Modification of porous polyetherimide hollow fiber membrane by dip-coating of Zonyl® BA for membrane distillation of dyeing wastewater

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ABSTRACT

Wetting and fouling have significantly affected the application of membrane distillation (MD). In this work, a dip-coating method was used for improving surface hydrophobicity of the polyetherimide (PEI) hollow fiber membrane. An air gap membrane distillation (AGMD) process was applied for treatment of the methylene blue (MB) solution. The porous PEI membrane was fabricated by a dry-wet spinning process and the hydrophobic 2-(Perfluoroalkyl) ethanol (Zonyl® BA) was used as the coating material. From FESEM, the modified PEI-Zonyl membrane showed an open structure with large finger-like cavities. The modified membrane displayed a narrow pore size distribution with mean pore size of 0.028 μm. The outer surface water contact angle of the PEI-Zonyl membrane increased from 81.3° to 100.4° due to the formation of an ultra-thin coated layer. The pure water flux of the PEI-Zonyl membrane was slightly reduced compared to the pristine PEI membrane. A permeate flux of 6.5 kg/m² h and MB rejection of 98% were found for the PEI-Zonyl membrane during 76 h of the AGMD operation. Adsorption of MB on the membrane surface was confirmed based on the Langmuir isotherm evaluation, AFM and FESEM analysis. The modified PEI-Zonyl membrane can be a favorable alternative for AGMD of dyeing wastewaters.

Key words: air gap membrane distillation, coating, dyeing wastewater treatment, polyetherimide hollow fiber membrane, Zonyl® BA fluorotelomer intermediate

HIGHLIGHTS

• The porous PEI membrane was modified by surface coating of Zonyl® BA.
• A narrow pore size distribution with mean pore sizes of 0.028 μm was observed.
• The outer surface water contact angle was increased from about 81° to 100°.
• A more stable AGMD of the MB solution was found for the modified membrane.
• A lower flux decline ratio was observed for the modified PEI-Zonyl membrane.

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INTRODUCTION

A large amount of wastewater is annually produced in the textile industries due to consumption of water in various wet processes (Ramlow et al. 2017). According to the World Bank, around 17–20% of industrial water pollution originates from the textile industry (Kant 2012). Approximately 280,000 tons of textile dyes are annually discharged as industrial waste worldwide (Ali 2010). Mostly, textile wastewaters contain a complex composition with reactive ingredients that can cause major global environmental issues. For dyeing wastewater treatment, several processes such as physicochemical, biochemical, and hybrid processes have been applied (Holkar et al. 2016). However, these processes have shown drawbacks such as low separation efficiency, high maintenance cost, and consumption of unsafe chemicals. In the biological processes, an increasing risk of environmental pollution is possible due to the impacts of temperature, pH, and different organic pollutants in the textile wastewater (Pazdzior et al. 2019). In the adsorption processes, the regeneration of the adsorbents is a challenging process and their disposal can cause environmental issues (Zhou et al. 2019).

Membrane technology has shown advantages over traditional wastewater treatment processes (Sójka-Ledakowicz et al. 1998; Rozzi et al. 1999). Superior quality of the produced water without addition of chemicals and a compact process due to modular configuration are the main advantages of the membrane technology. Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and also the membrane bioreactor (MBR) as pressure driven processes have been used for dyeing wastewater treatment (Lau & Ismail 2009; Abid et al. 2012; Jegatheesan et al. 2016; Zou et al. 2019). However, fouling has been a major problem for industrial application of the pressure-driven membrane processes. Membrane distillation (MD) processes have attracted attention for dyeing wastewater treatment due to their low fouling tendency. MD, as a temperature-driven process, has shown various benefits over the pressure-driven membrane processes such as total rejection of non-volatile elements, low sensitivity to the feed concentration, and low operating temperature and pressure (Mokhtar et al. 2014; Drioli et al. 2015). So far, several studies have been conducted for dyeing wastewater treatment by the MD processes. An et al. (2016) applied hydrophobic membranes of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) in a direct contact membrane distillation (DCMD) process for treatment of the dyeing wastewater discharged by the textile industry. Due to the strong negative charge and chemical structure of the PTFE membrane, the dye absorption mainly occurred on the membrane surface rather than in the pores, which can cause an easy flux recovery by water flushing. For treating 100 mg/L of dye mixtures, the
PTFE membrane indicated a stable flux and higher dye rejection during five days' operation. Mokhtar et al. (2016) fabricated nanocomposite hollow fiber membranes of PVDF-Cloisite 15A for treatment of industrial textile wastewater through a DCMD process. A treatment efficiency of over 89% was found for the industrial effluent. However, the permeation flux of the membrane was reduced about 50% during a few hours of the process and then the flux remained almost stable at 15 kg/m² h. Leaper et al. (2019) applied a commercial PTFE membrane in an air gap membrane distillation (AGMD) process to recover water from the simulated textile wastewater containing NaCl and either sunset yellow (SY) or rose bengal (RB) dyes and sodium dodecyl sulphate (SDS) surfactant. Their results showed that a stable flux of 11.7–12.6 L/m² h and 100% salt and dye removal for binary feed solutions (NaCl + SY or RB) were achieved for over 20 h of the operation. Based on a low flux deterioration and potentially higher thermal efficiency, they demonstrated that AGMD could be the most suitable configuration for dye removal. Criscuoli et al. (2008) used commercial polypropylene (PP) capillary membranes through a vacuum membrane distillation (VMD) process for treatment of several dyeing solutions. They found that the membrane swelling occurred because of the interaction between the dyes and the polymer, which could increase the permeation flux. Due to the membrane fouling, a flux reduction was observed during 30 min of operation. Hydrophobic surface modification of porous polyetherimide (PEI) hollow fiber membranes was performed by Mousavi et al. (2021) for dyeing wastewater treatment via a sweeping gas membrane distillation (SGMD) process. The membrane, surface coated by polydimethylsiloxane (PDMS), showed about 19% permeate flux reduction during about 140 h of the operation. The improved PEI membrane presented a good anti-fouling property with a flux recovery ratio of about 89%.

It should be noted that improving surface properties of the membrane plays an important role in minimizing wetting and fouling in the MD processes. The improved surface hydrophobicity and surface porosity are essential factors that can reduce wetting and increase the vapor-liquid contact area to increase the membrane permeation flux. In addition, a weak interaction with the foulant in the feed stream due to the modified surface can enhance the anti-fouling property of the membrane, resulting in a stable MD operation. Therefore, hydrophobic surface modification is usually required to improve the water-resistant and anti-fouling properties of the polymeric membranes for MD applications. Hydrophobic surface modification of the membranes has been conducted through different methods such as UV and plasma treatment, coating, and blending (Ahmad et al. 2015). Among the various modification methods, surface coating is known as an easy approach that has been applied at large scale for various applications.

The hydrophobic nature of fluorinated compounds makes them favorable alternatives for enhancing the hydrophobicity of the membranes. Fluorohydrocarbon macromolecules have unique properties such as high wetting resistance and good thermal stability, making them useful materials in wide variety of applications. From an extensive literature survey, almost all of the fluorinated surface-modifying macromolecules (SMM) were blended with the polymer solutions in order to enhance surface hydrophobicity of the polymeric membranes for various applications (Ho et al. 2000; Kim et al. 2009; Essalhi & Khayet 2012; Khayet 2013; Mansourizadeh et al. 2014). However, it should be noted that the complete migration of SMM to the membrane surface is the main challenge during the membrane fabrication process.

In the present study, a dip-coating process was used for complete deposition of 2-(Perfluoroalkyl) ethanol (Zonyl® BA fluorotelomer intermediate) as a fluorinated SMM on the surface of a highly porous PEI hollow fiber membrane. To the best of our knowledge, there is no research in the literature regarding surface modification of the PEI membranes by Zonyl® BA for MD of dyeing wastewater. The pristine and surface-modified PEI hollow fiber membranes were characterized in terms of field emission scanning electronic microscopy (FESEM), fourier transform infrared spectroscopy (FTIR), pore size distribution, mechanical strength, overall porosity, critical water entry pressure (CEPw) and water contact angle. The separation performance of the membranes for removal of methylene blue (MB) from the wastewater was evaluated through an AGMD process.

**EXPERIMENTAL**

**Materials**

PEI pellets (Utem®1000) were provided from General Electric Co. to fabricate porous hollow fiber membranes. 1-Methyl-2-pyrrolidone (NMP) was supplied by Merck and used as the solvent for preparation of the PEI solution. Glycerol (Merck) was used as non-solvent phase-inversion promoter additive in the PEI solution. 2-(Perfluoroalkyl) ethanol with the trade name of Zonyl® BA was purchased from Sigma-Aldrich for preparation of the
coating solution. The chemical structure of Zonyl® BA is shown in Figure 1. Acetone (Merck) was used as the solvent for Zonyl® BA. Ethanol (>99.8%, Sigma-Aldrich) was used for post-treatment of the membranes. Methylene blue (MB) was provided by Sigma-Aldrich and used as a cationic dye for preparation of the dyeing solution.

Fabrication and modification of PEI hollow fiber membranes

For the membrane fabrication, first a homogeneous PEI solution was prepared under continuous stirring at 60 °C for 12 h. The composition of the polymer solution was PEI/glycerol/NMP 14/4/82 wt%. Then the prepared solution was de-bubbled by an ultrasonic bath through a lenient condition (treatment time of 15 min; frequency of 25 kHz; and temperature of 60 °C) in order to minimize degradation of the polymer. The hollow fiber membranes were fabricated by a dry-wet spinning process under constant spinning conditions (Table 1). The prepared wet fibers were immersed in distilled water for 3 days to remove residual solvent and non-solvent. Before drying the fibers at room temperature, they were immersed in pure ethanol for 15 min to prevent the membrane pores’ deformation.

Surface modification of the dry hollow fibers was performed via a dip-coating process. The coating solution was prepared by dissolution of 2 wt% Zonyl in acetone. By immersion of the hollow fibers in the coating solution for 30 min, an ultra-thin coated layer was deposited on the outer surface. Then, curing of the hollow fibers was performed at 70 °C in a vacuum oven for 12 h. This coating condition was chosen to enhance surface hydrophobicity of the membrane without a considerable reduction in the surface porosity.

Characterization of the hollow fiber membranes

Morphology of the pristine and modified PEI hollow fiber membranes was analyzed by field emission scanning electronic microscopy (Hitachi S-4700 FESEM). The hollow fibers were cracked in liquid nitrogen and coated by sputtering platinum before analyzing the cross-section, inner surface and outer surface by FESEM. In addition, the inner skin layer of the modified PEI-Zonyl hollow fiber membrane was analyzed after the long-term AGMD experiment of the dyeing solution.

Functional groups on the outer surface of the prepared membranes were examined by Fourier transform infrared spectroscopy (FTIR) (Thermo Nicolet Nexus 870 FT-IR spectrometer). The scanning range of 3,700–700 cm⁻¹ was used for taking FTIR spectra at room temperature.

**Table 1 | Dry-wet spinning conditions for the porous PEI membrane fabrication**

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope extrusion rate (cm³/min)</td>
<td>1.8</td>
</tr>
<tr>
<td>Bore fluid rate (cm³/min)</td>
<td>0.6</td>
</tr>
<tr>
<td>Bore composition (wt.%)</td>
<td>NMP/H₂O 70/30</td>
</tr>
<tr>
<td>External coagulant</td>
<td>Tap water</td>
</tr>
<tr>
<td>Air gap distance (cm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Spinneret o.d./i.d. (mm/mm)</td>
<td>0.7/0.3</td>
</tr>
<tr>
<td>Spinning dope temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>External coagulant temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Jet-stretch ratio*</td>
<td>1</td>
</tr>
</tbody>
</table>

*The ratio of wind-up drum velocity to the dope extrusion velocity.
Pore size distribution and mean pore size of the hollow fiber membranes were evaluated through a capillary flow porometer (3H-2000PB, Beshide Instrument Technology Co., Ltd., China). For measuring the bubble point of the membranes, three pieces of the dead-ended hollow fibers with a length of 6 cm were fully wetted by immersion in isopropanol (surface tension 21.7 dynes/cm and density 786 kg/m³) and then sealed in the sample chamber. The chamber was gradually pressurized by pure nitrogen until it overcame the capillary force through the largest pore (bubble point). Then, the pore size was calculated by Laplace-Young equation (Rehman et al. 2019). After obtaining the bubble point, further increase of pressure in the chamber was achieved and the nitrogen permeation flow rate was measured until all the pores became empty and the membrane became dry. Nitrogen permeation flow rate of the dry sample was also measured as a function of pressure. By a computer software attached to the capillary flow porometer, the bubble point and pore size distribution were calculated based on the nitrogen flow rates of the wet and dry membranes.

The overall porosity of the hollow fiber membranes was measured based on the weighting method (Mansourizadeh & Ismail 2010; Kong et al. 2020). To measure the weight of the wet samples, three hollow fibers with a length of 50 cm were immersed in distilled water for three days. Then they were dried in a vacuum oven at 105 °C for about 2 h in order to measure weight of the dry samples. The overall porosity (ε_o) was calculated as the ratio of pore volume to total volume of the hollow fibers:

\[
\varepsilon_o(\%) = \frac{(W_w - W_d)/\rho_w}{(W_w - W_d)/\rho_w + W_d/\rho_p} \times 100
\]

where \(\rho_w\) and \(\rho_p\) are water density and polymer density (kg/m³), respectively. The density of PEI is 1,270 kg/m³. \(W_w\) and \(W_d\) are the weight of the wet and dry samples (kg), respectively.

Surface hydrophobicity of the PEI membranes was examined by water contact angle measurement. A contact angle goniometer (DSA20E, KRUSS), equipped with image-processing software, was used to measure the contact angle of the outer and inner surface of the hollow fiber membranes. The droplet size and rate were adjusted to be 0.2 μL and 0.5 μL/s, respectively. An average value of contact angle was reported at ten different locations of the membrane surface.

The pore wetting resistance of the hollow fiber membranes was estimated by measuring critical entry pressure of water (CEP_w). In fact, CEP_w is known as the applied pressure difference across the membrane that water can penetrate into the membrane pores. The CEP is related to surface tension of the liquid, contact angle of the liquid with the membrane surface and size and shape of the membrane pores (Dindore et al. 2004; Shirazi et al. 2020). The CEP is calculated by Laplace–Young equation (Franken et al. 1987) as:

\[
CEP = -\frac{2\gamma_l \cos \theta}{r_{max}}
\]

where \(\gamma_l\) is surface tension of the liquid; \(\theta\) is contact angle of the liquid with the membrane surface; \(r_{max}\) is the membrane maximum pore radius; and \(\beta\) is geometric coefficient of the pore. For uniform cylindrical pores, \(\beta\) is equal to 1 and it is in the range of \(0 <\beta < 1\) for the pores having irregular shapes.

In order to measure CEP_w, the membrane module was prepared by potting two dead-end hollow fibers in a stainless steel tube. The opening lumen side of the hollow fibers was connected to the discharge section of a diaphragm pump. Distilled water was pressurized into the lumen side of the hollow fibers and the pressure was gradually increased at 50 kPa intervals. The hollow fibers were retained at each constant pressure for 10 min and the appearance of the first water droplet on the outer surface was reported as CEP_w. Since the largest pores of the membrane are initially wetted, the CEP_w is related to the maximum pore size of the membrane. For each membrane sample, the test was repeated three times and the average value was reported.

Mechanical stability of the hollow fiber membranes was examined via a tensile strength machine (model: INSTRON 5564) according to ASTM D3379. A constant elongation velocity of 20 mm/min was applied to measure the Young’s modulus (MPa), stress at break (MPa) and strain at break (%) of the hollow fiber samples with a length of 10 cm.

For fouling analysis of the modified PEI-Zonyl membrane, 3D atomic force microscopy (AFM) images of the inner surface for the unused membrane and the membrane fouled by MB in the AGMD process were captured.
An AFM (DUALSCOPE 95-200E, DME, Denmark) was used to capture 3D images of the dried hollow fiber membrane.

**AGMD of dyeing solution and fouling analysis**

The hollow fiber membrane module was prepared and then it was applied in the AGMD system for treatment of the MB solution. The characteristics of the membrane module are given in Table 2 and the schematic illustration of the AGMD set up is shown in Figure 2. In order to prepare the module, 20 hollow fibers with a length of 30 cm were packed in a stainless steel tube. The gap between the fibers was adjusted to be 2 mm and the air gap between the bundle of fibers and the shell surface was 5 mm. Both end sides of the hollow fibers were sealed to the shell surface by an epoxy adhesive. The temperature of the shell surface was controlled at 5 °C by an outside cooling jacket using ice water circulation. The images of the experimental AGMD set-up and the membrane module are presented in Figure 3.

For preparation of the stock dyeing wastewater, MB powder was dissolved in distilled water to achieve 1,000 mg/L concentration. By dilution of the stock solution, a concentration of MB solution in the range of 50–200 mg/L was used in the AGMD experiments. The temperature of the MB solution in the tank was controlled by an electric heater in the range of 35–80 °C. In order to minimize the heat loss of the AGMD system, the module and all the tubes were insulated. Using a diaphragm pump, the MB solution was flowed into the lumen side of the hollow fiber membranes in a continuous mode of operation. The flowrate and pressure of the solution were set as 0.2 L/min and 50 kPa, respectively. The temperature of the module wall was set to 5 °C using a cooling heat exchanger. The permeate water vapor was condensed in the shell side of the module.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Characteristics of the experimental AGMD module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>Module o.d. (cm)</td>
<td>1.4</td>
</tr>
<tr>
<td>Module length (cm)</td>
<td>30</td>
</tr>
<tr>
<td>Effective fiber length (cm)</td>
<td>20</td>
</tr>
<tr>
<td>Fiber o.d. (mm)</td>
<td>0.7</td>
</tr>
<tr>
<td>Fiber i.d. (mm)</td>
<td>0.4</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>20</td>
</tr>
<tr>
<td>Effective membrane area (cm²)</td>
<td>88</td>
</tr>
<tr>
<td>Air gap width (cm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Cooling surface temperature (°C)</td>
<td>5</td>
</tr>
</tbody>
</table>

![Figure 2](image-url) Schematic illustration of the AGMD set up.
and the permeation flux \((J)\) was calculated as:

\[
J = \frac{m}{A_i \times t}
\]  

(3)

where \(J\) is the permeation flux (kg/m\(^2\) h); \(m\) (kg) is the weight of permeate water in time \(t\) (h); and \(A_i\) (m\(^2\)) is the inner surface of the hollow fibers in the module. The MB rejection (\(R\)) of the membranes was calculated as:

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

(4)

where \(C_p\) (mg/L) is the MB concentration in the permeate water and \(C_f\) (mg/L) is the MB concentration in the feed solution.

**Figure 3** | Image of the experimental AGMD system: (a) the membrane module and (b) the AGMD setup.
To measure the concentration of the MB solutions in the feed and permeate, a UV-VIS spectrophotometer (UV-2600, Shimadzu, Japan) at maximum wavelength of 664 nm was applied. At five standard concentrations of the MB solutions, a calibration curve was plotted to obtain the solution concentration during the AGMD experiments.

Antifouling property of the membranes was examined by flux recovery ratio (FRR). The pure water flux of the unused membrane and those used in the MB separation test were measured through the AGMD process. The used membranes were flushed by circulating distilled water at flowrate of 0.2 L/min in the lumen side of the hollow fibers for 20 min before measuring the pure water flux. The FRR of the membranes was calculated as (Johari et al. 2020):

$$FRR(\%) = \left( \frac{J_w}{J_{w0}} \right) \times 100$$ (5)

where $J_{w0}$ is the pure water flux of the unused membrane and $J_w$ is the pure water flux of the used membrane.

The flux decline ratio ($FD$) of the membranes was measured to evaluate the adsorption of MB on the surface. The $FD$ indicates the permeation performance of the membranes as a function of the MB concentration and is calculated as (An et al. 2017):

$$FD(\%) = \left( 1 - \frac{J_{op}}{J_{w0}} \right) \times 100$$ (6)

where $J_{op}$ is the permeate flux of the membrane after 500 min of the MB separation experiment.

The MB adsorption amount of the membranes can be evaluated by the dimensionless factor of the Langmuir isotherm ($R_L$) (Kundu & Gupta 2006):

$$R_L = \frac{1}{1 + \frac{b}{C_0}}$$ (7)

where $b$ is the Langmuir constant and $C_0$ is the initial concentration of MB in the feed solution. A favorable adsorption is occurred in $0 < R_L < 1$. While, $R_L > 1$, $R_L = 1$, and $R_L = 0$ demonstrate unfavorable, linear, and irreversible adsorption, respectively (Mckay et al. 1982).

When the equilibrium concentration ($C_e$) is considered to be equal to $C_0$ as the MB concentration in the feed solution is constant, the Langmuir constant of $b$ and $FD_{max}$ can be measured by the linear relationship between the $FD$ and $C_0$ as below equation (An et al. 2017):

$$\frac{C}{FD} = \frac{C_0}{FD_{max}} + \frac{1}{b \times FD_{max}}$$ (8)

**RESULTS AND DISCUSSION**

**Morphological study of the PEI and PEI-Zonyl hollow fiber membranes**

The FESEM images of the cross-section, outer surface and inner surface of the pristine PEI and modified PEI-Zonyl hollow fiber membranes are shown in Figure 4. The pristine PEI membrane presented the outer and inner layers with a large finger-like structure, which can confirm a fast solidification during the phase-inversion process. Since a weak non-solvent (aqueous solution of 70% NMP) was used for the bore fluid, the smaller finger-like of the inner layer can be related to a delay phase-inversion. In addition, the formation of an open micro-porous inner surface is correlated to a delay phase-inversion. A similar inner surface morphology with open structure was reported by Santos et al. (2019) for the PEI hollow fiber membrane prepared by the bore fluid of water/NMP (1:1 v/v). From the outer surface image, the pristine PEI membrane presented a high surface porosity with nano-scale pore sizes because of the fast phase-inversion of the polymer solution in water. The fabricated porous PEI membrane with open structure and high surface porosity can be a potential choice for surface coating to show a low mass transfer resistance.
From Figure 4(A2), the coating process couldn’t affect the cross-section morphology for the modified PEI-Zonyl membrane. It can be seen that the pore size of the inner and outer surface of the membrane was decreased due to the formation of an ultra-thin coated layer. The nano-scale pores on the outer surface of the PEI-Zonyl membrane were not clearly visible at high magnification (30 K) of FESEM due to the formation of a uniform coated layer. Although the coated layer can affect the membrane resistance to some extent, increasing the surface hydrophobicity can be a dominant effect for the MD process. In this work, an attempt was made to enhance surface hydrophobicity of the membrane by coating hydrophobic Zonyl in a way to have the minimum effect on the surface porosity and flux reduction.

**FTIR analysis of the PEI and PEI-Zonyl hollow fiber membranes**

Figure 5 represents the FTIR spectra of the pristine PEI and PEI-Zonyl hollow fiber membranes. The pristine PEI membrane demonstrated bands at 1,778, 1,726 and 1,356 cm\(^{-1}\) which are correlated to asymmetric imide carbonyl, symmetric imide carbonyl and C-N stretch of imide groups, respectively (Garcia et al. 2017). For the modified PEI-Zonyl membrane, the relative intensity of peaks was significantly decreased, which can be related to the formation of the ultra-thin coated layer of Zonyl. In addition, the PEI-Zonyl membrane showed peaks near 3,450 cm\(^{-1}\) and 1,200 cm\(^{-1}\) which can be associated to the stretching OH and CF\(_2\) functional groups of Zonyl, respectively. For the blend PVDF-Zonyl membrane, Kim et al. (2009) indicated that the O-H group was
not enough on the membrane surface to be detected by FTIR. It can be said that the coating method for enhancement of surface hydrophobicity by the SMM has advantages over the blending method since a complete deposition of the SMM on the membrane surface is possible.

**Characteristics of the pristine PEI and PEI-Zonyl hollow fiber membranes**

In the present study, an attempt was made to improve surface hydrophobicity of the highly porous PEI hollow fiber membrane. An ultra-thin coated layer of hydrophobic Zonyl was formed on the membrane surface in order to minimize the surface porosity reduction. The characteristics of the fabricated hollow fiber membranes were examined in terms of pore size distribution, $C_{EP\text{w}}$, outer and inner surface water contact angle, and overall porosity. The characterization results are shown in **Table 3**.

**Figure 6** represents the pore size distribution of the pristine PEI and PEI-Zonyl hollow fiber membranes and the mean pore size of the membranes is given in **Table 3**. The pristine PEI membrane presented a wider pore size distribution and a larger mean pore size compared to the modified PEI-Zonyl membrane which can be confirmed by the FESEM image of the outer surface. The pristine PEI and PEI-zonyl membranes presented mean pore size of 0.036 $\mu$m and 0.028 $\mu$m, respectively. It can be seen that the coated layer of Zonyl resulted in a narrow pore size distribution, which is an appropriate parameter for separation performance of the porous membranes. Moreover, application of membranes with small pore size and narrow pore size distribution may reduce the membrane fouling and wetting during the MD process. Indeed, the membranes with larger pore sizes are more favorable to irreversible internal pore fouling (Jin et al. 2010), while the membranes with smaller pore sizes can cause reversible fouling (cake layer formation). Internal pore fouling can reduce surface hydrophobicity of the pores, which may facilitate the membrane wetting (McGaughey et al. 2020). Membrane wetting can affect the permeation flux and the solute rejection of the MD process.

**Table 3** | Characteristics of the PEI hollow fiber membranes

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
<th>PEI</th>
<th>PEI-Zonyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean pore size ($\mu$m)</td>
<td>0.036</td>
<td>0.028</td>
<td></td>
</tr>
<tr>
<td>Outer surface contact angle (°C)</td>
<td>81.3 ± 2.5</td>
<td>100.4 ± 1.3</td>
<td></td>
</tr>
<tr>
<td>Inner surface contact angle (°C)</td>
<td>78.6 ± 3.4</td>
<td>92.3 ± 2.2</td>
<td></td>
</tr>
<tr>
<td>Overall porosity (%)</td>
<td>82.2</td>
<td>80.5</td>
<td></td>
</tr>
<tr>
<td>$C_{EP\text{w}}$ (kPa)</td>
<td>200</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>Pure water flux @ $T_f = 80$ °C (kg/m² h)</td>
<td>21.6</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>FRR (%)</td>
<td>76.5</td>
<td>87.6</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 6** | Pore size distribution of the pristine PEI and PEI-Zonyl hollow fiber membranes.
Surface hydrophobicity of the membranes was evaluated by measuring the outer and inner surfaces water contact angle, as the results show in Table 3. As can be seen, the coating of Zonyl resulted in improvement of the outer surface contact angle from about 81° to 100°, which is related to the increment of fluorine content at the membrane surface. Furthermore, a lesser improvement in contact angle of the inner surface was observed. It was found by Zhao et al. (2007) that not only the hydrophilic additives but also the produced larger pore size and high surface porosity can significantly reduce the contact angle of the PVDF membrane. Indeed, the larger pore sizes on the inner surface of the PEI-Zonyl membrane results in a greater diffusion of the water droplets in the pores, which presents a lower contact angle. It should be noted that the membrane surface hydrophobicity plays an important role in the stability and production flux of the MD process.

Wetting resistance of the pristine PEI and PEI-Zonyl membranes was measured in terms of CEPw. From Table 3, the pristine PEI and PEI-Zonyl membranes showed CEPw of 200 and 350 kPa, respectively. This significant improvement in the wetting resistance of the modified membrane is related to the enhanced surface hydrophobicity and the smaller pores due to the coated layer of Zonyl. Based on the Laplace-Young equation, wetting pressure of the porous membrane is proportional to the surface contact angle and the pore size. It should be noted that the pressure difference across the membrane should be lower than the CEPw to achieve a long-term stable MD operation. CEPw in the range of 42–240 kPa has been reported in the literature for MD applications (Shirazi et al. 2020). Indeed, the improved membrane structure with high surface hydrophobicity and small pore size has shown promising performance in the MD applications. In this study, the AGMD of the MB solution is performed at a pressure difference of 50 kPa. Hence, it is expected that the modified PEI-Zonyl membrane will present a stable AGMD operation.

The prepared pristine PEI membrane presented a high overall porosity of about 82% due to the produced open morphology with large finger-like cavities. In general, the finger-like structure of the asymmetric membranes provides a higher porosity compared to a sponge-like structure (Mansourizadeh & Ismail 2012). It is worth mentioning that the type and concentration of non-solvent additive and the polymer concentration in the casting solution play an important role in the membrane morphology and overall porosity. Usually, using a low polymer concentration and a strong non-solvent additive in the polymer solution can provide asymmetric membranes with high overall porosity. It was found by Bakeri et al. (2010) that the overall porosity of the PEI hollow fiber membrane decreased from 86.7 to 78.9% when the PEI concentration increased in the polymer solution from 10 to 15%. This porosity reduction was related to the increase of membrane density. In the present study, by using 14% PEI concentration and 4% glycerol as non-solvent additive in the polymer solution, the prepared PEI membrane presented a good overall porosity. In addition, the modified PEI-Zonyl membrane showed a slightly lower porosity than the pristine PEI membrane, which may be related to the blocking of the small pores and deposition of Zonyl on the finger-like cavities due to the coating process. Indeed, a high void fraction in the membrane matrix can decrease the membrane mass transfer resistance for the MD application.

A tensile strength experiment was performed to evaluate mechanical stability of the pristine PEI and PEI-Zonyl hollow fiber membranes in terms of Young’s modulus, stress at break and strain at break. The obtained results are given in Table 4. It can be seen that the modified PEI-Zonyl membrane presented a higher modulus and stress at break, which can be related to the formation of a coated layer on the membrane surface. In addition, the coated layer resulted in a slight increase of the strain at break, which represents a more flexible state of the membrane. Therefore, these values indicated that the membrane can easily withstand the AGMD process since it is operated at a low pressure.

From the AGMD process, the pure water flux of the membranes was measured and the results are presented in Figure 7. By increasing the temperature of water from 35 to 80 °C, a significant increase in the water flux of the membrane was observed due to the increment of driving force for mass transfer. Because of the lower surface porosity of the coated membrane, a small reduction in the water flux of the PEI-Zonyl membrane was observed.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Young’s modulus (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>122.6 ± 5.4</td>
<td>3.5 ± 0.2</td>
<td>2.7 ± 0.3</td>
</tr>
<tr>
<td>PEI-Zonyl</td>
<td>164.6 ± 7.2</td>
<td>5.5 ± 0.2</td>
<td>3.6 ± 0.4</td>
</tr>
</tbody>
</table>
compared to the pristine PEI membrane. At a feed temperature of 65 °C, the pristine PEI and PEI-Zonyl hollow fiber membranes presented a pure water flux of 12.8 and 10.5 kg/m² h, respectively. In fact, the reduction of pore sizes and blocking of the small pores by the ultra-thin coated layer can cause a lower vapor-liquid contact area during the AGMD process which can affect the mass transfer process and the subsequent permeation flux (Lu et al. 2016; Ajdar et al. 2019).

AGMD of the MB solution and fouling study
Surface hydrophobicity of the porous PEI hollow fiber membranes was improved by coating an ultra-thin layer of Zonyl and the membranes were used in an AGMD process for treatment of the dyeing solution. At the same conditions for the pristine PEI and PEI-Zonyl membranes, the AGMD operation was performed for about 500 min and the results are shown in Figure 8. The pristine PEI membrane showed an initial permeation flux of 12.3 kg/m² h and then a continuing flux reduction (about 40%) was observed during 500 min of the AGMD operation. This significant water flux reduction can be related to the membrane wetting due to the low surface hydrophobicity. In addition, in the MD processes, the surface fouling of the membrane by a non-volatile solute can also improve the membrane pore wetting and flux reduction (Choudhury et al. 2019). On the other hand, the modified PEI-Zonyl membrane presented a lower initial flux (10.3 kg/m² h) due to the coated Zonyl layer. The modified membrane showed a gradual 22% flux reduction during about 200 min and then the flux remained almost stable until the end of the operation. The lesser flux reduction of the modified membrane can be attributed to the enhanced surface hydrophobicity and a less fouling tendency. A similar trend of flux reduction was reported for the composite PVDF hollow fiber membrane during the VMD of the MB solutions (Li et al. 2019).
Since the permeation flux of the membrane is related to the rate of vapor diffusion in the pores, the surface porosity and pore size of the membrane have an important effect on the flux (Mousavi et al. 2021). Meanwhile, the surface hydrophobicity plays an important role in the stability of the permeation flux. Therefore, although the PEI-Zonyl membrane showed a lower initial permeation flux, a more stable flux was achieved for this membrane.

MB rejection performance of the modified PEI-Zonyl membrane is shown in Figure 8. In the MD processes, generally water vapor diffusion through the pores of a porous hydrophobic membrane provides the complete rejection of a non-volatile solute. However, when the membrane is wetted, the penetration of non-volatile solute into the permeate side can reduce the rejection percentage. As can be seen in Figure 8, at the initial stage of the operation, almost a complete rejection of MB was achieved and then a slight reduction in the rejection of MB was observed at the end of the operation (98.5%), which can be related to the total wetting of the larger pores. Due to the higher wetting tendency of the pristine PEI membrane (lower hydrophobicity), MB rejection of about 96.6% was observed after 500 min of the AGMD operation. It was observed by Ren et al. (2018) that non-volatile organic compounds can ideally pass through the wetted pores to the permeate side of the MD process, which can affect the membrane rejection.

Long-term performance of the modified PEI-Zonyl membrane was compared with a commercial PTFE membrane for dyeing wastewater treatment through a continuous mode of AGMD operation and the results are shown in Figure 9. The commercial PTFE membrane was used by Leaper et al. (2019) for treatment of a feed solution containing RB + NaCl + SDS surfactant. The PTFE membrane has a mean pore size, porosity and contact angle of 0.2 μm, 80% and 105°, respectively. From Figure 8, the PEI-Zonyl membrane presented a more stable operation with a gradual flux reduction of about 38% for over 72 h. On the other hand, the PTFE membrane showed a step-wise flux reduction of about 75% during 70 h of the operation. As mentioned by Leaper et al. (2019), the possible reason for such a trend of flux reduction was the formation of a fouling layer due to the amphiphilic structure of SDS and subsequent washing away of the weakly-bound fouling layer. Indeed, fouling and wetting are two interrelated phenomena that can affect each other (Choudhury et al. 2019). It can be said that although both compared membranes presented almost similar hydrophobicity, the higher operational stability of the PEI-Zonyl membrane can possibly be attributed to the improved asymmetric structure, with smaller pores and improved wetting resistance. It is worth mentioning that the porous PTFE membranes are usually fabricated by thermal and stretching methods (Feng et al. 2018; Li et al. 2018), which demonstrate symmetric structure with larger pore sizes compared to the asymmetric porous membranes fabricated by the non-solvent induced phase separation (NIPS) method.

In addition, the separation performance of various hydrophobic membranes for MD of the MB solutions was compared in Table 5. There is no research in the literature related to AGMD of the MB solution and most of the research conducted by VMD and DCMD. Although the production flux of the AGMD process is lower than the DCMD and VMD processes, it has been considered for installation of various desalination pilot plants (Khayet & Matsuura 2011). In comparison, the lower flux of the AGMD process is correlated to the applied air gap in the module, which results in a higher mass transfer resistance. It can be seen that most of the works on separation of MB by the MD processes have been performed by the commercial hydrophobic PP, PTFE and PVDF membranes. However, in order to achieve a long-term MD operation, more efforts should be made on improvement of the
membrane structure in future works. From Table 5, the fabricated PEI-Zonyl membrane demonstrated reasonable results in terms of flux and rejection in the AGMD process.

FRR of the membranes and adsorption of MB on the membrane surface were examined in order to study the membrane fouling. The FRR of the prepared membranes is given in Table 3. FRR of 76.5% and 87.6% was obtained for the pristine PEI membrane and PEI-Zonyl membrane, respectively. Based on the FRR values, it can be said that an irreversible fouling occurred for the membranes and the rate of fouling was more severe for the pristine PEI membrane due to the lower surface hydrophobicity. The adsorption of MB on the membrane surface can cause fouling, which is discussed in the following section.

In order to study the adsorption of MB on the membrane surface, FD ratio as a function of MB concentration in the feed solution was plotted in Figure 10. A higher MB adsorption on the membrane surface was confirmed.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pore size (μm)</th>
<th>MD process</th>
<th>Operating condition</th>
<th>Permeation flux (kg/m² h)</th>
<th>MB rejection (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PP</td>
<td>0.2</td>
<td>VMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 50 °C; vacuum pressure = 5 mm Hg; C&lt;sub&gt;0&lt;/sub&gt; = 18.5 ppm; Re = 6,000; operating time = 1 h.</td>
<td>8.2</td>
<td>NA</td>
<td>Banat et al. (2005)</td>
</tr>
<tr>
<td>PP capillary</td>
<td>0.2</td>
<td>VMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 50 °C; vacuum pressure = 10 mbar; C&lt;sub&gt;0&lt;/sub&gt; = 50 ppm; Re = 4,341; operating time = 100 min.</td>
<td>24.2</td>
<td>NA</td>
<td>Criscuoli et al. (2008)</td>
</tr>
<tr>
<td>Commercial PVDF</td>
<td>0.45</td>
<td>DCMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 60 °C; C&lt;sub&gt;0&lt;/sub&gt; = 100 mg/L; feed flow rate = 0.5 L/min; operating time = 24 h</td>
<td>17.75</td>
<td>98.3</td>
<td>An et al. (2017)</td>
</tr>
<tr>
<td>TEOS crosslinked polystyrene</td>
<td>NA</td>
<td>VMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 30 °C; vacuum pressure = 10 mmHg; C&lt;sub&gt;0&lt;/sub&gt; = 50 ppm; feed flow rate = NA; operating time = NA</td>
<td>5.04</td>
<td>98</td>
<td>Parakala et al. (2019)</td>
</tr>
<tr>
<td>Composite PVDF</td>
<td>0.21</td>
<td>VMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 50 °C; vacuum pressure = 31.3 kPa; C&lt;sub&gt;0&lt;/sub&gt; = 500 mg/L; feed flow rate = 0.85 L/min; operating time = 100 h</td>
<td>10.35</td>
<td>99.6</td>
<td>Li et al. (2019)</td>
</tr>
<tr>
<td>Commercial PTFE</td>
<td>0.2</td>
<td>DCMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 60 °C; C&lt;sub&gt;0&lt;/sub&gt; = 100 mg/L; feed flow rate = 0.5 L/min; operating time = 24 h</td>
<td>26.4</td>
<td>100</td>
<td>An et al. (2016)</td>
</tr>
<tr>
<td>Commercial PVDF</td>
<td>0.21</td>
<td>DCMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 60 °C; C&lt;sub&gt;0&lt;/sub&gt; = 100 mg/L; feed flow rate = 0.6 L/min; operating time = 50 h</td>
<td>22</td>
<td>100</td>
<td>Deng et al. (2020)</td>
</tr>
<tr>
<td>PEI-Zonyl</td>
<td>0.028</td>
<td>AGMD</td>
<td>T&lt;sub&gt;f&lt;/sub&gt; = 65 °C; C&lt;sub&gt;0&lt;/sub&gt; = 100 mg/L; feed flow rate = 0.2 L/min; operating time = 76 h</td>
<td>7.5</td>
<td>98</td>
<td>Present work</td>
</tr>
</tbody>
</table>

*Not available.

Table 5 | Performance comparison of hydrophobic membranes for MD of the MB solutions

Figure 10 | AGMD of the dyeing solutions: (a) FD vs. dye concentration; and (b) C/FD vs. dye concentration (C<sub>0</sub> = 50–200 ppm; T<sub>f</sub> = 65 °C; Q<sub>f</sub> = 0.2 L/min; and T<sub>c</sub> = 5 °C).
when the $FD$ ratio increased by increasing MB concentration in the feed solution during the AGMD process. In addition, increasing concentration of MB in the feed can decrease the driving force (vapor pressure) and the permeate flux reduction. From Figure 10(a), a lower $FD$ ratio was observed for the modified PEI-Zonyl membrane, which is related to the enhanced hydrophobicity and less wetting tendency. At MB concentrations in the range of 50–100 ppm, a higher increment in the $FD$ ratio of the membranes was observed, which is associated to the enhanced MB adsorption and fouling due to the concentration polarization phenomenon. The rate of $FD$ ratio was decreased at MB concentrations over 100 ppm.

Langmuir constant ($b$) and maximum flux decline ratio ($FD_{max}$) of the membranes were obtained by the intercept and slope of the lines in Figure 8(b). The Langmuir constant was found to be 0.035 and 0.009 L/mg for the pristine PEI membrane and the PEI-Zonyl membrane, respectively. The pristine PEI membrane and the PEI-Zonyl membrane presented $FD_{max}$ of about 56 and 53%, respectively. The dimensionless factor of the Langmuir isotherm was found for the pristine PEI membrane and the PEI-Zonyl membrane to be in the range of $0.125 < R_L < 0.36$ and $0.357 < R_L < 0.69$, respectively. Therefore, a sufficient MB adsorption on the inner surface of the membranes was confirmed, since $0 < R_L < 1$ indicates a favorable adsorption (Li et al. 2017). It is worth mentioning that MB as a cationic dye is dissociated in the aqueous solutions as $\text{Dye}^+ \text{Cl}^-$ (Liu et al. 2010), which can be adsorbed on the membrane surface of negative charge. The pristine PEI membrane and the coated membrane by fluorine compounds present a negative surface charge (Liu et al. 2018; Santos et al. 2019), which can adsorb MB due to electrostatic attraction. A similar trend of MB adsorption on the surface of the PEI membrane coated by polydimethylsiloxane (PDMS) was reported in our previous work (Mousavi et al. 2021).

The 3D AFM images of the inner surface of unused PEI-Zonyl membrane and those fouled by MB adsorption are shown in Figure 11. It can be seen that the surface roughness of the unused membrane is moderately higher than the fouled membrane. The average surface roughness ($R_s$) of the unused membrane and the fouled membrane was found to be 52.66 nm and 36.26 nm, respectively. The adsorption of MB on the membrane surface during the AGMD process could reduce the membrane surface roughness. It should be noted that the smoother surface can show a lower surface hydrophobicity according to the Cassie and Baxter model (Cassie & Baxter 1944). In fact, at higher surface roughness, the larger fraction of air pockets can cause a higher surface contact angle and hydrophobicity. In addition, the FESEM images of the inner skin layer of the unused and the fouled membranes were compared to confirm the adsorption of MB on the surface (Figure 12). As can be seen, the unused membrane presented a highly porous inner layer with an ultra-thin coated skin. However, due to the adsorption of MB and fouling of the surface during about 76 h of the AGMD operation, a fouled layer with thickness of about 0.15 μm was observed. Therefore, the formation of a fouling layer and reduction of surface roughness can decrease hydrophobicity, which can deteriorate the long-term performance of the MD process.

**CONCLUSION**

The main purpose of this study was to improve surface hydrophobicity of the porous PEI hollow fiber membrane by a dip-coating method for the AGMD of the MB solution. Hydrophobic fluorohydrocarbon macromolecules of

**Figure 11** AFM image of the inner surface of the PEI-Zonyl hollow fiber membrane: (a) unused membrane; and (b) fouled membrane.
Zonyl® BA were used as the coating material. The characteristics of the pristine PEI and the modified PEI-Zonyl membranes were evaluated through pore size distribution, overall porosity, water contact angle, FESEM, CEPw, FTIR, and mechanical stability. In addition, surface fouling of the membranes was studied via FRR, MB adsorption and AFM. The outcomes of this study can be summarized as below:

- From the FTIR analysis, the PEI-Zonyl membrane showed peaks associated to the stretching OH and CF2 functional groups of Zonyl which confirmed the formation of a coated layer.
- The PEI-Zonyl membrane presented an open finger-like structure with an inner skinless surface via FESEM examination. In addition, an outer surface with less porosity was observed due to the formation of an ultra-thin coated layer.
- The PEI-Zonyl membrane showed a narrower pore size distribution compared to the pristine PEI membrane. The mean pore sizes of 0.036 μm and 0.028 μm were found for the pristine PEI membrane and the modified PEI-zonyl membrane, respectively.
- By coating an ultra-thin layer of Zonyl, the outer surface water contact angle of the membrane was increased from about 81° to 100°.
- A significant improvement in the wetting resistance (CEPw) of the modified membrane was observed, which is related to the enhanced surface hydrophobicity and the smaller pores.
- The modified PEI-Zonyl membrane demonstrated a high overall porosity of about 82% due to the open morphology with a finger-like structure.
- The modified PEI-Zonyl membrane presented a higher mechanical stability in terms of Young’s modulus and stress at break due to the formation of the coated layer.
- In the AGMD process, a small reduction in the pure water flux of the PEI-Zonyl membrane was observed compared to the pristine PEI membrane. At feed temperature of 65 °C, the pristine PEI and PEI-Zonyl hollow fiber membranes presented a pure water flux of 12.8 and 10.5 kg/m² h, respectively.
- Due to the enhanced properties of the PEI-Zonyl hollow fiber membrane, a lower flux reduction was observed compared to the pristine PEI membrane during about 500 min of the AGMD operation for treatment of the MB solution.
- MB adsorption on the surface of the membranes was confirmed according to the Langmuir isotherm evaluation. A lower flux decline ratio was observed for the modified PEI-Zonyl membrane which is related to the enhanced hydrophobicity and less wetting tendency.
- From 3D AFM images, a decrease in average surface roughness of the PEI-Zonyl membrane used in the AGMD of MB solution confirmed the adsorption of MB on the membrane surface. In addition, a fouling layer with thickness of about 0.15 μm on the inner surface was observed by analyzing FESEM image.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


