Enhanced Performance of Thin Film Composite Forward Osmosis Membrane by Chemical Post-Treatment

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Abstract. Forward osmosis is an attractive technique in water purification and desalination fields. Enhancement of the forward osmosis membrane performance is essential to the application of this technique. In this study, an optimized chemical post-treatment approach which was used to improve RO membrane performance was employed for enhancing water flux of thin film composite forward osmosis membrane. Home-made polysulfide-based forward osmosis membrane was prepared and nitric acid, sulfuric acid, ethanol, 2-propanol were employed as post-treatment solutions. After a short-term treatment, all the membrane samples manifested water flux enhancement compared with their untreated counterparts. Over 50% increase of water flux had been obtained by ethanol solution treatment. The swelling, changes of hydrophobicity and solvency in both active layer and substrate were verified as the major causes for the enhancement of the water flux. It is noted that the treatment time and solution concentration should be controlled to get both appropriate water flux and reverse salt flux. The results obtained in this study will be useful for further FO membrane development and application.

1. Introduction

In the recent decade, forward osmosis (FO) technique developed rapidly. It has gained increased attention in fields of water/wastewater treatment, seawater desalination, etc. due to its low energy consumption and anti-fouling potential advantages [1]. However, the application performance of FO membrane could be greatly hampered by its inherent internal concentration polarization (ICP) which leads to a significant decline in permeation flux. Especially in the case of using RO membrane in FO process [2]. Plenty of efforts have been made for developing high performance FO membranes, such as cellulose acetate-based (CA) membrane with double skinned active layer and thin film composite (TFC) membrane with finger-like substrate [3,4]. The performance could be effectively enhanced by the improvement of the microstructure of the FO membranes. However, few attentions have been given to the post-treatment of the FO membrane although it could have impact on the performance in practical usage.

In previous, chemical post-treatment has been reported to be beneficial in improving TFC RO membrane performance. Kulkarni et al. [5] investigated the use of hydrofluoric acid, hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, ethanol, and ethanol–acid–water ternary solutions to treat commercial RO membranes. Significant increase of water flux was observed without significant loss
of salt rejection. Mukherjee et al. [6] studied the use of hydrofluoric, fluosilicic and isopropanol alcohol to treat TFC RO membranes. It is found that the limited hydrolysis of the barrier layer on polyamide membrane and the increase in hydrophilicity lead to the increase in permeability. However, FO and RO have completely different operation conditions. The reverse salt flux in FO process could lower the driven force which leads the decrease of the water flux. Hence, the results obtained under RO conditions could not be directly used in FO process. X Wang et al. [7] investigated the FO performance (PRO mode) of commercial available TFC polyamide RO membranes which were treated with acids, ethanol and combinations of acid-ethanol mixtures. It was demonstrated significant flux enhancement (as much as 40 times higher) compared to their untreated counterparts.

Based on previous works done on the chemical post-treatment for improving TFC RO performance, we sought to investigate the potential improvement of TFC FO membrane performance through similar treatment. In this study, home-made TFC FO membrane was treated with acids and alcohols. The performance of the treated membranes was measured by the water flux and reverse salt flux. Morphologies and surface characterization of the resultant FO membranes were also included for further investigated. The optimized treatment approach is expected to be useful for the application of FO membrane.

2. Experimental

2.1. Membrane fabrication.

The TFC FO membranes were prepared via two steps: (1) a phase inversion step to form the membrane substrate, and (2) an interfacial polymerization step to form the active layer. The casting solution of FO substrate contained certain amount of PSf/DMAc/additives and hand casted onto a glass plate to form the uniform film using an Elcometer 4340 Motorised Film Applicator. DI water mixed with solvent was used as coagulant and the nascent substrate was stored in ultrapure water before use. The morphology of the TFC FO membrane was shown in Fig. 1. It is shown that the substrate has a sponge-like porous structure with a thickness of about 100μm. The active layer was prepared on the surface of a pre-casted PSf substrate via an interfacial polymerization reaction between MPD and TMC.

![Fig. 1 The morphology of PSf-based TFC FO membrane (left: active layer; right: substrate)](image)

2.2. Chemical post-treatments.

Two inorganic acids (nitric acid, sulfuric acid) and two alcohols (ethanol, 2-propanol) were employed as treatment solutions at controlled conditions of various times and concentrations. The membrane samples were first presoaked in deionized (DI) water and then soaked in treatment solutions. At last, the treated membranes were immediately immersed in DI water for further rinsing and stored at 4 °C for further characterization. The initial concentrations used were as follows: 70% nitric acid, 24% sulfuric acid, and 100% ethanol and 50% 2-propanol according to the references [5,7].
2.3. *Forward osmosis performance measurement.*

FO experiments were conducted using a lab-scale cross-flow filtration unit with an effective membrane area of 20 cm$^2$. FO performance in terms of water flux and reverse salt flux of the membrane samples was determined by FO test in FO mode. Water flux and the reverse salt flux from the draw solution to the feed were determined by the method reported elsewhere previously [8, 9]. DI water (1L) was used as the feed and 1 M NaCl aqueous solution (5L) was used as the draw solution.

2.4. *Instrumental characterization.*

Water contact angles of the TFC FO membranes were measured using an optical contact angle measuring device (Shanghai Zhongchen Digital Technology Apparatus Co. Ltd) by sessile drop method.

The morphology and mean roughness (Ra) of the membranes were measured using an atomic force microscope (AFM, AIST-NT SmartSPM$^\text{TM}$-1000).

The mean pore size of the PSf substrate was tested by capillary flow porometer (Porolux$^\text{TM}$ 1000, German) based on the gas-liquid displacement method.

Surface morphology TFC FO membrane was characterized by field emission scanning electron microscopy (SEM) (GEMINISEM).

3. Results and Discussion

3.1. *Forward osmosis performances after treating by different solutions.*

Fig. 2 presents the water flux and reverse salt flux of the home-made PSf-based TFC FO membrane with or without treating by inorganic acids and alcohols. The exposure time for treated membrane samples were 5min except for treatment with nitric acid which was limited to 30s due to excessive membrane degradation. It is showed that the water flux and salt flux of all the treated membranes increase to a greater or lesser degree. Meanwhile, reverse salt flux raised as well. The membrane was especially sensitive to the treatment with ethanol solution. The increment of water flux is over 50% compared with the untreated counterpart.

![Fig. 2 Water flux and salt flux of home-made TFC FO membranes treated by different solutions](image)

It was reported that the increase of the hydrophobicity and the partial hydrolysis of the active layer by inorganic acids took the major responsibilities for the increase of the water and salt fluxes of the RO membrane [6]. The partial hydrolysis reactions between inorganic acids and polyamide layers...
have been illustrated by A. Kulkarini et.al. [5] And similar trend of hydrophobicity changes on the polyamide active layer and PSf substrate are observed by contact angle tests (Table 1).

Unlike the performance after inorganic acids treating, it is reported that the water flux increased often came along without any loss of ion rejection for RO membrane treatment by alcohols [5]. This is a different phenomenon between RO and FO processes. In RO process, high hydraulic pressures can induce more ordered conformation which resulting in tightened polymer chains and a polyamide layer with few defects [10]. Unfortunately, if more defects exist on the membrane surface, there will be no hydraulic pressures covering the shortage of the defects in FO process.

Table 1. Specification of the polysulfone based TFC FO membrane

|                | Polyamide active layer | PSf substrate |
|----------------|------------------------|---------------|
|                | Mean roughness (Ra)    | Water contact angle | Water contact angle | Mean pore size |
| Untreated membrane | 0.0588nm              | 65.6°          | 83.0°          | 84.36nm        |
| Ethanol 5min    | 0.1111nm              | 61.0°          | 72.0°          | 92.64nm        |
| 2-propanol 5min | 0.1304nm              | 54.5°          | 76.9°          | 81.49nm        |
| nitric acid 30s | 0.0673nm              | 57.8°          | 74.2°          | 80.27nm        |
| sulfuric acid 5min | 0.0630nm            | 51.4°          | 76.0°          | 82.23nm        |

Furthermore, since ethanol and 2-propanol are both good swelling agents (the value of the solubility parameters of ethanol and 2-propanol are 26.6 MPa$^{1/2}$, 23.6 MPa$^{1/2}$ and polyamide membrane is 23 MPa$^{1/2}$ [5]), the exposure to the alcohols could make the membrane swell and wash off alcohols could remove small molecular residuals from the polyamide active layer. This process could make the membrane to a more porous structure. We tested the surface morphology (Fig.3) of active layer and found that the mean roughness of the ethanol and 2-propanol treated membranes increased (Table 1) more obviously than inorganic acids treated ones. It is indicated that the alcohol treatment could aggravate the defects of the active layer and increase the leakage of the salt.

![Fig. 3 The morphology of membranes which treatment by inorganic acids and alcohols](image_url)
In addition, it is found that the mean pore size of the PSf support layer increased obviously by the ethanol treating method. It is implied that the additives within the support layers were more likely to be dissolved by the ethanol than other solutions after a period of exposure. That is a critical reason for the obvious increase of water flux treating by the ethanol solution.

3.2. Optimization for ethanol treatment.
Based on the comparison of forward osmosis performances after different solutions’ treatments, it is obvious that ethanol could be the best solution to improve TFC FO membrane flux. However, the exposure time and concentration must be carefully controlled due to the leakage of salt. Fig.4 shows the changes of water and salt fluxes treated by ethanol of different exposure times and concentrations.

![Fig 4 Variation of water flux and salt flux treated by ethanol of different concentration and time (the s in brackets represented salt flux and the w in brackets represented water flux)](image)

As a result, the water flux increased more obviously with the increase of concentration. Comparatively, the salt flux increased rapidly when the solution is pure ethanol (100%). It is indicated that low concentration of the solution could alleviate the leakage of salt. From the aspect of exposure time, it is manifested that the extension of exposure time between ethanol and membrane could not only enhancing the water flux but also aggravating the leakage of salt. Therefore, a short-time contact within 5-10min is recommended in consideration of balance of water and salt flux.

4. Conclusion
In this study, home-made TFC FO membrane was treated by nitric acid, sulfuric acid, ethanol and 2-propanol in the aim of enhancing its performance. It was found that the water flux and reverse salt flux could be raised simultaneously after treatment. The performance of FO membrane after chemical post-treatment was different with RO due to the absence of hydraulic pressure. Swelling, hydrophobicity and solvency effects were identified to be responsible for improving performance by the ethanol and 2-propanol treatment. It is found that the ethanol treatment was the best solution if the concentration and exposure time were carefully controlled. Low concentration and short-term exposure time were recommended for the usage of further application.

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