Study on the Influence of Interfacial Polymerization Process on Thin–Film Composite (TFC) Forward Osmosis (FO) Membrane Synthesis

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In this paper, interfacial polymerization conditions, such as monomer concentrations, interfacial polymerization reaction time and post treat temperature in the process were systematically studied for thin–film composite forward osmosis membrane synthesis and performance. Results show that with the increase of MPD and TMC monomer concentration, FO membrane water flux decline while the selectivity enhance. Interfacial polymerization reaction time and heating temperature both have significant effect on the properties of FO membrane. With the extension of polymerization time, FO composite membrane water flux decreased, selectivity performance reduces at first and improve then. While the FO membrane performance results illustrate the existence of the best processing temperature is 90 ∘C.

1. Introduction

The beginning of 21st century marks the start of an era of energy and water crises due to the tremendous population growth across the globe (Alessia Viola, 2016, Cannistraro et al., 2015, Ciampi et al., 2015). Forward osmosis (FO) has attracted growing attention as an energy-saving technology in many potential applications such as power generation, desalination, wastewater treatment and food processing (Zhao et al., 2012). The forward osmosis water purification technology taking natural osmotic pressure difference between the draw solution and feed solution on both sides of the membrane as the driving force has received people attention because of low energy consumption (Valladares Linares et al. 2016), low tendency of membrane pollution(She et al., 2016, Wang et al., 2015), high water recovery (Yang et al., 2015) and good rejection capacity of pollutants (Ansari et al., 2017, Li et al., 2016). Idea membranes with high water flux, low salt leakage and outstanding anti-fouling performance, as the most important part in FO process, are always focused by researchers.

Traditionally, aromatic polyamide composite membrane with good chemical stability and hydrophilicity are widely applied in the process of forward osmosis. This kind of membrane with high salt rejection, water permeability, wide range of pH application and chemical stability. PA composite membranes are synthesised by a porous support layer and a dense active layer. Normally, porous support layers are made of ultrafiltration membrane or microfiltration membrane while the active layer are synthesised by interfacial polymerization process. Interfacial polymerization process for FO composite membrane synthesis using a porous support layer soaked in aqueous solution with the contain active monomers for a period of time, followed by dipping the organic solution containing another kind of active monomer (Xiang et al., 2014). Then, in a relatively short period of time, rapid polymerization composite formation takes place via water monomer and oil phase interface. In order to obtain enough mechanical strength and crosslinking degree for the active layer materials, more than 2 functional monomer group materials and at least one aromatic compounds are commonly used in the process. Multiple amine and multivariate chloride are chosen as traditional active layer monomers. Water phase monomers are commonly multivariate amine materials, mainly divided into two categories, aliphatic and aromatic. Common aliphatic amine monomer, for example, like Diethylenetriamine, (DETA), Piperazine (PIP),

Polyethyleneimine (PEI) and Chitosan are preferable. And the commonly used aromatic amine including m - phenylenediamine, (MPD), o-phenylendiamine, (opd), p - phenylenediamine, (PPD), etc. Apart from this, multiple amine materials are choosing for oil phase monomers such as1,3,5 Benzenetricarbonyl Trichloride, (TMC), Phthaloyl Dichloride, (OPC), and 1, 3 - benzenedicarboxylicacid Dichloride, (IPC), etc. However, the relationship between the conditions for interfacial polymerization thin–film composite FO Membrane synthesis and performance aren't clear enough.

This paper, therefore, systematically investigates m-phenylene diamine MPD as water phase monomers, and 1, 3, 5 Benzenetricarbonyl Trichloride, TMC as oil phase monomers in interfacial polymerization process for FO composite membrane synthesis. Polysulfone, (PSf) ultrafiltration as support layer are self-made in the laboratory. MPD and TMC in interfacial polymerization reaction was studied respectively in the process of monomers concentration, interfacial polymerization reaction time, processing temperature for FO composite membrane synthesis.

2. Experimental

2.1 Materials

PSf beads (Sigma-Aldrich), polyvinylpyrrolidone (K30, Sigma-Aldrich) 1-me-thyl-2-pyrrolidinon (NMP, anhydrous, 99.5%), MPD (Sigma-Aldrich), TMC (Sigma-Aldrich), NaCl (Sigma-Aldrich) were used as received. TMC was dispersed in n-hexane, (Sigma-Aldrich). For membrane performance tests, sodium chloride (NaCl, Sigma-Aldrich) was dissolved in deionized (DI) water obtained from a Milli-Qultra pure water purification system (Millipore, Billerica, MA).

2.2 Substrate preparation and thin-film composite forward osmosis membrane synthesis

The cast solution was prepared by dissolving 15 g of polysulfone (PSf) and 8 g of polyvinylpyrrolidone (PVP) into77 g of anhydrous 1-methyl-2-pyrrolidinone (NMP) under vigorous stirring at room temperature for 24 h (Dong et al., 2015). The air bubbles in the cast solution could be dissipated after about 8-12 h at room temperature. A thin film of the obtained cast solution was casted onto a flat glass plate by using a casting blade, as showed in figure1. The film was exposed in the air for about 20 s before it was immersed into the water bath at 60°C. The membrane was removed from the water bath, thoroughly rinsed with Milli-Q water and stored in regularly replaced Milli-Q water (4 °C) prior to future tests.
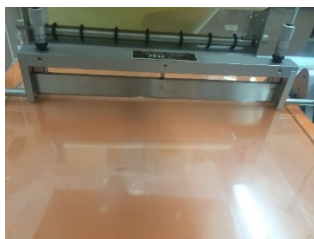

Figure 1: PSf membrane preparation with phase inversion method

TFC-FO membranes were fabricated on the top surface of PSf substrate by the interfacial polymerization reaction between MPD and TMC (Lu et al., 2016). The membrane substrate was firstly immersed in a 3.0wt% MPD aqueous solution for 5min.Then, the excess water droplets on the substrate were removed by an air-knife in 30s. Subsequently, the top surface of the substrate was brought into a 0.2wt% TMC/hexane solution for 120s. In the whole process, substrates were fixed in a PTFE frame so that only the top surface of the substrate was in contact with reactants. The obtained TFC-FO membranes were heat treated in 900C Oven for 5mins, and then kept in 4 °C deionized water until testing.

2.3 FO performance Tests

Water flux(Jw) and reverse solute flux(Js) are both important indexes for forward osmosis, whose calculate formulas and details were reported in our previous work (Wang, 2016). The specific reverse solute flux, which is defined as the ratio of the reverse solute flux to forward water flux, has been introduced as a measure of membrane selectivity. This parameter offers a new parameter to evaluate the FO membrane performance in addition to the permeate flux and reverse solute flux. The specific reverse solute flux calculation formula of forward osmosis is as follows:

$$F_s = J_s / J_w \tag{1}$$

where Fs is specific reverse solute flux (mMol/L); Js is solute flux (mmol/m^2 h); where JW is the water flux (L/m^2 h).

3. Result and Discussion

3.1 Effects of MPD concentrations on TFC membranes FO performance

Figure 2 manifests the relationship between MPD monomer concentrations and FO membrane performance. The results in Figure 2a show that the concentration of the monomer MPD in the water phase in interfacial polymerization for FO process has distinct effect on the water flux of FO membrane. The higher as the concentration of MPD monomer, the more of MPD molecules can participate in the interfacial polymerization reaction, then the polyamide layer are more likely to happen polymer chain crosslink reaction, which will further improve the degree of polymerization of polyamide layer. As a result the active layer become denser and not conducive for water molecules to pass through. The larger monomer concentration of MPD, the FO membrane water flux basically remain unchanged. When the concentration of monomer was greater than 3.0 wt. %, may be due to too much unreacted MPD molecules were detained in molecular chain polyamide, which results a denser active layer. So, in a high concentration of MPD, the decline of composite membrane water flux was larger.

On the other hand, the paper also studied the relationship between the MPD aqueous monomer concentration and reverse solute fluxes/ specific reverse solute fluxes in the interfacial polymerization process for FO membrane synthesis, as shown in figure 2b. This demonstrates that as the MPD aqueous monomer concentration increased, the obtained denser polyamide active layer increase the rejection of salt ion while not the selectivity of the membrane. When the concentration of MPD was 1 wt. %, the reverse solute flux for FO membrane was 109.35 mmol•m-2h-1 and specific reverse solute flux was 15.95 mmol/L. As the MPD concentration increased to 3 wt. %, the reverse solute flux decreased to 74.15 mmol•m^{-2}h^{-1} as well as the specific reverse solute flux dropped to 13.44 mmol•m-2h-1. When the concentration of MPD continued to increase to 5.0 wt. %, the reverse solute flux dropped to 61.58 mmol•m^{-2}h^{-1}, while the specific reverse solute flux increased to 18.70 mmol/L. This may be due to a large number of unreacted MPD molecules containing residual amino group (NH2), increasing the polyamide chain crosslinking effect, in the same time enhancing the charge strength within the membrane. Therefore, the process of the salt ions passing through the membrane are more effectively prevented, thus increasing the salt rejection of the permeable membrane. But due to the effect of high crosslinking, the water molecules are more difficult than salt to pass through, therefore, the membrane selectivity increased sharply at first and then decreased gradually.
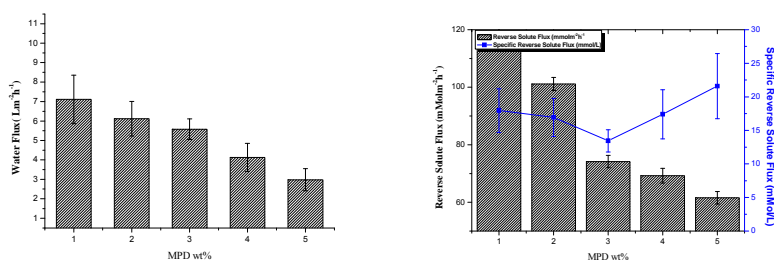
(a) Water Flux   *(b) Reverse Solute Flux and Specific Reverse Solute Flux*
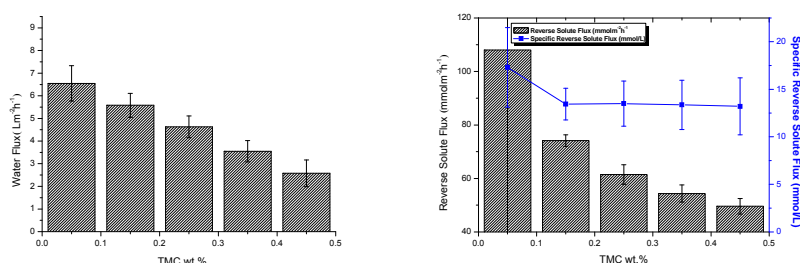
Figure 2: Effects of MPD concentrations on TFC membranes FO performance

3.2 Effects of TMC concentrations on TFC membranes FO performance

Figure 3 demonstrates the relationship between TMC monomer concentrations and FO membrane performance. As has been shown in the graph, similar experimental principles were found in the TMC and MPD monomer concentration on membrane water flux. As the TMC monomer concentration increased, the water flux of the composite membrane decreased gradually, but unlike MPD concentration on the influence of membrane water flux, the decrease trend of FO membrane water flux were approximate linearly with of concentration of TMC increase trend. When the concentration of TMC was 0.05 wt. %, membrane water flux was 6.55 L•m^{-2}h^{-1}, as the concentration increased to 0.15 wt. %, water flux decreased to 5.58 L•m^{-2}h^{-1}. When the concentration of MPD monomer increased per 0.1 wt. %, average decreased water flux was about 1.01 L•m^{-2}h^{-1}. These results show that when the TMC monomer concentration increased, the more TMC monomer

involved in interfacial polymerization process, which makes the activity of polyamide layer become denser, cause more difficult for water molecules pass through the membrane.

At the same time, the paper also studied the relationship between the TMC monomers concentration in the organic phase and reverse solute fluxes/specific reverse solute fluxes in the interfacial polymerization process for FO membrane synthesis, as shown in figure 3b. As we can see from the picture, the polyamide FO membrane reverse solute fluxes decreased gradually and the specific reverse solute fluxes decreased initially and then remained steady as the concentration of TMC increased. When the concentration of TMC was 0.05 wt %, the reverse solute flux and specific reverse solute fluxes was 108.00 mmol•m^{-2}h^{-1} and 17.30mmol/L, respectively. As the TMC concentration increased to 0.15 wt. %, the reverse solute flux decreased to 74.15 mmol•m^{-2}h^{-1} as well as the specific reverse solute flux dropped to 13.44 mmol•m^{-2}h^{-1}. When the concentration of TMC continued to increase to 0.45 wt %, the reverse solute flux dropped to 55.60 mmol•m^{-2}h^{-1}, while the specific reverse solute flux increased slightly to 14.79 mmol/L, basically remained steady. These results show that when the organic phase TMC monomers concentration increased, the interfacial polymerization reaction also increased the density of polyamide layer as well as the rejection of salt ions. This may be because, interfacial polymerization takes place in the oil-water interface, and TMC chloride groups are easily converted into carboxyl in the water, thus lose activity. A lot of carboxyl of the negatively charged, results in charge repulsion effect on salt ions in the process of FO, which improved the membrane's ability to reject salt and the stability for the membrane selectivity.
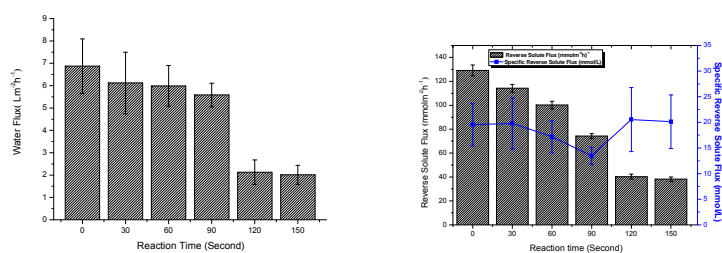

(a) Water Flux   (b) Reverse Solute Flux and Specific Reverse Solute Flux

Figure 3: Effects of TMC concentrations on TFC membranes FO performance

3.3 Effects of interfacial polymerization reaction time on TFC membranes FO performance

This section studies the influence of different reaction time of interfacial polymerization process on polyamide composite membranes FO performance, the results show that when the monomer concentration for interfacial polymerization was the same, in a relatively short period of time, full reaction cannot happen between monomers, cause a lot of residual functional group in molecular polyamide, thus a loose polyamide molecular network was formed and advantageous to the water molecules pass through. While the interfacial polymerization reaction time was long, more monomers were involved into the reaction and monomer functional groups can make full reaction, which makes polyamide active layer denser, but decrease the water flux at the same time. When the interfacial polymerization reaction time was too long (more than 120s), no obvious water flux reductions would be observed, this suggests that functional group can be fully involved in the reaction monomer reaction, but lead to polyamide active layer becomes too dense and not conducive to water molecules. Interfacial polymerization reaction time also has important effect on the salt rejection and selectivity of composite membrane. Figure 3b shows the relationship between the interfacial polymerization reaction time and reverse solute fluxes/specific reverse solute fluxes in the interfacial polymerization process for FO membrane synthesis. When the reaction time of 0 s, reverse solute flux and specific reverse solute fluxes was 129.12mmol•m^{-2}h^{-1} and 19.53mmol/L, respectively. When the reaction time increased to 30 s, 60 s and 90 s, when the reverse solute flux and specific reverse solute fluxes of the membrane continued to decline, and specific reverse solute flux achieved its minimum during the 90 s. When the reaction time continuous increase to 120 s and 150 s, the reverse solute fluxes were reduced to 40.32mmol•m^{-2}h^{-1} and 38.15mmol•m^{-2}h^{-1}, respectively, whilst the specific reverse solute flux rise to 20.54mmol/L and 20.10mmol/L, respectively. Therefore, extend the interfacial polymerization reaction time would improve polyamide composite membrane FO performance, but when the interfacial polymerization reaction time was more than 120s, the high selectivity of membrane performance would slightly decrease mainly due to the density of active layer level reached a certain high degree.
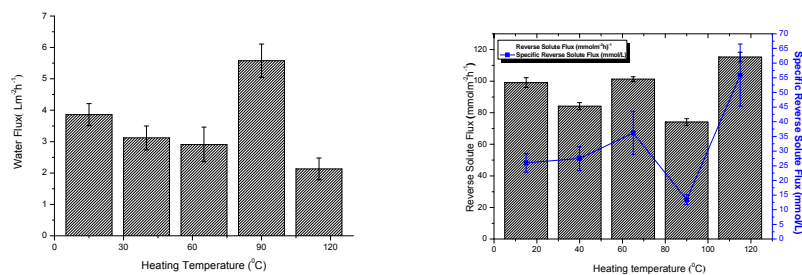
(a) Water Flux   *(b) Reverse Solute Flux and Specific Reverse Solute Flux*

Figure 4: Effects of interfacial polymerization reaction time on TFC membranes FO performance

3.4 Effects of heat-treatment temperature on TFC membranes FO performance

When the polymerization is completed, heat treatment is needed on the initial polyamide composite membrane which helps the organic solvent volatilization on the surface of the membrane and prompt further monomer reaction to improve the polyamide molecules within the network as well as the mechanical properties at the same time. The results show that the membrane permeability and selectivity performance are non-linear with the increase of heat treatment temperature. There is the optimum heat treatment temperature (90 °C). As shown in figure 5a, with the increase of processing temperature, the water flux of the composite membrane dropped initially, and then reached to its peak at 90 °C, about 5.58 L•m^{-2}h^{-1}. Therefore, when the interfacial polymerization reaction times are the same while and heat treatment temperature are not, the membrane permeability exists the best processing temperature to ensure that the molecular structure of the active layer of polyamide is most conducive to water molecules. From the perspective of the chemical reaction kinetics of interfacial polymerization reaction, when heating temperature is low, the reaction rate is slow, polyamide active layer approximately maintains the basic initial molecular structure. While when the heat treatment temperature is increased, molecular motion is accelerated as well as the reaction rate, result in a more compact molecular polyamide structure. Therefore, if a low or high temperature heat treatment was carried out on the membrane, the formation of the molecular structures of polyamide are unfavourable to the water molecules permeate. Obviously, appropriate heat treatment temperature for the preparation of high water flux FO polyamide composite film is of great significance.

Figure 4b shows the relationship between the heat treatment temperature and FO membrane reverse solute fluxes and specific reverse solute fluxes. With the increase of heat treatment temperature, membrane salt permeability and selectivity performance did not appear monotonic increase or decrease. When the temperature was 10 °C and 40°C, respectively, the selectivity performance was almost the same, specific reverse solute fluxes were 25.97 mmol•m^{-2}h^{-1} and 27.47 mmol•m^{-2}h^{-1}, respectively. When the heat treatment temperature was 90 °C, the FO membrane selectivity, showed the best, specific reverse solute flux 13.45mmol•m^{-2}h^{-1}. To sum up, the heat treatment temperature has significant impact on the FO membrane performance. The results show that the membrane permeability and selectivity performance are non-linear with the increase of heat treatment temperature. There is the optimum heat treatment temperature (90 °C).

(a) Water Flux   *(b) Reverse Solute Flux and Specific Reverse Solute Flux*

Figure 5: Effects of heat-treatment temperature on TFC membranes FO performance

4. Conclusions

This paper systemically studies the interfacial polymerization process in the preparation of the polyamide FO composite membrane. NaCl was chosen as draw solution, DI water as feed solution, and the monomer concentrations, reaction time, heat treatment temperature as processing conditions, following conclusion were obtained: The influence of different concentrations of MPD and TMC on the properties of polyamide FO composite membrane was studied. Results show that with the increase of MPD and TMC concentration, FO membrane water flux decline while the selectivity enhance. Interfacial polymerization reaction time and heating temperature both have significant effect on the properties of FO membrane, with the extension of polymerization time, FO composite membrane water flux decreased, selectivity performance reduce at first and improve then. While, the membrane permeability and selectivity performance is non-linear increase or decrease with the increase of heat treatment temperature, the most suitable heat treatment temperature is 90 °C.

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