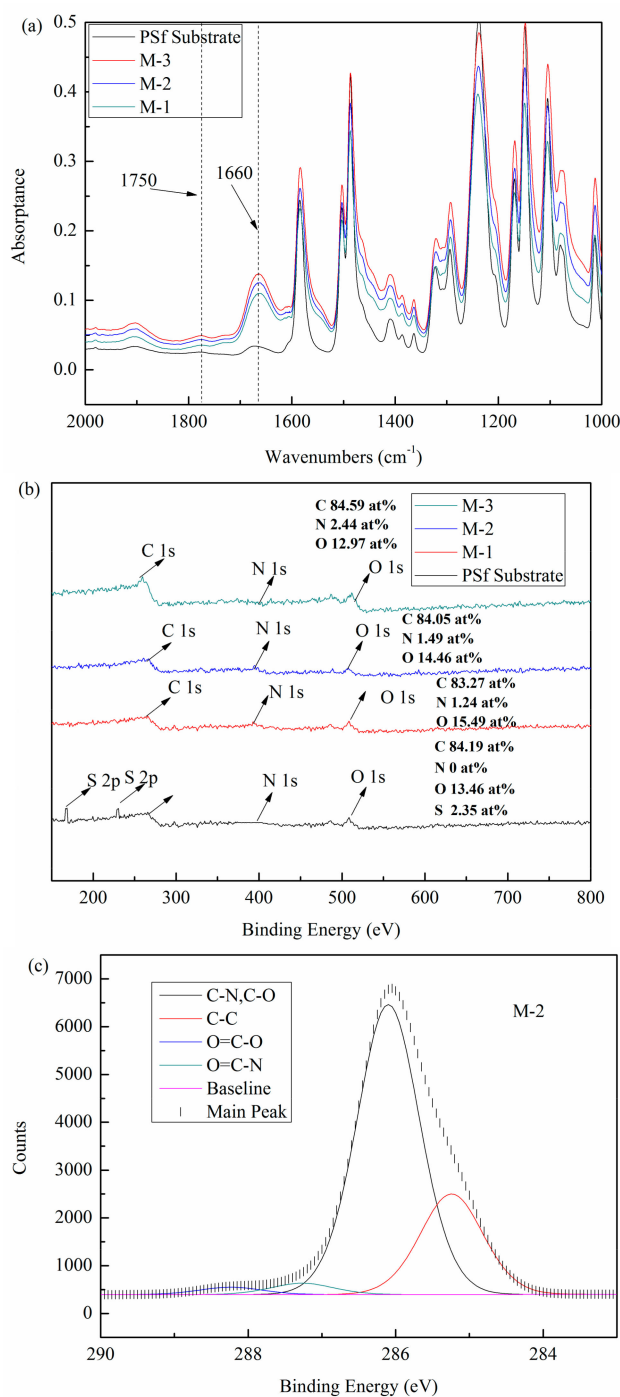


Figure 1. (a) Attenuated Total Reflection-Fourier Transform Infra-Red (ATR-FTIR) spectra of PSf substrate, M-1, M-2 and M-3; (b) X-ray photoelectron spectroscopy (XPS) spectra of the M-1, M-2 and M-3 membrane surface and (c) High-Resolution XPS spectrum C 1s spectra of M-2 surface.

3.1.2. Membrane Surface Morphology

Figure 2 shows the surface SEM images of these as-prepared membranes. Obviously, the PSf substrate surface was smooth, but after DA immersion, the surface of M-DA was rougher due to the DA self-polymerization. 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 [33]. As for the DA/TMC membrane surface (M-1, M-2 and M-3), structures with globules 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 globules could be found. As the DA concentration increased to 0.3 wt% (M-2), the appearance of these globules became more uniform and frequent, resulting in a rougher surface could be beneficial for enhancing water molecules transfer while reject salt ions. However, when the DA concentration was increased to 0.5 wt% (M-3), PDA particles agglomeration were clearly observed, which may reduce the membrane rejection due to their limited salt rejection abilities.

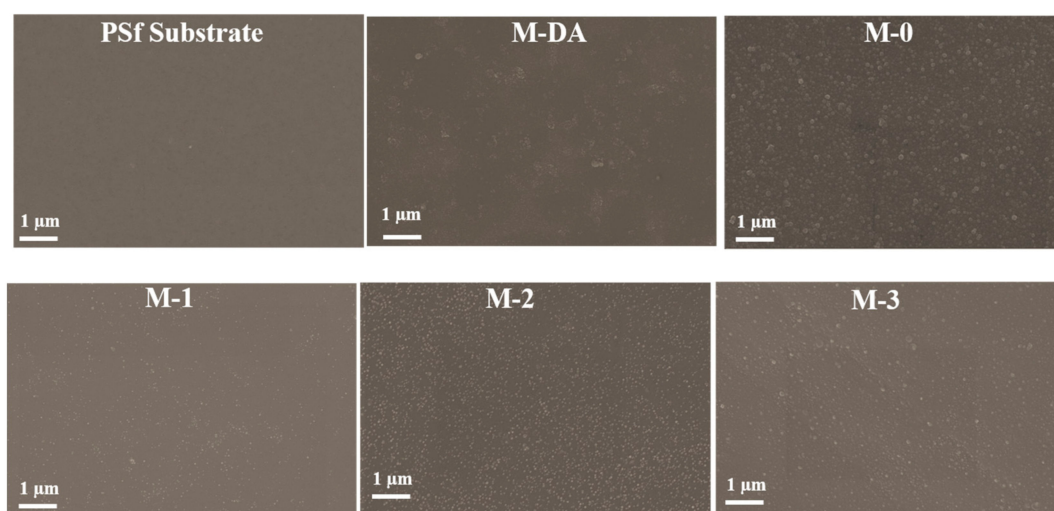


Figure 2. SEM images of PSf substrate, M-DA, M-0, M-1, M-2 and M-3 membrane surface.

3.1.3. Membrane Surface Hydrophilicity

The DA monomers and PDA particles in the aqueous phase with abundant amine and hydroxyl groups would improve the membrane surface hydrophilicity, as shown in Figure 3. WCA is a classical measurement to test the wettability of membrane surfaces: the lower the WCA, the easier for water molecules to wet the membrane surface and the higher the hydrophilicity. The WCA of the PSf substrate was relatively high at 75.3° , after the DA immersion, the WCA of M-DA was improved, indicating DA has been incorporated in the substrate. The WCA of the conventional membrane (M-0) was 51.0° , which is similar to Mohsen et al.'s work [34]. For the DA/TMC membranes with different DA concentrations, the WCAs only decreased from 55.9° to 50.2° when the DA concentration in aqueous phase was increased 5 times (from 0.1 wt% to 0.5 wt%). These results indicate that the incorporation of DA in the aqueous phase would enhance the membrane hydrophilicity while the concentrations of DA had slight influence on the membrane surface hydrophilicity.

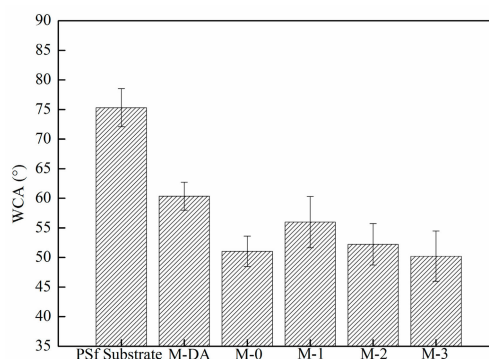


Figure 3. Water contact angles of PSf substrate, M-DA, M-0, M-1, M-2 and M-3.

3.2. Membrane FO Performance and Preparation Parameter Optimization

Figure 4a shows the influence of DA monomers concentration in the aqueous phase on FO performance of the obtained TFC membranes. The FO water flux increased from 3.22 to 6.55 LMH when the DA concentration was increased from 0.1 wt% to 0.3 wt%. However, further increasing the DA concentration showed little influence on the water flux in the meanwhile 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 particles formed globules (see Figure 2) might randomly increase the FO water flux but at the price of FO membrane selectivity. Based on, 0.3 wt% was selected in the following work.

The formation the novel active layer was determined by not only the concentration of DA monomers, but also the pH value of the aqueous phase. This is because, firstly, according to Zhu's study, DA self-polymerization of activity would be highly enhanced in alkaline solutions and reached the most drastic level at pH 8.5 [35]. Apart from this, this IP reaction between amine and phenol groups in DA monomers and acyl chloride groups in TMC monomers would produce hydrochloric acid. Thus, pH value of the aqueous phase would certainly have influence on the processing of the reaction of the chemical equilibrium [36]. Therefore, Figure 4b shows the influence of the pH value of the 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 ($1.62 \text{ g}\cdot\text{L}^{-1}$), which indicated that acidic aqueous environment had an adverse impact the formation of the active layer. When the pH value was increased to 7, the water flux decreased to 6.55 LMH, and the specific reverse solute flux decreased further to $0.4 \text{ g}\cdot\text{L}^{-1}$, indicating an enhanced FO membrane selectivity and a dense active layer was formed. 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 in alkali solution [37], thus, more PDA particles was formed thus less amine and phenolic hydroxyl groups of DA can react with TMC in IP process. As a result, a low salt selectivity and loose active layer was thus formed. From this, pH 7 was chosen in the following experiments.

Figure 4c shows the influence of IP 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 monomers could react with TMC, as a result, the main component of the active layer was loose PDA particles, which is attributed to the high FO water flux and low salt selectivity. 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 $0.4 \text{ g}\cdot\text{L}^{-1}$. However, further increase in the reaction time did not decrease the specific reverse solute flux obviously as well as the FO water flux. Therefore, 120 s was selected in the following experiments to reduce the membrane fabrication time.

Figure 4d shows the influence of IP 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 ($0.65 \text{ g}\cdot\text{L}^{-1}$) 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 $0.32 \text{ g}\cdot\text{L}^{-1}$, respectively. This might be attributed to the fact that higher IP reaction temperature increased the reaction between DA and TMC. The obtained relative dense active layer lowered the FO water flux but maintained membrane selectivity. Based on the above experimental results, the synthesis parameters for IP process were fixed at 25°C and 120 s, 0.3 wt% DA and pH value 7 in the aqueous phase, respectively.

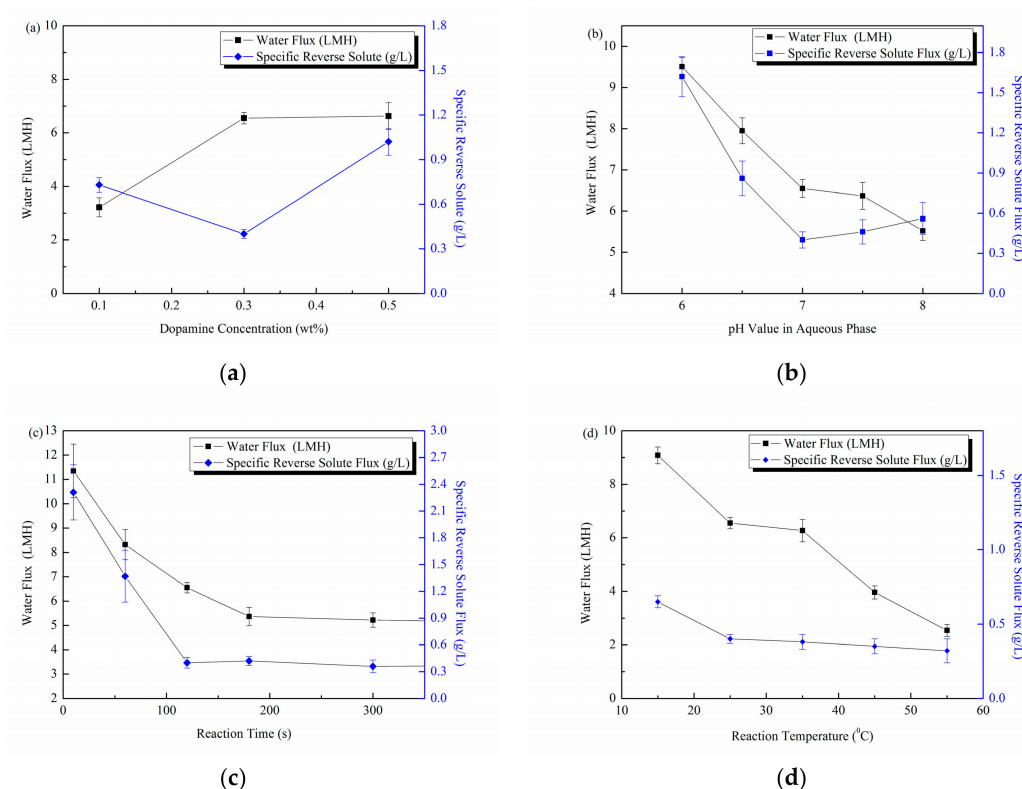


Figure 4. (a) The influence of dopamine (DA) concentration (0.1 wt%, 0.3 wt% and 0.5 wt%) in aqueous phase on the forward osmosis (FO) performance of the DA/trimesoyl chloride (TMC) TFC membranes; (b) The influence of pH value (6, 6.5, 7, 7.5 and 8) in aqueous phase on the FO performance of the DA/TMC 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 lifetime 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 lifetime and increasing the total cost of membrane separation applications. In the second scenario, in order to control the bio-fouling in FO process, some disinfectants with free chloride are widely used, which can inevitably cause the conformational changes of the PA chains, leading to drastic damages for 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 increase value in specific reverse solute flux was chosen as an upper limit [38], 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 test the structural stability, their FO performances are shown in Figure 5. For M-2, its FO water flux gradually increased from 6.55 to 9.22 LMH after the ethanol immersion, and the specific reverse solute flux also increased to $0.81 \text{ g} \cdot \text{L}^{-1}$. The whole process for the initial specific reverse solute flux value to double took as long as 228 h. 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 novel active layer and the substrate under the selected optimal conditions. Namely, when the pH value of the aqueous phase was fixed at 7.0, DA monomers in the aqueous phase were readily able to self-polymerize [35] to form tightly adhesive PDA particles with plenty of π - π and hydrogen-bonding interactions in between the newly-formed active layer and substrate [39].

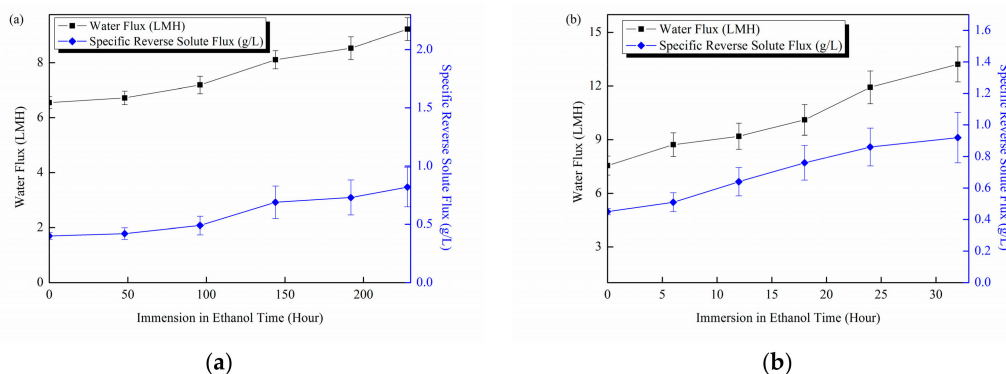


Figure 5. (a) The influence of ethanol immersion on the FO performance of M-2 membrane; (b) The influence of ethanol immersion on the FO performance of M-0 membrane. The FO performance was tested in active layer-feed solution (AL-FS) mode with 1 M MgCl₂ as draw solution and deionized water (DI) water 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, similar to the test in ethanol immersion, a gradual increase of water flux and specific reverse solute flux were observed during the test of chlorine exposure, which lasted up to as high as 12,000 ppm·h, before the specific reverse solute value was doubled. Both the water flux and specific solute flux increase of M-2 for the whole chlorine resistance test (up to 18,000 ppm·h) were mild and slow. This is because the ester bonds in M-2's active layer were much more stable than amide bonds of conventional PA layers when exposed to active chlorine. Therefore, a gradual increase of water flux due to the slow degradation of the novel active layer was observed. Meanwhile, due to a relatively complete active layer structure, the sudden rise in reverse solute flux on top of the membrane was avoided. As for the M-0 membrane, the water flux increase was firstly observed like the trend for M-2 but eventually decreased to approximately 65% of the initial flux in 500 ppm·h, while the specific reverse solute flux was finally increased from 0.45 to 3.05 g·L⁻¹. 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 FO selectivity. Such significant failure of membrane separation performance may hinder the application of PIP/TMC TFC-PA membranes in wastewater treatment, which usually involves frequently chemical cleaning to avoid high bio-foulants. On the contrary, the M-2 portrayed by the novel dense and stable active layer showed a much slower destruction due to its ester bonds, which are much stronger than amide bonds of conventional PA layers 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.

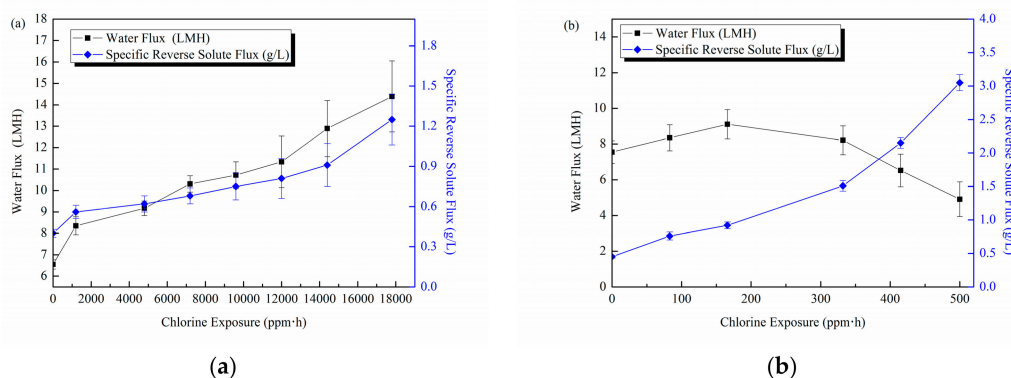


Figure 6. (a) The influence of chlorine immersion on the FO performance of M-2 membrane; (b) The influence of chlorine immersion on the FO performance of PIP/TMC conventional membrane. The FO performance was tested in active layer-feed solution (AL-FS) mode with 1 M MgCl_2 as draw solution and DI water as the feed solution.

4. Conclusions

A new type of DA/TMC TFC membranes was prepared via the IP reaction of DA monomers and TMC monomers on PSf substrates. DA as an amine was first explored in aqueous phase in IP process for TFC FO membrane preparation. Uniform hydrophilic structure with globules was generated on the membrane surface of the novel membranes at a moderate (0.3 wt%) DA concentration. The optimized parameters for this novel membrane synthesis process were obtained, including DA concentration (0.3 wt%), IP reaction temperature (25 °C), IP reaction time 120 s and the 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 to the poly-dopamine (PDA) strong linkage between the active layer and substrate as well as the polyester groups in the active layer. 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, Y.W. and Z.X.; Methodology, Y.W.; Investigation, Y.W. and D.N.; Resources, C.X.; Writing-Original Draft Preparation, Y.W.; Writing, Review and Editing, Y.W., D.N., S.Z. and Z.X.; Supervision, Z.X., Z.F. and C.X.; Funding Acquisition, Y.W., C.X. and Z.X.

Funding: This research received no external funding.

Acknowledgments: The authors would like to express their gratitude for the financial support received from CSIRO Manufacturing. The first author acknowledges the scholarship from China Scholarship Council (CSC 201503170336). Special thanks go to Madeline from Swinburne University, Guang Yang from Victoria University and Yi Wang's good friend, Durga, in CSIRO, for the English grammar proof work and Daneshfar in CSIRO for PSf substrates and XPS data analysis.

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

References

1. Zhao, S.; Zou, L.; Mulcahy, D. Brackish water desalination by a hybrid forward osmosis–nanofiltration system using divalent draw solute. *Desalination* **2012**, *284*, 175–181. [[CrossRef](#)]
2. Choi, Y.-J.; Choi, J.-S.; Oh, H.-J.; Lee, S.; Yang, D.R.; Kim, J.H. Toward a combined system of forward osmosis and reverse osmosis for seawater desalination. *Desalination* **2009**, *247*, 239–246. [[CrossRef](#)]
3. Zhao, S.; Zou, L. Effects of working temperature on separation performance, membrane scaling and cleaning in forward osmosis desalination. *Desalination* **2011**, *278*, 157–164. [[CrossRef](#)]
4. Korenak, J.; Basu, S.; Balakrishnan, M.; Helix-Nielsen, C.; Petrinic, I. Forward osmosis in wastewater treatment processes. *Acta. Chim. Slov.* **2017**, *64*, 83–94. [[CrossRef](#)] [[PubMed](#)]

5. Xue, W.; Yamamoto, K.; Tobino, T. Membrane fouling and long-term performance of seawater-driven forward osmosis for enrichment of nutrients in treated municipal wastewater. *J. Membr. Sci.* **2016**, *499*, 555–562. [[CrossRef](#)]
6. Wang, X.; Zhao, Y.; Yuan, B.; Wang, Z.; Li, X.; Ren, Y. Comparison of biofouling mechanisms between cellulose triacetate (CTA) and thin-film composite (TFC) polyamide forward osmosis membranes in osmotic membrane bioreactors. *Bioresour. Technol.* **2016**, *202*, 50–58. [[CrossRef](#)] [[PubMed](#)]
7. Wang, X.; Chang, V.W.C.; Tang, C.Y. Osmotic membrane bioreactor (ombr) technology for wastewater treatment and reclamation: Advances, challenges, and prospects for the future. *J. Membr. Sci.* **2016**, *504*, 113–132. [[CrossRef](#)]
8. Sahebi, S.; Phuntsho, S.; Eun Kim, J.; Hong, S.; Kyong Shon, H. Pressure assisted fertiliser drawn osmosis process to enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium. *J. Membr. Sci.* **2015**, *481*, 63–72. [[CrossRef](#)]
9. Phuntsho, S.; Shon, H.K.; Hong, S.; Lee, S.; Vigneswaran, S.; Kandasamy, J. Fertiliser drawn forward osmosis desalination: The concept, performance and limitations for fertigation. *Rev. Environ. Sci. Bio/Technol.* **2011**, *11*, 147–168. [[CrossRef](#)]
10. Altaee, A.; Sharif, A.; Zaragoza, G.; Ismail, A.F. Evaluation of fo-ro and pro-ro designs for power generation and seawater desalination using impaired water feeds. *Desalination* **2015**, *368*, 27–35. [[CrossRef](#)]
11. He, W.; Wang, Y.; Shaheed, M.H. Energy and thermodynamic analysis of power generation using a natural salinity gradient based pressure retarded osmosis process. *Desalination* **2014**, *350*, 86–94. [[CrossRef](#)]
12. McCutcheon, J.R.; McGinnis, R.L.; Elimelech, M. Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. *J. Membr. Sci.* **2006**, *278*, 114–123. [[CrossRef](#)]
13. Faria, A.F.; Liu, C.H.; Xie, M.; Perreault, F.; Nghiem, L.D.; Ma, J.; Elimelech, M. Thin-film composite forward osmosis membranes functionalized with graphene oxide–silver nanocomposites for biofouling control. *J. Membr. Sci.* **2017**, *525*, 146–156. [[CrossRef](#)]
14. Shen, L.; Xiong, S.; Wang, Y. Graphene oxide incorporated thin-film composite membranes for forward osmosis applications. *Chem. Eng. Sci.* **2016**, *143*, 194–205. [[CrossRef](#)]
15. Jia, Q.; Xu, Y.; Shen, J.; Yang, H.; Zhou, L. Effects of hydrophilic solvent and oxidation resistance post surface treatment on molecular structure and forward osmosis performance of polyamide thin-film composite (TFC) membranes. *Appl. Surf. Sci.* **2015**, *356*, 1105–1116. [[CrossRef](#)]
16. Han, G.; Zhang, S.; Li, X.; Widjojo, N.; Chung, T.-S. Thin film composite forward osmosis membranes based on polydopamine modified polysulfone substrates with enhancements in both water flux and salt rejection. *Chem. Eng. Sci.* **2012**, *80*, 219–231. [[CrossRef](#)]
17. Salter, R.J. Forward osmosis. *Water Cond. Purif.* **2005**, *48*, 36–38.
18. Qin, J.; Chung, T.S. Effect of dope flow rate on the morphology, separation performance, thermal and mechanical properties of ultrafiltration hollow fibre membranes. *J. Membr. Sci.* **1999**, *157*, 35–51. [[CrossRef](#)]
19. Mi, B.; Elimelech, M. Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents. *J. Membr. Sci.* **2010**, *348*, 337–345. [[CrossRef](#)]
20. Sun, J.; Zhu, L.-P.; Wang, Z.-H.; Hu, F.; Zhang, P.-B.; Zhu, B.-K. Improved chlorine resistance of polyamide thin-film composite membranes with a terpolymer coating. *Sep. Purif. Technol.* **2016**, *157*, 112–119. [[CrossRef](#)]
21. Do, V.T.; Tang, C.Y.; Reinhard, M.; Leckie, J.O. Degradation of polyamide nanofiltration and reverse osmosis membranes by hypochlorite. *Environ. Sci. Technol.* **2012**, *46*, 852–859. [[CrossRef](#)] [[PubMed](#)]
22. McCloskey, B.D.; Park, H.B.; Ju, H.; Rowe, B.W.; Miller, D.J.; Chun, B.J.; Kin, K.; Freeman, B.D. Influence of polydopamine deposition conditions on pure water flux and foulant adhesion resistance of reverse osmosis, ultrafiltration, and microfiltration membranes. *Polymer* **2010**, *51*, 3472–3485. [[CrossRef](#)]
23. Arena, J.T.; McCloskey, B.; Freeman, B.D.; McCutcheon, J.R. Surface modification of thin film composite membrane support layers with polydopamine: Enabling use of reverse osmosis membranes in pressure retarded osmosis. *J. Membr. Sci.* **2011**, *375*, 55–62. [[CrossRef](#)]
24. Huang, Y.; Jin, H.; Li, H.; Yu, P.; Luo, Y. Synthesis and characterization of a polyamide thin film composite membrane based on a polydopamine coated support layer for forward osmosis. *RSC Adv.* **2015**, *5*, 106113–106121. [[CrossRef](#)]

25. Guo, H.; Yao, Z.; Wang, J.; Yang, Z.; Ma, X.; Tang, C.Y. Polydopamine coating on a thin film composite forward osmosis membrane for enhanced mass transport and antifouling performance. *J. Membr. Sci.* **2018**, *551*, 234–242. [[CrossRef](#)]
26. Zangmeister, R.A.; Morris, T.A.; Tarlov, M.J. Characterization of polydopamine thin films deposited at short times by autoxidation of dopamine. *Langmuir* **2013**, *29*, 8619–8628. [[CrossRef](#)] [[PubMed](#)]
27. Hong, S.; Na, Y.S.; Choi, S.; Song, I.T.; Kim, W.Y.; Lee, H. Non-covalent self-assembly and covalent polymerization co-contribute to polydopamine formation. *Adv. Funct. Mater.* **2012**, *22*, 4711–4717. [[CrossRef](#)]
28. Wang, Y.; Fang, Z.; Zhao, S.; Ng, D.; Zhang, J.; Xie, Z. Dopamine incorporating forward osmosis membranes with enhanced selectivity and antifouling properties. *RSC Adv.* **2018**, *8*, 22469–22481. [[CrossRef](#)]
29. Zhao, J.; Su, Y.; He, X.; Zhao, X.; Li, Y.; Zhang, R.; Jiang, Z. Dopamine composite nanofiltration membranes prepared by self-polymerization and interfacial polymerization. *J. Membr. Sci.* **2014**, *465*, 41–48. [[CrossRef](#)]
30. Zhao, S.; Zou, L.; Tang, C.Y.; Mulcahy, D. Recent developments in forward osmosis: Opportunities and challenges. *J. Membr. Sci.* **2012**, *396*, 1–21. [[CrossRef](#)]
31. She, Q.; Wang, R.; Fane, A.G.; Tang, C.Y. Membrane fouling in osmotically driven membrane processes: A review. *J. Membr. Sci.* **2016**, *499*, 201–233. [[CrossRef](#)]
32. Freger, V. Nanoscale heterogeneity of polyamide membranes formed by interfacial polymerization. *Langmuir* **2003**, *19*, 4791–4797. [[CrossRef](#)]
33. Dong, L.-X.; Huang, X.-C.; Wang, Z.; Yang, Z.; Wang, X.-M.; Tang, C.Y. A thin-film nanocomposite nanofiltration membrane prepared on a support with in situ embedded zeolite nanoparticles. *Sep. Purif. Technol.* **2016**, *166*, 230–239. [[CrossRef](#)]
34. Jahanshahi, M.; Rahimpour, A.; Peyravi, M. Developing thin film composite poly(piperazine-amide) and poly(vinyl-alcohol) nanofiltration membranes. *Desalination* **2010**, *257*, 129–136. [[CrossRef](#)]
35. Xi, Z.-Y.; Xu, Y.-Y.; Zhu, L.-P.; Wang, Y.; Zhu, B.-K. A facile method of surface modification for hydrophobic polymer membranes based on the adhesive behavior of poly(dopa) and poly(dopamine). *J. Membr. Sci.* **2009**, *327*, 244–253. [[CrossRef](#)]
36. Lee, K.P.; Arnot, T.C.; Mattia, D. A review of reverse osmosis membrane materials for desalination—development to date and future potential. *J. Membr. Sci.* **2011**, *370*, 1–22. [[CrossRef](#)]
37. Lee, H.; Dellatore, S.M.; Miller, W.M.; Messersmith, P.B. Mussel-inspired surface chemistry for multifunctional coatings. *Science* **2007**, *318*, 426–430. [[CrossRef](#)] [[PubMed](#)]
38. Lu, P.; Liang, S.; Zhou, T.; Xue, T.; Mei, X.; Wang, Q. Layered double hydroxide nanoparticle modified forward osmosis membranes via polydopamine immobilization with significantly enhanced chlorine and fouling resistance. *Desalination* **2017**, *421*, 99–109. [[CrossRef](#)]
39. Li, B.; Liu, W.; Jiang, Z.; Dong, X.; Wang, B.; Zhong, Y. Ultrathin and stable active layer of dense composite membrane enabled by poly(dopamine). *Langmuir* **2009**, *25*, 7368–7374. [[CrossRef](#)] [[PubMed](#)]

