Effect of Additives on the Performance of PPBES Composite Forward Osmosis Hollow Fiber Membranes

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ABSTRACT: A polyamide composite forward osmosis (FO) hollow fiber membrane was successfully prepared with a novel copoly(phthalazinone biphenyl ether sulfone) (PPBES) polymer. Effects of different additives including ethylene glycol methyl ether (EGME) and lithium chloride anhydrous (LiCl) in the dope solution on the morphologies and properties of PPBES support membranes and composite FO hollow fiber membranes were investigated. With the increase of EGME content in the dope solution, the water flux of PPBES support membranes and FO hollow fiber membranes decreased. When LiCl was added into the dope solution, the water flux of FO hollow fiber membranes improved significantly with the increase of LiCl content. Additionally, the FO performance of the PPBES membrane was further optimized by adding triethylamine (TEA) in the interfacial polymerization (IP) process. In comparison with other FO membranes, the novel PPBES composite FO hollow fiber membrane displayed a remarkably high water flux of 45.3 L/m² h and a low specific reverse salt flux of 0.15 g/L.

1. INTRODUCTION

Due to the rising world population, inexorably increasing consumption, and unbalanced distribution of water resources, the water crisis has become a worldwide problem.¹⁻³ To solve this challenge, tremendous efforts have been devoted to exploring new types of water treatment technologies at reduced energy consumption. For the past few years, a forward osmosis (FO) process has been used as a promising energy-effective separation tool in various applications including wastewater reclamation, pharmaceutical products, liquid food concentration, and power generation.⁴⁻⁸ However, the lack of proper FO membranes with desirable performance has severely impeded the further development and large-scale application of this membrane technology.⁹,¹⁰

An ideal FO membrane should have an active layer with high water permeability and low solute permeability and a support layer with high porosity, small structural parameters, and good chemical stability.¹¹,¹² The structures and physicochemical properties of FO support membranes could not only affect the degree of the internal concentration polarization (ICP) phenomenon but also determine the formation and perfection of the polyamide active layer of composite FO membranes.¹³⁻¹⁵ Shi et al. investigated that the desired molecular weight cutoff (MWCO) range of the support membranes is very important to develop new FO membrane materials, and a support layer with an MWCO of less than 300 kphthalazinone and aromatic structure Da is preferred to achieve a desirable RO-like active layer.¹⁶ Additionally, interfacial polymerization (IP) solution formulation may influence the morphologies of active layers, thus affecting the separation selectivity of composite FO membranes.¹⁷,¹⁸

Copoly(phthalazinone biphenyl ether sulfone) (PPBES) shown in Figure 1 is composed of a unique phthalazinone and aromatic structure as well as flexible ether linkages, which endow the PPBES material with outstanding comprehensive properties.¹⁹⁻²¹ With these unique characteristics, PPBES as a membrane material has been successfully applied in the preparation of thermally stable composite FO membranes.²² Due to the use of pure PPBES materials and stringent

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Figure 1. Chemical structure of copoly(phthalazinone biphenyl ether sulfone).
conditions of the interfacial polymerization process, the water flux of the PPBES FO membrane is not very outstanding in comparison with other FO membranes.

Additives are one of the commonly used materials to regulate the structure and properties of FO membranes. Usually, various additives are added into the dope solution to adjust the properties of support membranes. Different amounts and kinds of additives could provide FO support membranes with different structures and separation performance. Ma et al. developed a new composite FO membrane by adding poly(vinyl butyral) (PVB) in the dope solution and found that the incorporation of the PVB additive could significantly improve the hydrophilicity and reduce the ICP effect in FO. Xu et al. explored the correlations between the cis–trans isomers (trans-2-butenedioic acid, TBA, and cis-2-butenedioic acid, CBA) additives and membrane properties and found that the molecular configuration of the additive had a considerable influence on the FO membrane structure and water transport performance. In addition, some additives are also added into the component of the interfacial polymerization solution to modify the morphologies of active layers. Amini et al. found that the introduction of modified TiO₂ nanoparticles in the aqueous solution of m-phenylenediamine (MPD) could significantly change the performance of composite FO membranes. Compared with other modification methods (surface coating, surface grafting, plasma treatment, etc.), the additive blending method is not only simple and easy but also can make use of the advantages of the original components of the blend to complement each other and significantly improve the membrane performance. The limitation of low water flux of PPBES FO membranes might be overcome via the incorporation of additives in the dope solution or IP formulation.

In this work, a novel polyamide/PPBES composite forward osmosis hollow fiber (TFC-FO-HF) membrane was prepared by adding different additives in the dope solution or IP formulation. Effects of ethylene glycol methyl ether (EGME), lithium chloride anhydrous (LiCl), and triethylamine (TEA) additives in the dope solution or IP formulation on the performance of the support membranes and TFC-FO-HF membranes were investigated.

2. RESULTS AND DISCUSSION

2.1. Effect of Dope Solution Formulation on the Properties of PPBES TFC-FO-HF Membranes. Various PPBES support membranes were fabricated using different dope solution compositions, and then, PPBES TFC-FO-HF membranes were fabricated through identical optimized IP conditions regardless of the employed support membranes.

2.1.1. Properties of TFC-FO-HF Membranes as a Function of EGME Content. Different concentrations of EGME were used as nonsolvent additives (NSAs) to investigate their influence on the properties of PPBES TFC-FO-HF membranes. The effects of EGME content on the cross sections of PPBES support membranes and surface morphologies of PPBES TFC-FO-HF membranes are exhibited in Figures 2 and 3, respectively. As shown in Figure 2, the PPBES support membranes had a straight fingerlike structure on the sublayer.
and spongelike structure on the top layer when the EGME content increased from 8 to 20 wt %. Furthermore, with the increase of EGME content, the thickness of the top layer of the PPBES support membrane increased. It was also found from Figure 3 that all of the surfaces of active layers exhibited a typical ridge-and-valley structure. However, with the increase of EGME content from 8 to 20 wt %, more and more obvious peak–valley protuberances appeared on the surface of the composite FO membrane.

The corresponding performance of PPBES TFC-FO-HF membranes fabricated from different EGME contents is shown in Figure 4. The FO water flux of PPBES TFC-FO-HF membranes had a trend of decreasing markedly from 24.0 to 10.0 L/m² h when the EGME content was improved from 8 to 20 wt %. The corresponding specific reverse salt flux decreased slightly from 0.17 to 0.10 g/L. A lower $J_s/J_v$ ratio indicates a less severe reverse solute leakage for the same water production. The FO membrane prepared using 8 wt % EGME showed the highest water flux of 24.0 L/m² h but the most severe salt leakage as well. The reason may be that the varying EGME content changed the structures of PPBES support membranes, which further affected the performance of TFC-FO-HF membranes. The introduction of EGME into the dope solution could suppress the precipitation rate of the polymer solutions during the spinning process, which eventually produced a thicker spongelike top layer. The substrate membrane prepared with low EGME content produced a thinner and looser top layer. It is well confirmed in the literature that a spongelike morphology is more unfavorable to reduce the ICP phenomenon in the FO process than a fingerlike morphology. Increasing the thickness of the top layer of the support membrane could contribute to adverse effects of ICP and cause an additional resistance to mass transfer, thus decreasing the performance of the PPBES TFC-FO-HF membrane. In addition, the denser substrate skin layer is favorable to produce a less permeable and more compact active layer, which provides additional resistance to...
water and solute transport in the polyamide active layer. Therefore, the PPBES TFC-FO-HF membrane using higher EGME content displayed lower water flux and less salt leakage.

2.1.2. Properties of TFC-FO-HF Membranes as a Function of LiCl Content. LiCl has been widely utilized as a hydrophilic inorganic additive to fabricate hollow fiber UF membranes. Typically, 12 wt % EGME was chosen as a nonsolvent additive, and different contents of LiCl were used as an inorganic additive in the dope solution. The effects of LiCl content on the PPBES substrate morphologies and the performance of TFC-FO-HF membranes were studied. Figure 5 exemplifies the variation of PPBES support membrane structures as a function of LiCl content. As one can see, the substrate membranes had more uniform fingerlike macrovoids with the enhancement of LiCl content from 0.5 to 2.0 wt %.

Figure 6 depicts the influence of LiCl content on the top surface morphologies of PPBES TFC-FO-HF membranes. As seen from Figure 6, the top surface morphologies of TFC-FO-HF membranes exhibited a larger portion of a ridge-and-valley layer and prominent protuberance with the increase of LiCl content.

Figure 7 presents the performance impact of LiCl content on the PPBES TFC-FO-HF membranes. The water flux of TFC-FO-HF membranes increased sharply from 18.3 to 25.1 L/m² h, while the specific reverse salt flux increased gradually with the increase of LiCl concentration up to 2.0 wt %. The changes in FO performance may be attributed to the fact that the addition of LiCl could regulate the properties of the substrate morphologies and change the surface morphologies of TFC-FO-HF membranes. The introduction of LiCl could promote the formation of a porous substrate membrane dominated by fingerlike macrovoids. The macrovoid structure could mitigate the phenomenon of internal concentration polarization and reduce the resistance to water diffusion. Meanwhile, the increasing ridge-and-valley structure and protuberance could enhance the surface area of composite FO membranes. The increase surface area of the active layer may result in coming into contact more water molecules, which in turn may improve the water flux of TFC-FO-HF membranes correspondingly. To get a better water flux and a lower specific reverse salt flux, 1.5 wt % LiCl was selected for further research.

2.2. Properties of TFC-FO-HF Membranes as a Function of the TEA Additive During the IP Process. To further modify the performance of TFC-FO-HF membranes, different concentrations of TEA were introduced into the aqueous phase during the interfacial polymerization process. The influence of the TEA additive in the aqueous solution on the surface morphologies of PPBES TFC-FO-HF membranes is shown in Figure 8. As can be seen, with increasing TEA content in the aqueous solution from 0.5 to 2.0 wt %, an increased ridge-and-valley layer and prominent protuberance were exhibited in the top surface of TFC-FO-HF membranes.

Figure 9 exemplifies the impact of the TEA additive on the performance of TFC-FO-HF membranes. As exhibited in
Figure 9, with the increase of TEA concentration from 0.5 to 2.0 wt %, the water flux of TFC-FO-HF membranes could be remarkably improved without a significant change of the specific reverse salt flux. The TFC-FO-HF membrane prepared with 2.0 wt % TEA displayed a superior water flux of 45.3 L/m² h. However, the FO water flux of PPBES membranes decreased slightly when the TEA content exceeded 2.0 wt %. These phenomena may be mainly explained by the fact that the introduction of TEA as an accelerator in the aqueous solution would promote the cross-linking reaction rate of polyamide, resulting in a thinner and more cross-linked active layer. Furthermore, the addition of TEA could remove the byproduct of IP reaction (HCl), which might increase the pH value of the aqueous solution and ultimately change the physicochemical properties of the active layer.

2.3. Performance Comparison of FO Membranes. A performance comparison of PPBES TFC-FO-HF membranes with various FO at sheets or hollow fiber membranes that one can see, in comparison appeared in the literature is summarized in Table 1. As one can see, in comparison with membranes of other works, the novel PPBES TFC-FO-HF membrane developed in the current work displayed an excellent water flux of 45.3 L/m² h. Furthermore, the PPBES membrane also exhibited a relatively low specific reverse salt flux of 0.15 g/L. The development of novel PPBES TFC-FO-HF membrane with excellent performance may pave the way for their further application.

2.4. Seawater Desalination Potential of the PPBES TFC-FO-HF Membrane. The FO water flux of the PPBES TFC-FO-HF membrane with varying draw solution concentrations using a simulated seawater (3.5 wt % NaCl) sample is illustrated in Figure 10. It was found that the water flux of the TFC-FO-HF membrane improved steadily with the enhancement of draw solution concentration. Furthermore, the water flux under the AL-FS mode was much smaller than the value under the AL-DS mode due to the lointernal concentration polarization under the latter mode. With simulated seawater as
feed and 2.0 M NaCl as the draw solution, the novel PPBES TFC-FO-HF membrane could achieve an excellent water flux of 52.1 L/m² h for the AL-DS mode and 20.0 L/m² h for the AL-FS mode, which is higher than those of other reported FO membranes.17,43

3. CONCLUSIONS

Novel polyamide/PPBES TFC-HF-FO membranes were prepared by adding different additives in the dope solution or IP formulation. Experimental results demonstrated that different dope solution formations could change the morphologies and performance of PPBES TFC-FO-HF membranes. With increasing EGME content from 8 to 20 wt %, water flux of TFC-FO-HF membranes declined sharply from 24.0 to 10.0 L/m² h and the specific reverse salt flux decreased slightly from 0.17 to 0.10 g/L. However, with the increase of LiCl content from 0.5 wt % up to 2.0 wt %, the water flux improved significantly from 18.3 to 25.1 L/m² h, while the specific reverse salt flux changed gradually. Furthermore, the water flux of TFC-FO-HF membranes improved remarkably without a significant change of the specific reverse salt flux when TEA was added into the MPD aqueous solution. The PPBES TFC-FO-HF membrane prepared with 2.0 wt % TEA exhibited a remarkably high water flux of 45.3 L/m² h and low specific reverse salt flux of 0.15 g/L under the AL-DS mode. Using simulated seawater as feed and 2.0 M NaCl as the draw solution, the PPBES TFC-FO-HF membrane could achieve a high water flux of 52.1 L/m² h for the AL-DS mode and 20.0 L/m² h for the AL-FS mode.

4. MATERIALS AND METHODS

4.1. Experimental Materials and Reagents. The PPBES polymer was supplied by Dalian Polymer New Material Co., Ltd. (PR China). Ethylene glycol methyl ether, lithium chloride anhydrous, and triethylamine were all analytically pure and used without further treatment. Trimesoyl chloride (TMC) with a purity of overall 98% and m-phenylenediamine were further purified in our laboratory.

4.2. Preparation of PPBES Support Membranes. The PPBES support membranes were fabricated by employing the Loeb–Sourirajan phase inversion method.29,33 The hollow fiber membrane spinning apparatus was designed in our laboratory. A brief introduction to the preparation process of PPBES support membranes is described as follows. First, the
dried PPBES polymer powder was dissolved in the additive/solvent mixture system. Deionized water was used as the bore liquid, while filtered water was used as the coagulation medium. Then, the homogeneous casting solution was extruded at a controlled volume rate of 1.5 mL/min and immersed into the coagulation bath at 23 ± 2 °C. The resultant PPBES support membranes were collected by a gear pump and preserved in the water basin for future use.

### 4.3. Preparation of PPBES TFC-FO-HF Membranes

The PPBES TFC-FO-HF membranes were prepared by interfacial polymerization.²² For different support membranes, polyamide active layers adopted the same interfacial polymerization formulation. First, the prepared PPBES support membranes were immersed in 2.0 wt % MPD aqueous phase for 120 s. Then, the excess amine solution was removed by purging with nitrogen gas for 6 min. Subsequently, 0.1% (w/v) TMC organic solution reacted with the residual MPD monomers for 60 s. Subsequently, the nascent FO membranes were cured at 50 °C for 5 min. Finally, PPBES TFC-FO-HF membranes were washed and immersed in deionized water before performance evaluation.

In addition, different concentrations of the TEA additive varying from 0.5 to 3.0 wt % were added into the MPD aqueous phase. The novel PPBES TFC-FO-HF membranes with TEA additives were fabricated via an identical kind of interfacial polymerization formulation. First, the prepared PPBES support membranes were collected by a gear pump and preserved in the water basin for future use.

### Table 1. Performance Comparison of FO Membranes

| Membranes            | Water Flux (L/m²h) | Specific Reverse Salt Flux (g/L) | Draw Solution | Feed Solution | Refs |
|----------------------|--------------------|----------------------------------|---------------|--------------|------|
| PPBES-TFC            | 45.3               | 0.15                             | 0.5 M NaCl    | DI water     | this work |
| HTI-CTA              | 8.5                |                                   | 0.5 M NaCl    | DI water     | 36   |
| PES TFC #8-FO        | 17.0               | 0.85                             | 0.5 M NaCl    | 10 mMNaCl    | 37   |
| TFC-TB3 Tri-bore     | 32.2               | 0.11                             | 1.0 M NaCl    | DI water     | 38   |
| PSI/PES TFC-FO       | 27.6               | 1.36                             | 2.0 M NaCl    | DI water     | 39   |
| PDA-SWCNTs/PES TFC-FO | 35.7              | 0.04                             | 1.0 M NaCl    | DI water     | 40   |
| UTFN-0.075           | 75.0               | 0.06                             | 0.5 M (NH₄)₂HPO₄| DI water     | 41   |
| TFC-PS-MOF           | 16.0               | 0.78                             | 0.5 M NaCl    | DI water     | 42   |

²²All of the FO membranes are in the AL-DS configuration at 23 ± 2 °C.³³ HTI commercial FO membrane on a cellulose triacetate support.³⁴ TFC-FO hollow fiber membrane on a poly(ethersulfone) (PES) support (#B-FO dope formula).³⁵ TFC-FO tri-bore hollow fiber membrane on a Matrimid S218 polymer (with 1 wt % SDS and 0.5 wt % TEA in an aqueous solution).³⁶ TFC-FO flat sheet membrane on a polysulfone (PSf)/poly(ethersulfone) (PES) blend substrate.³⁷ Polydopamine-modified SWCNTs (PDA-SWCNTs) on a poly(ethersulfone) (PES) microfiltration (MF) support.³⁸ Thin-film nanocomposite forward osmosis (UTFN) membrane containing UiO-66-NH₂ particles.³⁹ TFC-FO membrane on functionalized membranes comprising silver-based MOFs.

**Figure 10.** Water flux of the FO membrane with varying draw solution concentrations using 3.5 wt % NaCl as feed.

**4.4. Performance Tests for PPBES TFC-FO-HF Membranes.** A forward osmosis test instrument was used to measure the performance of PPBES TFC-FO-HF membranes.⁴⁴ The experiments were carried out under room-temperature conditions maintained at 23 ± 2 °C. The PPBES TFC-FO-HF membranes were measured in the active layer facing the draw solution (AL-DS) or the active layer facing the feed solution (AL-FS) configuration.⁵³,⁵⁴ In addition, a certain concentration of NaCl was used as the draw solute, and deionized water or a seawater sample served as feed. The FO water flux was evaluated by measuring the change of feed solution weight and was calculated by the following equation

\[ J_V = \frac{\Delta V}{A \Delta t} \]  

where \( J_V \) (L/m²h) denotes the FO water flux, \( A \) (m²) is the membrane area, \( \Delta V \) (L) represents the absolute change of feed solution, and \( \Delta t \) (h) is the test time intervals.

The reverse salt flux was obtained by calculating the change of feed solute concentration using the following formula

\[ J_S = \frac{\Delta (C_i V_f - C_o V_o)}{A \Delta t} \]  

where \( J_S \) (g/m²h) represents the reverse salt flux, \( C \) (mol/L) is the salt concentration, and \( V \) (L) denotes the volume of feed solution.

The specific reverse salt flux, \( J_S / J_V \) ratio (g/L), was the ratio value between \( J_S \) and \( J_V \), which is a practical indicator of the nonperfectness degree of a composite FO membrane.⁵⁵ The smaller specific reverse salt flux indicates less severe reverse salt leakage under the same conditions.

**4.5. Membrane Characterization.** The cross-sectional structures of PPBES support membranes and surface morphologies of TFC-FO-HF membranes were characterized using a scanning electron microscope (Quanta 450, FEI). The samples must be fractured using liquid nitrogen before spraying a layer of gold.
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Notes
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