Zwitterionic Triamine Monomer for the Fabrication of Thin-Film Composite Membranes

Ngoc Lieu Le,* Phuoc H.H. Duong, Bruno A. Pulido, and Suzana P. Nunes*

**ABSTRACT:** A new zwitterionic triamine monomer prepared from tris(2-aminoethyl)amine and 1,3-propane sulfone is proposed for the interfacial polymerization with trimesoyl chloride to form thin-film composite membranes for nanofiltration with antifouling properties. The positive effects of the zwitterionic monomer fraction on the surface characteristics of the polyamide layer, fouling resistance, and filtration performance are demonstrated. Increasing the zwitterionic monomers in the selective layer significantly improves the water permeance (two-fold) without affecting the rejection for dyes tested with a molecular weight in the range of 637 and 1673 g/mol. The smoother and more hydrophilic membrane surface of the newly developed membrane provides excellent fouling resistance confirmed by the negligible protein adsorption and permeance drop during the filtration.

1. INTRODUCTION

Nanofiltration has found its applications in dye removal, water softening, chemical oxygen demand (COD) and biological oxygen demand (BOD) reduction, and concentration of organics with the molecular weights of 300–1000 in the food and pharmaceutical industries. The most successfully commercialized nanofiltration membranes are thin-film composite (TFC) membranes, which comprise a thin active layer on a mechanically strong support, such as nanofiltration membranes from Filmtec Corporation, Nitto Denko, Toray Industries, Desalination Systems, and Advanced Membrane Technology Inc. The most commonly used technique to fabricate TFC membranes is interfacial polymerization, where the water-soluble and organic-soluble monomers are dissolved into two immiscible phases and react at their interface (i.e., on the substrate surface) to form a highly-cross-linked polymeric network as the ultra-thin selective skin. The resultant membranes exhibit excellent performance in desalination and water purification in terms of water permeability and solute rejection. However, the polyamide layer is susceptible to fouling, which is still a major hindrance for their extensive applications. Significant interest still remains in discovering fouling-resistant TFC membranes.

Membrane fouling is strongly determined by membrane surface morphology and properties such as roughness, nodule structure, hydrophilicity, charge, and the presence of certain functional groups. Many research efforts have been dedicated to modify the membrane surface properties to enhance its fouling-resistant capability. The incorporation of highly hydrophilic and neutrally charged segments into the selective layer has been widely applied to achieve simultaneous positive effects such as reduced surface charge, improved hydrophilicity, smoothened membrane surface, and in certain cases, enhanced water permeability and solute rejection.

Zwitterionic polymers such as polyphosphobetaine, polysulfobetaine, and polycarboxybetic have been introduced as non-fouling segments to prepare a fouling-resistant surface. Membrane surfaces coated or grafted with zwitterionic polymers have been demonstrated to be more resistant against the adsorption of organic and biological components. These characteristics are attributed to their effective zero-charge (i.e. pseudo-neutrality) due to the coexistence of negative and positive charges in the same monomer unit and their high hydrophilicity. The strong electrostatic bonds between water molecules and zwitterionic groups favor the formation of a hydration layer, which is even more stable than those observed on neutral hydrophilic polymers (e.g., polyethylene glycol and its derivatives). This seems to be the primary reason for the high water...
permeability and antifouling characteristics of zwitterionic polymers compared to common hydrophilic polymers.30

Despite that, zwitterionic polymers suffer a critical challenge of poor solubility and processability.33 An important aspect is how to incorporate the zwitterionic segments into the membrane matrix.20–23,32–35 For TFC membranes, zwitterionic polymers have been introduced by membrane surface modifications,6–30 by initiated chemical vapor deposition,39,40 and by interfacial polymerization with zwitterionic monomers.1 For example, Liu et al.32 employed the ARGET-ATRP technique (activators regenerated by electron transfer–atom transfer radical polymerization) to tailor TFC membranes with zwitterionic poly(sulfobetaine methacrylate) (PSBMA), using dopamine hydrochloride and α-bromoisobutyryl bromide as the adhesion agent and initiator, respectively. Yang et al.40 applied initiated chemical vapor deposition to synthesize a random copolymer, poly[2-(dimethylamino)-ethyl methacrylate-co-ethylene glycol dimethacrylate], deposited on TFC membranes, which then reacted with 1,3-propane sulfonate at the solid–gas interface to generate a zwitterionic polymer. Ma et al.41 synthesized a new zwitterionic diamine monomer, N-aminoethyl piperazine propane sulfonate (AEPPS), to react with TMC via interfacial polymerization and form a zwitterionic polyamide layer for TFC membranes.

In this study, we proposed a new zwitterionic triamine monomer formed by the reaction between tris(2-aminoethy1) amine and 1,3-propane sulfone for the interfacial polymerization with TMC to prepare nanofiltration TFC membranes for dye removal. The small size of the amine monomer (~146 g/mol) and its triamine chemistry are expected to tighten the polyamide network and increase the density of zwitterionic units in the network, which may improve the anti-fouling effects. In addition, the presence of tertiary amine and formed sulfate groups could open the opportunities to bind with silver for additional antibacterial effects.42 The surface chemical structure, morphology, and properties were characterized to demonstrate the successful incorporation of the zwitterionic moiety into the polyamide layer. We mainly focus on the effect of the zwitterion on the nanofiltration performance (i.e., water permeance and dye rejection) and its fouling-resistant performance.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyetherimide (PEI) Ultem 1000 from Sabic (Saudi Arabia), N-methyl-2-pyrrolidinone (NMP, ≥99.5%, Merck), and diethylene glycol (DiEG, 99%, Alfa-Aesar) were employed to formulate the dope solution. A nonwoven sheet (TH100, Hirose) was employed to support the porous substrate for improved mechanical strength. Ethanol from Merck was employed to prepare the non-solvent mixture. Poly(ethylene glycol) with the molecular weight of 200 g/mol (PEG) from Sigma-Aldrich was used as the pore-filling liquid. Tris(2-aminoethyl)amine and 1,3-propane sulfone from Sigma Aldrich were used to synthesize new amine monomers. Trimesoyl chloride (TMC), m-phenylenedi-amine (MPD), and n-hexane for the preparation of the polyamide layer on the top of the substrates were purchased from Sigma-Aldrich. Three different dyes from Sigma-Aldrich were used to test the dye rejection of the resultant membranes. Their properties are listed in Table 1. For fouling tests, bovine serum albumin (BSA) and fluorescein isothiocyanate-conjugated BSA from Sigma-Aldrich were used.

2.2. Triamine Monomer Synthesis. A total of 17 mL tris(2-aminoethyl) amine was prepared in 20 mL dry acetonitrile. Under stirring, 10 mL 1,3-propane sulfone was added. The mixture was then heated up to 35 °C and stirred for 3 h. After completing the reaction, the mixture was cooled down and the solvent was discarded. The product was washed three times with 30 mL dry acetonitrile each and once with diethyl ether and then dried in vacuum at room temperature overnight. The successful formation of a zwitterionic sulfobetaine group by the reaction of a tertiary amine with 1,3-propanesulfonate has been extensively demonstrated in previous studies.40,43–45 The new monomer was abbreviated as ZTM.

2.3. TFC Membrane Preparation. TFC membranes were prepared by an interfacial polymerization on the top of PEI porous substrates to form dense thin selective polyamide layers. The PEI porous substrates were fabricated by non-solvent-induced phase separation of the polymer solutions containing 10.5 wt % PEI, 8.0 wt % DiEG and 81.5 wt % NMP cast on a nonwoven fabric using a 200 μm gap casting knife and immersed in the non-solvent mixture of water and ethanol (80/20 wt %) at ambient temperature to form porous substrates. They were then kept in cold water at 4 °C for further experiments.

Before conducting the interfacial polymerization, the substrates were immersed in PEG for 1 h. The high viscosity of PEG could prevent the deep diffusion of amine monomers into the substrate and hence facilitate the formation of a more uniform polyamide layer during interfacial polymerization. After discarding the liquid, their excess amount on the substrate surface was removed gently by tissue papers. The substrates were then fit in an acrylic/silicone frame. Amine in water (1 wt %) was added into the frame. After 2 min, water was completely removed without any excess. The weight percentages of the new amine monomer in the amine mixture were 0, 25, 50, 75 and 100%. Afterward, 0.15 wt % TMC in hexane was added in and drained off after 1 min. The newly formed TFC membranes were then washed with the excess amount of hexane, dried in air at ambient temperature, and then kept in water to liberate any unreacted chemicals. The membranes were then kept at 4 °C for further analyses. The reactions to synthesize the new amine monomer and form the polyamide layer are depicted in Figure 1.

2.4. Substrate and Membrane Characterization. The morphologies of the freeze-dried substrate and membranes were analyzed by field emission scanning electron microscopy (FESEM) on Nova NanoSEM 630 (FEI, USA) and Quanta 600 FESEM (FEI, USA) microscopes. The substrates or membranes were coated with a 3 nm layer of iridium before observation. Their surface topography was imaged by atomic force microscopy (AFM, Agilent 5400 SPM, Agilent Technologies) with the aid of a silicon AFM cantilever (Nanosensors) to conduct the tapping mode in air. The substrates or membranes were coated with a 3 nm layer of iridium before observation. Their surface topography was imaged by atomic force microscopy (AFM, Agilent 5400 SPM, Agilent Technologies) with the aid of a silicon AFM cantilever (Nanosensors) to conduct the tapping mode in air. The membrane surface roughness was expressed by root-mean-squared roughness (Rq), which was analyzed by the Pico Image

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Table 1. Different Dyes Used for Nanofiltration

<table>
<thead>
<tr>
<th>dye</th>
<th>molecular weight (g/mol)</th>
<th>maximum absorption wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>red direct 80</td>
<td>1373</td>
<td>528</td>
</tr>
<tr>
<td>brilliant blue R250</td>
<td>826</td>
<td>589</td>
</tr>
<tr>
<td>reactive blue 4</td>
<td>637</td>
<td>595</td>
</tr>
</tbody>
</table>

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The contact angles between membrane surface and water were determined by a Kruess Easydrop (Kruess GmbH, Germany) at ambient temperature.

The chemical structures of the substrate or membrane surfaces were analyzed using Fourier transform infrared spectroscopy (FTIR) (is10, ThermoFisher) using the attenuated total reflectance (ATR) mode over the range of 1000–2000 cm\(^{-1}\) and the crystal type of diamond with ZnSe lens with a resolution of 1 cm\(^{-1}\). The penetration depth (\(d_p\)) of the beam into the studied sample can be calculated as follows:

\[
d_p = \frac{\lambda}{2 \pi n_1 \sqrt{\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2}}
\]  

(1)

where \(\lambda\) is the light wavelength, \(\theta\) is the angle of incidence of the beam, and \(n_1\) and \(n_2\) are the refractive indices of the crystal and sample, respectively. \(n_1 = 2.4\) and \(\theta = 42^\circ\) are for the crystal type of diamond with ZnSe lens. \(n_2 = 1.5\) is for general organic compounds.

2.5. Nanofiltration Performance. The water permeance and dye rejection of TFC membranes were evaluated through a nanofiltration process. A dead-end permeation cell was used for filtration experiments conducted under a transmembrane pressure of 1 bar. The pure water permeance (PWP, in L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) was determined when deionized water was used as feed and calculated as follows:

\[
PWP = \frac{\Delta V}{\Delta t \times A \times \Delta P}
\]  

(2)

where \(\Delta V\) (L) is the permeate volume, \(\Delta t\) is the duration (h), \(A\) is the effective membrane surface area (m\(^2\)), and \(\Delta P\) is the transmembrane pressure (bar).

Dye rejection was determined by the experiments with aqueous solutions of 200 ppm dye. The retentate volume was maintained at >95% of the initial feed volume by using a large feed amount.

Dye rejection \((R)\) was calculated as follows:

\[
R = \left(1 - \frac{C_p}{C_r}\right) \times 100\%
\]  

(3)

where \(C_p\) and \(C_r\) are the dye concentrations in the permeate and the retentate, respectively, which were determined by their
absorption values at their maximum absorption wavelengths presented in Table 1, using a NanoDrop 2000/2000C spectrophotometer (Thermo Fisher Scientific).

2.6. Fouling Tests. The static protein adsorption was analyzed using 0.5 mg/mL solution of fluorescein isothiocyanate-conjugated bovine serum albumin (BSA-FITC) in phosphate-buffered saline. The membranes were kept in the buffer for 10 min and then in the BSA-FITC solution at room temperature for 1 h. The protein density absorbed on the membrane surface was observed using an Olympus BX41 microscope and then determined by calculating its fluorescence intensity using ImageJ software (National Institutes of Health, Bethesda, MD).

In addition, the hydrodynamic protein adsorption was evaluated through fouling tests, which were conducted by filtrating a 500 ppm BSA solution until the flux was unchanged. After this, the fouled membrane was cleaned with deionized water before re-measuring the pure water flux (PWP). The flux recovery ratio (FRR) was calculated as follows:

$$\text{FRR} = \frac{\text{PWP}_2}{\text{PWP}} \times 100\%$$

3. RESULTS AND DISCUSSION

3.1. Morphology of PEI Substrates. Figure 2 illustrates the surface and cross-sectional morphology of PEI substrates, which consists of finger-like macrovoids underneath a sponge-like porous substructure, which contributes to the good mechanical strength of the membranes. The substrates have a molecular weight cut-off (MWCO) of approximately 430 kg mol\(^{-1}\). Poly(ethylene glycol) and poly(ethylene oxide) of various molecular weights were used in determination of solute rejection and the molecular weight cut-off (MWCO) by a procedure previously detailed elsewhere.

3.2. Characterization of TFC Membranes. Figure 3 shows the surface and cross-sectional morphologies of the TFC membranes prepared with different weight ratios of MPD and ZTM. The membrane prepared with 100% MPD has the typical ridge and valley morphology, which is mostly found in TFC membranes prepared by the cross-linking reaction of MPD and TMC. By increasing the amount of ZTM in the amine mixture, the ridges become flattened and disappear when 100% ZTM is used. Along with that, the thickness of the selective layer decreases from 452 to 67 nm. This morphological change is probably induced by differences in the diffusion rate of MPD and ZTM during the interfacial polymerization. When the organic and aqueous phases contact, an incipient film is quickly formed at the interface. The reaction is governed by two steps. At a first stage, the polymer network growth is kinetically limited by the monomer diffusion in the solvent. Due to the low solubility of TMC in water and relatively higher solubility of MPD in the organic phase, the diffusion of MPD from the aqueous phase toward the organic phase is indeed the limiting factor for the reaction. The first stage lasts until a dense layer of polymer is formed. A waved morphology is obtained due to the convective monomer transport and reaction. Subsequently, the growth of the polyamide layer is controlled by the transport of the monomer through the densely formed film. The reaction eventually stops when the mass transfer resistance becomes large enough to terminate the MPD transport. The shape of the formed polyamide layer describes the liquid–liquid interface pattern during the polymerization. If no convection occurs during the interdiffusion of monomers, the formed polymerized layer will be smooth. Otherwise, any convection at the interface will urge a pronounced roughness. MPD and ZTM have differential diffusion rates. Since ZTM molecules (268 g/mol) have a much larger size than MPD (108 g/mol), their diffusion to the interface is much lower. Therefore, by increasing the ZTM fraction in the amine mixture, the formation rate of the polyamide is lower and the convection is minimized, leading to a smooth and thin film.

Figure 3. SEM images of the surfaces of the TFC membranes prepared using different ZTM monomer concentrations (wt %) in the amine solution.

The formation of the polyamide layer on the PEI substrate was also verified by FTIR spectra as illustrated in Figure 5. The characteristic peaks of the PEI substrate were observed at 1781 and 1736 cm\(^{-1}\), assigned to the asymmetric and symmetric stretching vibrations of C==O in imide groups. Another peak is at 1356 cm\(^{-1}\), corresponding to the C–N bond stretching vibration in the phthalimide ring, while the 1275 to 1017 cm\(^{-1}\) vibrations are assigned to the aryl ether bonds. These spectra are consistent with the literature report for PEI. Since the penetration of the infrared light in ATR measurements is deeper than the thickness of the polyamide layers, peaks relative to PEI are still present in the recorded spectra after the interfacial polymerization on substrates. As calculated using eq 1, the penetration depth of the IR beam fluctuates from approximately 1.4 (at 2000 cm\(^{-1}\)) to 2.8 \(\mu\)m (at 1000 cm\(^{-1}\)). The thickness of the polyamide layers is 0.067 to 0.452 \(\mu\)m.
New peaks relative to amide groups are seen at 1535 and 1640 cm\(^{-1}\). The peak intensity decreases with the increase of the ZTM fraction due to the reduced thickness of the polyamide layer. On the other hand, no obvious peaks are observed for the sulfonate group. This may be due to the overlap of its characteristic peaks (at 1040 cm\(^{-1}\) for SO\(_3\)\(^{-}\)) with the existent peaks of PEI.

A semi-quantitative evaluation of the surface roughness was obtained by AFM, as shown in Figure 6. The darker regions correspond to the valleys, and the brighter regions indicate the higher hills. The surface roughness is expressed as the root mean square of the height values (\(R_q\)) and is presented in Table 2. The membranes prepared with 100% MPD have the largest fraction of dark areas. When the ZTM fraction in the amine mixture increases, the surfaces become brighter and more uniform in color, reflecting the lower thickness and smoother surfaces, consistent with the SEM results (Figures 3 and 4). The roughness decreases with the increase of the ZTW fraction, as presented in Table 2. According to the Wenzel equation,\(^{54,55}\) the roughness affects the hydrophilicity of a surface according to:

\[ \cos \theta_W = r \cos \theta_Y \]  

where \(\theta_W\) is the effective contact angle on a rough surface and \(\theta_Y\) is the value on the same material if the surface would be completely smooth and \(r\) is the ratio between the total rough surface area and the equally sized smooth surface. The roughness could lower the water contact angle if \(\theta_Y < 90^\circ\), while it promotes a higher water contact angle if \(\theta_Y > 90^\circ\). The

Table 2. Surface Characteristics of TFC Membranes Prepared with Different ZTM Monomer Concentrations (Wt %) in the Amine Solution

<table>
<thead>
<tr>
<th>% zwitterionic monomer (ZTM)</th>
<th>contact angle</th>
<th>roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39 ± 2</td>
<td>75.5</td>
</tr>
<tr>
<td>25</td>
<td>43 ± 2</td>
<td>64.8</td>
</tr>
<tr>
<td>50</td>
<td>23 ± 4</td>
<td>58.7</td>
</tr>
<tr>
<td>75</td>
<td>56 ± 5</td>
<td>33.5</td>
</tr>
<tr>
<td>100</td>
<td>35 ± 2</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Figure 5. ATR-FTIR spectra the TFC membranes prepared with different ZTM monomer concentrations (wt %) in the amine solution.

Figure 6. AFM images of the TFC membranes prepared with different ZTM monomer concentrations (wt %) in the amine solution.
results in Table 2 show that the change in contact angles does not follow a simple trend with the roughness variation. That is due to the fact that both the roughness and the intrinsic hydrophilicity of the groups on the membrane surface are being changed. The lowest contact angles were observed for the 50 and 100% ZTM membranes, while the highest ones were obtained for the 25 and 75% ZTM membranes.

3.3. Nanofiltration Performance of TFC Membranes. The performance of TFC membranes in nanofiltration experiments was evaluated by measuring their pure water permeance and the rejection of three types of dyes: Red Direct 80, Brilliant Blue R250, and Reactive Blue 4 with their molecular weights of 1373, 826 and 637 g/mol, respectively. The results in Table 3 show that the water permeance increases with the increase in the ZTM fraction except the membrane prepared with 100% ZTM. The water permeation is governed by the hydrophilicity of the surface and its effective area. It is commonly agreed that the effective surface area increases with the increase of surface roughness. Considering the 100% ZTM membrane, the effect of reduced roughness and hence effective surface area may be more dominant than the effect of increased hydrophilicity by zwitterionic groups, leading to the decreased water permeance. All the membranes have 100% rejection toward Red Direct 80 and approximately 90 and 80% toward Brilliant Blue and Reactive Blue, respectively. This indicates that incorporation of new zwitterionic monomers into the polyamide layer would not affect membrane separation efficiency. Performance comparison of the membrane developed in this study with others in the literature as presented in Table 4 indicates that the ZTM-based TFC membrane has relatively high flux with comparative dye rejection.

3.4. Fouling Tests of TFC Membranes. The fouling resistance of the TFC membranes was studied by evaluating the static protein adsorption and the water permeation using protein solutions as feed. Bovine serum albumin (BSA) was used as foulant. Figure 7 displays the surface of TFC membranes exposed to fluorescence-labeled BSA, imaged on a fluorescence microscope. A brighter surface corresponds to higher adsorption levels, indicating that the incorporation of zwitterionic groups significantly decreases the protein adsorption. The zwitterionic groups are known to bind a great quantity of free water, preventing the protein molecules from approaching and/or tightly attaching to the membrane surface. This effectively reduces the protein adsorption. In addition, several studies have pointed out that a membrane surface with lower roughness could better resist fouling.

Figure 8 depicts the permeance patterns of the TFC membranes prepared with 100% MPD, 75% ZTM, and 100% ZTW. A BSA solution of 500 ppm was used as feed. All membranes can practically reject 100% BSA and only allow the buffer to pass through. Although the 100% MPD and 75% ZTM membranes have high pure water permeances (24.2 and 43.4 L m⁻² h⁻¹ bar⁻¹), these values rapidly dropped to around 0.6 and 8.7 L m⁻² h⁻¹ bar⁻¹, respectively, when the feed contained the foulant. These values correspond the flux declines of 97.5 and 80%, respectively, as in Table 5. In the opposite, the permeance through the 100% ZTW membrane only slightly decreased from 13.3 to 12.7 L m⁻² h⁻¹ bar⁻¹ with the flux decline of 4.5%. The smooth and highly hydrophilic surface of the 100% ZTW membrane provides the favorable morphology and hydrophilicity to stabilize a hydration layer, which minimizes the protein accumulation and facilitates their removal (if any adsorbed) by hydrodynamic forces.

<p>| Table 3. Pure Water Permeance and Dye Rejection of the TFC Membranes Prepared with Different ZTM Concentrations (wt %) in the Amine Solution |
|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>wt% zwitterionic monomer (ZTM)</th>
<th>pure water permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>dye rejection (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.2 ± 2.4</td>
<td>Red Direct 80 100</td>
<td>Brilliant Blue R250 92.5</td>
</tr>
<tr>
<td>25</td>
<td>30.2 ± 8.8</td>
<td>Brilliant Blue R250 92.7</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>33.8 ± 9.5</td>
<td>Reactive Blue 4 77.9</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>43.4 ± 15.2</td>
<td>Reactive Blue 4 79.2</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>13.3 ± 3.9</td>
<td>Reactive Blue 4 80.2</td>
<td></td>
</tr>
</tbody>
</table>

increases with the increase in the ZTM fraction except the membrane prepared with 100% ZTM. The water permeation is governed by the hydrophilicity of the surface and its effective area. It is commonly agreed that the effective surface area increases with the increase of surface roughness. Considering the 100% ZTM membrane, the effect of reduced roughness and hence effective surface area may be more dominant than the effect of increased hydrophilicity by zwitterionic groups, leading to the decreased water permeance. All the membranes have 100% rejection toward Red Direct 80 and approximately 90 and 80% toward Brilliant Blue and Reactive Blue, respectively. This indicates that incorporation of new zwitterionic monomers into the polyamide layer would not affect membrane separation efficiency. Performance comparison of the membrane developed in this study with others in the literature as presented in Table 4 indicates that the ZTM-based TFC membrane has relatively high flux with comparative dye rejection.

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**Table 4. Pure Water Permeance and Dye Rejection Comparison of the Membrane Prepared in this Study with Others in the Literature**

<table>
<thead>
<tr>
<th>membrane composition</th>
<th>membrane type</th>
<th>PWP (L m⁻² h⁻¹ bar⁻¹)</th>
<th>dye rejection (%)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(tpa)@GO/PES</td>
<td>composite flat-sheet membrane</td>
<td>~39</td>
<td>methylene blue: ~15</td>
<td>48</td>
</tr>
<tr>
<td>PANI/PVP/PSf</td>
<td>hollow fiber membrane</td>
<td>~30</td>
<td>methyl orange: ~65</td>
<td>57</td>
</tr>
<tr>
<td>PA/PSf</td>
<td>thin-film composite membrane</td>
<td>~4</td>
<td>congo red: ~99</td>
<td>58</td>
</tr>
<tr>
<td>PA/PSf</td>
<td>TFC membrane</td>
<td>~13</td>
<td>setazol red: ~99.7</td>
<td>59</td>
</tr>
<tr>
<td>AA/PSf</td>
<td>flat-sheet membrane</td>
<td>~8</td>
<td>congo red: ~99.6</td>
<td>60</td>
</tr>
<tr>
<td>GO/PDA/CA</td>
<td>flat-sheet membrane</td>
<td>~60</td>
<td>neutral red: ~81</td>
<td>61</td>
</tr>
<tr>
<td>ceramic</td>
<td>UF flat-sheet membrane</td>
<td>~14</td>
<td>various dyes: ~87 to 99</td>
<td>62</td>
</tr>
<tr>
<td>ceramic</td>
<td>tight UF flat-sheet membrane</td>
<td>~32</td>
<td>various dyes: 97 to 99.5</td>
<td>63</td>
</tr>
<tr>
<td>TiO₂/bentonite</td>
<td>UF flat-sheet membrane</td>
<td>~16</td>
<td>direct red: 98</td>
<td>64</td>
</tr>
<tr>
<td>clay</td>
<td>UF flat-sheet membrane</td>
<td>~16</td>
<td>acid orange: 85</td>
<td>65</td>
</tr>
<tr>
<td>PA/PEI</td>
<td>TFC membrane</td>
<td>~43</td>
<td>methylene blue: 94</td>
<td>this study</td>
</tr>
</tbody>
</table>

results imply that zwitterionic groups should be completely distributed over the surface for effective antifouling effects, as even a small fraction of MPD (25 wt %) in the 75 wt % ZTM membranes causes a significant flux decline. With a short cleaning period of 10 min, the 100 wt % ZTM membrane could fully recover its initial flux while the 75 wt % ZTM and 100 wt % MPD membranes have FRR values of 66.4 and 4.7%, respectively, implying the needs of longer cleaning duration or harsh cleaning agents. This result again emphasizes the efficiency of ZTM for fouling resistance.

4. CONCLUSIONS

In this study, a new zwitterionic amine (ZTM) was synthesized and employed to develop thin film composite membranes with high fouling resistance. The following conclusions could be drawn:

1. The incorporation of ZTM monomers into the amine solution for the interfacial polymerization reduced the thickness of the polyamide layer and smoothened its surface.

2. The water contact angle on the membrane surface was governed by the amount of zwitterionic groups and the roughness.

3. The incorporation of the ZTM fraction in TFC membranes improved the water permeance without losing their dye rejection capability.

4. The presence of zwitterionic groups in the membrane surface prevented the protein adsorption and hence efficiently maintained the permeance.

Table 5. Flux Declines and Flux Recovery Ratios of the TFC Membranes Prepared with 0, 75, and 100 wt % ZTM in the Fouling Test

<table>
<thead>
<tr>
<th>membrane</th>
<th>flux decline (%)</th>
<th>FRR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt % ZTM</td>
<td>97.5</td>
<td>4.7</td>
</tr>
<tr>
<td>75 wt % ZTM</td>
<td>80.0</td>
<td>66.4</td>
</tr>
<tr>
<td>100 wt % ZTM</td>
<td>4.5</td>
<td>~100</td>
</tr>
</tbody>
</table>

Figure 7. Fluorescence microscopic images and the respective relative fluorescence intensities of the TFC membranes prepared with different ZTM concentrations (wt %) after exposure to a 0.35 mg/mL BSA-FITC solution for 1 h.

Figure 8. Fouling test of the TFC membranes prepared with 0, 75, and 100 wt % ZTM in the amine mixture, using BSA as the foulant. The transmembrane pressures were normalized to provide the same initial water fluxes for all membranes.

Table 5. Flux Declines and Flux Recovery Ratios of the TFC Membranes Prepared with 0, 75, and 100 wt % ZTM in the Fouling Test

<table>
<thead>
<tr>
<th>membrane</th>
<th>flux decline (%)</th>
<th>FRR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt % ZTM</td>
<td>97.5</td>
<td>4.7</td>
</tr>
<tr>
<td>75 wt % ZTM</td>
<td>80.0</td>
<td>66.4</td>
</tr>
<tr>
<td>100 wt % ZTM</td>
<td>4.5</td>
<td>~100</td>
</tr>
</tbody>
</table>
Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.0c04738

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS

AA        acrylic acid
AFM       atomic force microscopy
ATR       attenuated total reflectance
BSA       bovine serum albumin
CA        cellulose acetate
DiEG      diethylene glycol
FESEM     field emission scanning electron microscope
FITC      fluorescein isothiocyanate-conjugated
FTIR      Fourier transform infrared spectroscopy
GO        graphene oxide
MPD       m-phenylenediamine
MWCO      molecular weight cut-off
NMP       N-methyl-pyrrolidone
PANI      polyaniline
PDA       polydopamine
PEG       poly(ethylene glycol)
PEI       polyethylenimine
PEO       poly(ethylene oxide)
PES       polyethersulfone
PSI       polysulfone
PVP       polyvinylpyrrolidone
TFC       thin-film composite
TMC       trimesoyl chloride
ZTM       zwitterionic triamine monomer

Nomenclatures

A            membrane area (m²)
FRR          flux recovery ratio (%)
R            dye rejection (%)
Rq           root mean squared roughness (nm)
r           roughness
Cp          dye concentration in the permeate (ppm)
Cf          dye concentration in the feed (ppm)
t           time (s)
ΔP          transmembrane pressure (bar)
ΔV           volume (L)
θ           water contact angle (°)

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