Synthesis of thin-film composite forward osmosis membranes for removing organic micro-pollutants from aqueous solutions
Alireza Saeedi-Jurkuyeh and Ahmad Jonidi Jafari

ABSTRACT

In this study, a thin-film composite (TFC) forward osmosis membrane was synthesized and characterized with various concentrations (15%, 16%, 17% and 18%) of polysulfone for the removal of two organic micro-pollutants, namely phenol and benzene from the aqueous solutions. Synthesis of a thin-film composite membrane with a support layer carried out by dissolving an amount of polysulfone polymer and polyvinyl pyrrolidone in N-methyl,2-pyrrolidone via phase inversion process and a thin-film layer of the polyamide M-phenylenediamine (MPD) and 1,3,5-benzene trichloride by interfacial polymerization reaction for the fabrication of the TFC were examined. Water flux and reverse salt flux decreased with increasing the concentration of polysulfone polymer. The composite membranes with polysulfone at 16% and 17% had even higher efficiencies. Also, by increasing the concentration of the draw solution, further phenol and benzene could be removed. The highest rejection rates of phenol (polar) and benzene (nonpolar) were found to be 79% and 90%, respectively. The results showed the capability of the thin-film composite forward osmosis (TFC-FO) membranes for removing organic micro-pollutants from the aqueous solutions under different operating conditions, with the efficiency of removing nonpolar compounds being higher.

Key words | benzene, forward osmosis, organic micro-pollutants, phenol, rejection, thin-film composite membrane

HIGHLIGHTS

• A thin-film composite (TFC) forward osmosis membrane was employed to remove organic micro-pollutants.
• Removal of benzene and phenol from aqueous solutions by forward osmosis.
• Application of TFC forward osmosis membrane has been presented.

INTRODUCTION

Benzene is widely used as a solvent for synthesis of organic material. It often permeates into groundwater due to leakage in underground storage tanks and incorrect waste disposal methods (Tawabini & Makkawi 2018). Benzene is a carcinogenic substance for humans such that the United States Environmental Protection Agency has placed it on the list of the top ten priority pollutants (Iqbal et al. 2017). Phenol is present in agricultural wastes, and industrial wastewater, such as petrochemicals (Mukherjee & De 2016). Common methods for the removal of organic matter, such as benzene, phenol and their derivatives, are divided into three categories: chemical (e.g. electrochemical techniques and oxidation), physical (e.g. adsorption and steam stripping) and biological treatments (e.g. activated sludge and biosorption) (Cui et al. 2016). Compared with
the membrane treatment methods, these technologies deal with problems such as cost considerations and production of toxic by-products (Dahili et al. 2015). In the past decade, studies have shown that membrane-assisted separation technology is more common than conventional separation technologies for wastewater treatment because of such advantages as simplicity, minimal need for secondary chemicals and applicability for removing various pollutants at a reasonable cost (Zaviska et al. 2015). The membrane separation process is increasingly being used as a common method for treatment of industrial effluents; this process not only provides standards for industrial effluent, but also makes it possible to reuse a large percentage of water (Qdais & Moussa 2004). Membrane processes, such as reverse osmosis (RO), can produce high-quality water (Lutchmiah et al. 2014). Among different membranes, RO is the most suitable for treatment of wastewater containing organic micro-pollutants (Zaviska et al. 2015). Application of higher pressures in RO increases the cost of treatment resulting in increase of concentration and polarization and increased risk of fouling (Cath et al. 2006). Unlike those pressure-driven membrane processes based on RO, forward osmosis (FO) is an osmotic-driven membrane process which is performed under no/low hydraulic pressure. FO has a higher water recovery rate, lesser membrane fouling problem, and lower energy consumption than those in pressure-driven membrane processes (Kumar et al. 2017). FO process is an emerging technology for molecule separation (Ge et al. 2013). To the present, FO membranes have been made from cellulose materials and polyamide thin-film composites. The cellulosic membranes have such limitations as little water flux, poor salt rejection, narrow pH range and susceptibility to biological degradation (Han et al. 2012). TFC membranes have a polyamide active layer on top of a support layer (Han et al. 2012). Modified fabrication procedures have made it possible to achieve higher water flux and improved separation performance (Han et al. 2012).

In this study, the effects of different concentrations of polymer solution and the removal efficiency of benzene and phenol were determined using a TFC-FO membrane, providing a useful insight into the use of thin-film composite FO membranes to remove polar and nonpolar organic micro-pollutants from aqueous solutions.

EXPERIMENTAL

Materials

Polysulfone beads (average $M_n \sim 22,000$ by MO, Sigma-Aldrich) as polymer, $N$-methyl,2-pyrrolidone (NMP, $\geq 99.5\%$, Sigma-Aldrich) as solvent, and polyvinyl pyrrolidone (PVP, $M_w = 25,000$ gmol$^{-1}$, Merck) as pore former were used to prepare the membrane support layer. M-phenylenediamine (MPD, $\geq 99\%$, Sigma-Aldrich), trimesoylchloride (TMC, $\geq 98\%$, Sigma-Aldrich) and $n$-hexane ($\geq 95\%$, Sigma-Aldrich) were used to synthesize the active layer.

Fabrication of membrane support layer

At first, a particular amount of polysulfone (PSF) polymer and PVP were dissolved in NMP. The solution was mixed on a magnetic mixer for at least 8 hours to form a completely homogeneous solution. The solution was bubbled at room temperature (25 $^\circ$C) for at least 24 hours. Using a film casting knife, a film with thickness of about 100 $\mu$m was created on a clean glass. The film was placed in a bath containing deionized water (DW) for the purpose of phase inversion. It took at least 24 hours in the DW bath to remove the remaining solvent and excess material before undertaking the next steps on the support layer.

Fabrication of polyamide active layer of TFC

The formation of an active layer on top of the support layer was accomplished upon an interfacial polymerization reaction between the aqueous MPD and TMC hexane solutions. Initially, the support layer was in contact with an aqueous 2% MPD solution for 2 minutes. Then, the remaining MPD solution was removed from the surface of the support layer using filter paper. Next, the MPD-saturated substrate was immersed in 0.15% TMC hexane for approximately 60 seconds followed by rinsing and storing in DW for at least 5 minutes. Then, the prepared TFC membrane was stored in DW at 4 $^\circ$C (Emadzadeh et al. 2014).
Membrane characterizations

Membrane morphology

In order to determine the morphological properties of the membrane, cross-section and top surface imaging was performed using a high-resolution emission scanning electron microscope (FE-SEM, TESCAN-MIRA3, Czech Republic). For the cross-sectional scanning, the membranes were first dried at room temperature for 24 h and then fractured in liquid nitrogen and coated with a gold layer by a sputter coater for observation purposes. Substrate thickness was measured by a digital micrometer (293–330 Mitutoyo, Japan).

Membrane porosity

Membrane porosity ($\varepsilon$) was obtained by weighting the wet mass ($w_1$) and the dry mass ($w_2$) of the samples based on Equation (1) (Tang et al. 2010):

$$\varepsilon = \frac{w_1 - w_2}{\rho_w} \times \left( \frac{w_2 - w_2}{\rho_m} \right) \times 100 \quad (1)$$

where $\rho_w$ and $\rho_m$ are water and membrane densities, respectively.

Evaluation of FO membrane performance

Performance of the membrane was analyzed in terms of water flux ($J_w$), reverse salt flux (RSF), specific reverse salt flux (SRSF) and solute rejection rate (SRR).

In order to recycle the water using the FO process, the draw solution (DS) (100 mL of aqueous solution of NaCl) at concentrations of 0.5, 1 and 2 molL$^{-1}$ was driven through the membrane toward the feed solution (FS) (400 mL of DW) at concentrations of 50, 100 and 150 mg L$^{-1}$. Aqueous solutions were circulated at 18 L h$^{-1}$ on either sides of the membrane. Then, the active layer membrane was contacted with the FS.

Accordingly, water flux ($J_w$, Lm$^{-2}$ h$^{-1}$, LMH) was calculated using Equation (2) (Cui et al. 2016):

$$J_w = \frac{\Delta m}{\Delta t \cdot A_m} \quad (2)$$

where $J_w$ denotes water flux, $\Delta m$ (g) is absolute weight loss on the FS side, $A_m$ refers to effective surface area for the membrane (6.7 cm$^2$), and $\Delta$ (h) is the measured time, which was set to 0.5 h. For each experiment, a fresh DS (NaCl) was prepared and used. RSF of the DS was calculated according to Equation (3) (Cui et al. 2016):

$$J_s = \frac{\Delta C_i V}{\Delta t \cdot A_m} \quad (3)$$

where $J_s$ (gm$^{-2}$ h$^{-1}$) denotes the RSF and $\Delta C_i$ (g L$^{-1}$) and $V$ (L) refers to changes in salt concentration and FS volume, respectively.

SRSF was calculated as the ratio of RSF to water flux, as expressed in Equation (4):

$$\text{SRSF} = \frac{J_s}{J_w} \quad (4)$$

Equation (5) gives the percentage of feed solutes rejected by the FO membrane (Cui et al. 2016):

$$\text{SRR} = 1 - \frac{C_d \times V_d / V_p}{C_f} \quad (5)$$

where SRR (%) is the solute rejection rate, $C_d$ (mg L$^{-1}$) refers to the concentration of benzene and phenol in the DS by the end of each FO test, $V_d$ (L) is the final volume of the DS, $V_p$ (L) is the volume of the permeate water, and $C_f$ (mg L$^{-1}$) is the cumulative concentration of benzene and phenol in the FS.

Selected organic micro-pollutants

Benzene and phenol (>99%, Merck, Germany) are herein considered as organic micro-pollutants. Dissolving benzene and phenol in DW, two compounds were synthesized and used as wastewater samples (FS). Following a one-factor-at-a-time approach, the rejection rate was examined at different concentrations of FS (50–150 mg L$^{-1}$) and DS (0.5–2 mol L$^{-1}$). Sodium chloride (Merck, Germany) was used as DS. In order to add to the accuracy of the results while lowering the level of error, all experiments were conducted in triplicate and mean values were reported as results.
Analytical methods

Concentrations of benzene and phenol were determined using the GC (Varian CP-3800, USA), HPLC (CE4200, England), and UV-Vis spectrophotometry (DR6000, HACH), respectively. The maximum absorption wavelength was determined as 260 and 280 nm for benzene and phenol, respectively.

RESULTS AND DISCUSSION

Membrane characterizations

Membrane morphology

Figure 1 shows SEM images of the cross-section and top surface of the (TFC-FO) membrane. The support layer of these membranes had high porosity with long finger-like pores via the phase inversion process for better water passage and reduced internal concentration polarization (ICP) (Emadzadeh et al. 2014) with its top surface (polyamide thin film layer) being a relatively smooth and dense structure by interfacial polymerization between MPD and TMC for better rejection performance.

Membrane porosity

The results showed that, upon increasing the concentration of PSF from 15% to 18%, the membrane thickness ranged from 34 to 66.8 μm, with the membrane porosity measured as 68% to 39%, respectively (Table 1). Previous studies have shown that an increase in thickness and/or a decrease in porosity leads to an increase in ICP (Manickam et al. 2017). Accordingly, with increasing the concentration of PSF, it is expected to end up with a decreased rate of water transmission and removal of dissolved materials from the FS is expected to increase.

Performance of TFC-FO membrane

Effect of polysulfone concentration on membrane performance

According to Table 2, by increasing the concentration of PSF, water flux and (RSF) decreased. Indeed, as the concentration of polymer increases, the membrane becomes thicker and denser, thereby increasing ICP and hence decreasing the water flux (Mustaffar et al. 2004; Kajitvichyanukul et al. 2011; Tiraferri et al. 2011). For comparison purposes, the results of this study and some other studies are presented in Table 2. In order to select the optimal membrane, one shall pay attention to two indicators simultaneously: the membrane must have (1) a minimum RSF and (2) a good water flux. Among other membranes, those synthesized with polysulfone at 15% exhibited the highest water flux and RSF, while those fabricated with polysulfone at 18% had the lowest water flux and RSF values, with the water flux and RSF values being significantly different between the two membranes (p < 0.05). The membranes formed with polysulfone at 16% and 17% were more suitable in terms of water flux, RSF and SRSF. There was no significant difference in water flux and RSF values between these two membranes (p > 0.05). It can be concluded that the flux passing through the membrane is directly related to the surface porosity of the membrane; in other words, the higher the

Figure 1 | SEM images of (a) the cross-section and (b) top surface.
The porosity of the surface of a membrane, the greater is the flow of pure water through the membrane.

### Performance of TFC-FO membrane for removing phenol and benzene

Figure 2 shows that by increasing the concentration of the polymer, the rejection rate and contents of phenol and benzene increase. As the concentration of polymer increases, the interaction between PSF and 1-methyl,2-pyrrolidone increases, forming a high-viscosity membrane solution. This increase in viscosity reduces the driving force for polymer film deposition, which leads to the formation of membranes with thicker layers (Mustaffar et al. 2004). At lower concentrations of PSF, a thin porous layer of membrane is created; such a layer tends to increase water flux and decreases its rejection for liquid separation (Mustaffar et al. 2004). According to the results, the rate of phenol removal is lower than that of benzene. The reason for the difference between the removal of benzene and that of phenol may be the differences in molecular size and dipole moments of these organic compounds. In general, the smaller the molecular size and the higher the dipole moments, the greater is the transfer of dissolved matter and the lower is the rejection rate (Cui et al. 2014). Considering the molecular sizes and weights and dipole moments of these two organic compounds (phenol (0.57 nm) > benzene (0.43 nm); phenol (94 g mol⁻¹) > benzene (78 g mol⁻¹); and phenol (1.7 Debye) > benzene (0 Debye), respectively), it can be stipulated that, despite the larger molecular size and higher molecular weight of phenol, the corresponding rejection rate of phenol is lower, possibly due to its polarity. Given that the TFC surface is charged, the electrostatic attraction between the TFC layer and phenol may lead the phenol toward the membrane surface, as the phenol can easily pass through the membrane, resulting in a lower rejection rate (Cui et al. 2016). In general, the maximum rejection rates of phenol and benzene were obtained as 79% and 90%, respectively.

### Table 1 | Structural properties of synthesized TFC-FO

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Top surface morphology</th>
<th>Cross-section morphology</th>
<th>Thickness (μm)*</th>
<th>Porosity (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFC1</td>
<td>Smooth</td>
<td>Finger-like pore</td>
<td>34 ± 3</td>
<td>68 ± 2</td>
</tr>
<tr>
<td>TFC2</td>
<td>Smooth</td>
<td>Finger-like pore</td>
<td>55.7 ± 1</td>
<td>51 ± 3</td>
</tr>
<tr>
<td>TFC3</td>
<td>Smooth</td>
<td>Finger-like pore</td>
<td>63.4 ± 3</td>
<td>45 ± 1</td>
</tr>
<tr>
<td>TFC4</td>
<td>Smooth</td>
<td>Finger-like pore</td>
<td>66.8 ± 1</td>
<td>39 ± 2</td>
</tr>
</tbody>
</table>

*Mean ± standard deviation.

### Table 2 | Comparison between performances of the thin-film composite forward osmosis membranes considered in this study and some other studies

<table>
<thead>
<tr>
<th>Reference ID</th>
<th>PSF substrate (wt %)</th>
<th>Feed</th>
<th>Draw solution</th>
<th>Water flux (LMH)*</th>
<th>Reverse salt flux (gMH)*</th>
<th>Jw/Jw</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFC1</td>
<td>15</td>
<td>DW</td>
<td>2 M NaCl</td>
<td>12.5 ± 0.5</td>
<td>2.5 ± 0.1</td>
<td>0.2</td>
<td>In this work</td>
</tr>
<tr>
<td>TFC2</td>
<td>16</td>
<td>DW</td>
<td>2 M NaCl</td>
<td>11.9 ± 0.2</td>
<td>1.5 ± 0.05</td>
<td>0.13</td>
<td>In this work</td>
</tr>
<tr>
<td>TFC3</td>
<td>17</td>
<td>DW</td>
<td>2 M NaCl</td>
<td>10.8 ± 0.4</td>
<td>1.3 ± 0.2</td>
<td>0.12</td>
<td>In this work</td>
</tr>
<tr>
<td>TFC4</td>
<td>18</td>
<td>DW</td>
<td>2 M NaCl</td>
<td>8.9 ± 0.6</td>
<td>0.9 ± 0.1</td>
<td>0.1</td>
<td>In this work</td>
</tr>
<tr>
<td>TFC</td>
<td>16.5</td>
<td>DW</td>
<td>2 M NaCl</td>
<td>13.9</td>
<td>5.3</td>
<td>0.38</td>
<td>Emadzadeh et al. (2014)</td>
</tr>
<tr>
<td>TFC</td>
<td>16.5</td>
<td>DW</td>
<td>0.5 M NaCl</td>
<td>9.54</td>
<td>3.0</td>
<td>0.31</td>
<td>Emadzadeh et al. (2014)</td>
</tr>
<tr>
<td>TFC</td>
<td>18</td>
<td>DW</td>
<td>2 M NaCl</td>
<td>7.5</td>
<td>0.37</td>
<td>0.05</td>
<td>Han et al. (2012)</td>
</tr>
</tbody>
</table>

*Mean ± standard deviation.
Effects of draw solutions

Figure 3 shows that, with increasing the concentration of the DS, the rejection rates of phenol and benzene increased. As the concentration of DS increases from 0.5 to 2 molL$^{-1}$, in the PSF at 16%, the water flux increases from 8.1 LMH to 11.9 LMH, and the amount of phenol and benzene rejection is increased from 70.0% and 76.0% to 78.5% and 88.0%, respectively. This is due to the degree of rise in water flux through the concentration of the DS being more than that in solute flux. Also the RSF was observed to increase with DS concentration, which could hinder the forward transfer of organic micro-pollutants through the membrane to the DS, leading to lower permeation of the organic micro-pollutants within the membrane and, in turn, higher rejection rates in the TFC-FO process. The others showed that, in TFC-FO, when DS concentration increased from 0.5 M to 2 M, rejection rates of phenol, aniline and nitrobenzene increased from 66.0% to 80%, 88% to 92% and 73% to 81%, respectively (Cui et al. 2016). Also, it was observed that there was a significant difference between increasing the concentration of DS, rejection rates of phenol and benzene ($p < 0.05$).

CONCLUSIONS

This study showed that, by increasing the concentration of polysulfone, the membrane thickness (49.0%) and porosity (43.0%) decreased. The effects of different concentrations of PSF polymer were investigated for synthesizing TFC-FO membranes, indicating better results in terms of water flux, RSF and SRSF when the PSF was applied at 16% and 17%. Then, the TFC-FO membrane separation function was investigated for the removal of phenol (polar) and benzene (nonpolar) from wastewater. The results showed that the rejection rate of benzene was higher than that of phenol.
and an increase in the concentration of DS led to an increase in the content of micro-pollutants (phenol and benzene). The maximum phenol and benzene removal rates were 79.0% and 90.0%, respectively. According to this investigation, it can be concluded that, as far as the synthesis of a TFC-FO membrane is concerned, one may obtain higher efficiency by using a PSF polymer at 16% or 17%. Also, despite the relatively good potential of the TFC-FO membrane for removing polar (e.g. phenol) and nonpolar compounds (e.g. benzene), it is more efficient for removing nonpolar compounds.

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