Tuning the performance of polypyrrole-based solvent-resistant composite nanofiltration membranes by optimizing polymerization conditions and incorporating graphene oxide

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A B S T R A C T
Solvent-resistant nanofiltration (SRNF) is considered an emerging process capable of replacing conventional energy-consuming methods of separating organic mixtures in diverse industrial fields. This study optimized the performance of polypyrrole (PPy) composite SRNF membranes by varying the polymerization conditions, including the types and concentrations of oxidants and pyrrole concentrations, forming integral selective layers on hydrolyzed polyacrylonitrile (PAN-H) support membranes with better separation properties. The PAN-H support was partially hydrolyzed as indicated by the FTIR spectrum and was compatible with the PPy selective layer, as demonstrated by the apparent lack of an interfacial phase observed in the cross-sections of the composite membranes. The PPy/PAN-H composite SRNF membrane fabricated by reacting 0.5 mol L⁻¹ (NH₄)₂S₂O₈ and 5.0 wt% pyrrole exhibited a Rose Bengal (RB) rejection of 99.2% in isopropanol (IPA), with a relatively high solvent permeance. For the first time, graphene oxide (GO) was incorporated into the PPy/PAN-H composite SRNF membrane by dispersing GO into the pyrrole ethanol solution before polymerization. GO led to a significant enhancement in solvent permeance without compromising RB rejection. Compared with pure PPy/PAN-H composite SRNF membranes, the methanol (MeOH), ethanol (EtOH), and isopropanol (IPA) permeances of the GO-PPy/PAN-H membrane were approximately 945%, 635% and 302% higher, respectively. In a long term experiment, the GO-PPy/PAN-H composite SRNF membrane exhibited a constant IPA permeance of 1.21 L m⁻² h⁻¹ bar⁻¹ and an RB rejection of approximately 99.0%. Therefore, the newly developed GO-PPy/PAN-H composite SRNF membranes in this study have significant potential for practical applications.

1. Introduction

In many industrial fields, processes must be designed to separate active molecules while limiting organic solvent waste, which can lead to high energy consumption and significant environmental contamination. The emerging approach of membrane separation technology may be able to effectively alleviate such critical issues [1–5]. Among various membrane separation processes, solvent-resistant nanofiltration (SRNF) seems to be the most suitable strategy to solve such issues in production processes requiring large amounts of organic solvents. SRNF is a recently developed membrane process applied in non-aqueous media that can replace traditional separation systems. SRNF uses a membrane with a pore size diameter between 0.5 and 2.0 nm and is typically a pressure-driven separation process without phase transfer. Highly efficient SRNF is required to ensure the recovery of organic solvents and the purification of active molecules such as catalysts and pharmaceutically active ingredients. SRNF can be used to significantly reduce energy consumption and solvent contamination while retaining profits. Therefore, SRNF has attracted increasing attention over the last several decades [6–15]. The performance of SRNF membranes has received less investigation than traditional NF membranes. The lack of high-performance and low-cost membrane materials has been the major problem for SRNF. The membrane materials for commercial SRNF are primarily cross-linked polyimides (PI) or polydimethylsiloxane (PDMS). The typically high price of PI and the serious swelling of PDMS limit the practical applications of SRNF. Therefore, recent studies have explored the development of new types of low cost membrane materials and the fabrication of composite membranes consisting of thin selective layers for SRNF [16].

Sirkar and co-workers have studied polyamide (PA) composite SRNF membranes (on polypropylene (PP) supports) via IP (interfacial polymerization) of polyethyleneimine (PEI) and isophthaloyl...
Polypyrrole (PPy) is highly chemically stable but is insoluble in most organic solvents [33,34]. PPy has been used as the selective layer material for gas separation and pervaporation [35,36]. However, only Vankelecom’s group [37] initiated a study on PPy as the SRNF membrane material, investigating the effects of support type and the concentration of the pyrrole monomer on the performance of PPy composite SRNF membranes. They reported that PPy composite SRNF membranes exhibited a high selectivity (over 96%) for negatively charged solutes with a greater permeance in the range of 0.12–1.57 L m⁻² h⁻¹ bar⁻¹ and Rose Bengal retention up to 99% [19–22]. Other materials such as polyurethane (PU), poly[1-(trimethylsilyl)-1-propyne] (PTMSP) on a porous polyacrylonitrile (PAN) support and PANI have been investigated for use in the fabrication of composite SRNF membranes [23–32].

The conducting polymer polypyrrole (PPy) is highly chemically stable but is insoluble in most organic solvents [33,34]. PPy has been used as the selective layer material for gas separation and pervaporation [35,36]. However, only Vankelecom’s group [37] initiated a pioneering study using PPy as the SRNF membrane material, investigating the effects of support type and the concentration of the pyrrole monomer on the performance of PPy composite SRNF membranes. They reported that PPy composite SRNF membranes exhibited a high selectivity (over 96%) for negatively charged solutes with a greater permeance in the range of 0.12–1.57 L m⁻² h⁻¹ bar⁻¹ and Rose Bengal retention up to 99% [19–22]. Other materials such as polyurethane (PU), poly[1-(trimethylsilyl)-1-propyne] (PTMSP) on a porous polyacrylonitrile (PAN) support and PANI have been investigated for use in the fabrication of composite SRNF membranes [23–32].

2. Experimental

2.1. Materials

Methanol (MeOH), ethanol (EtOH), isopropanol (IPA) (Xilong Chemical Industrial Co., Ltd.), pyrrole (Sinopharm Chemical Reagent Co., Ltd.), Rose Bengal (RB) (Aladdin Industrial Co., Ltd.), N-methyl-2-pyrrolidone (NMP) (Tianjin Guangfu Fine Chemical Research Institute), NaOH, HCl (35%), (NH₄)₂S₂O₈, FeCl₃, and H₂O₂ (30%), (Xilong Chemical Co., Ltd.) were used as received. Graphite powder was manufactured by Qingdao Baichuan Graphite Co., Ltd. The PAN was provided by Qilu Petrochemical Company with Mw ≈ 90,000 and used to prepare the support membranes.

2.2. Preparation of GO, PAN support and the composite SRNF membranes

Graphene oxide was synthesized using a modified Hummer’s method as reported in the literatures [45,46]. The detailed procedure was as follows: 5 g graphite powder and 5 g NaNO₃ were added into a 1000 ml three-neck bottle. Then, after slowly adding 240 ml H₂SO₄ (98 wt%) to the mixture, 30 g KMnO₄ was added slowly while stirring in an ice-water bath to keep the temperature under 10 °C. After 4 h, the ice-water bath was removed, and the resulting mixture was heated to 35 °C for 30 min. Then, 200 ml H₂SO₄ (5 wt%) was added slowly under stirring. The temperature of the mixture was then held at 98 °C for 30 min. To reduce the residual KMnO₄ and MnO₂, 400 ml distilled water and 50 ml H₂O₂ (30 wt%) were added to the mixture, which was then stirred for 30 min. The resulting mixture solution was left to stand for a certain period of time, and then the supernatant was poured. Then, 250 ml HCl (3 wt%) and 250 ml H₂O₂ (0.5 wt%) were added to the mixture to wash the product. The obtained mixture was rinsed and centrifuged repeatedly in distilled water until the pH of the solution reached approximately 7.0. Finally, the mixture was dried in a vacuum freeze drier for 24 h.

PAN membranes were obtained by the phase inversion method from an 18 wt% NMP solution, with a steel blade used to obtain a thickness of 200 μm. The PAN-H membrane was prepared via hydrolysis of the original PAN membranes in 10 wt% NaOH for 3 h at room temperature. Before fabricating PPy or GO-PPy composite SRNF membranes on the PAN support, the PAN-H support membrane was immersed in 0.2 mol L⁻¹ HCl for approximately 3 h for activation. The PAN-H membranes were stored in distilled water before the fabrication of SRNF composite membranes.

The GO-modified PPy composite SRNF membrane was fabricated by casting the GO/ppyrole monomer mixture on the PAN-H support, followed by polymerization using selective oxidants. First, 0.05 g GO was dispersed into 100 g ethanol with the aid of ultrasound to obtain a homogenous solution. Then, pyrrole monomers were added, and a certain amount of the GO/ppyrole monomers/ethanol solution was poured into a 15 × 15 cm² steel ring fixed firmly on top of the support membranes. After immersion for approximately 2 h, the solution was removed and the residual ethanol on the membrane was evaporated. Then, the PPy was polymerized by immersing the membrane in the oxidant for approximately 3 h. The GO-modified PPy composite SRNF membrane was rinsed and immersed in distilled water for more than 12 h to remove all residual oxidants. Finally, the GO-PPy/PAN-H composite SRNF membrane was submerged in methanol overnight. The fabrication process of PPy/PAN-H composite membranes without GO was similar to that of the GO-PPy/PAN-H composite membranes. The fabrication process of composite SRNF membranes and the polymerization mechanism are described in Fig. 1. Each fabrication condition was repeated at least twice to improve the reliability of the results.

2.3. Characterization

FTIR-ATR was performed using a Spectrum One instrument (Perkin Elmer, USA). ZnSe was used as the crystal plate and the penetration depth was approximately 50 Å with a 45° incident angle. All spectra were recorded over the wave number range from 4000 to 600 cm⁻¹. XPS measurements were carried out using an AXIS ULTRA DLD spectrometer (SHIMADZU, Japan) with a monochromatized Al Kα X-ray source (1486.6 eV photons) at a constant dwell time of 250 ms and a pass energy of 40 eV. Wide-angle X-ray diffraction (WAXD) spectra were recorded using a RINT D/MAX-2500/PC XRD instrument (Cu Kα1 (λ = 0.154 nm), 40 kV × 30 mA, Rigaku, Japan). The samples were measured from 5° to 60° with a 0.02° step. The d-spacing can be calculated by Bragg’s Law, Eq. (1):

\[ d = \frac{\lambda}{2 \sin \theta} \]
where $\lambda$ represents the wavelength of Cu Kα radiation (1.54 Å), and $\theta$ is the angle of the reflection peak.

The morphology of the fabricated membranes was characterized by a scanning electron microscope (SEM, SEM Quanta 200F, FEI Company). The cross-section morphologies of the membranes were prepared by breaking the membranes in liquid nitrogen to avoid destroying the pore structures of the membranes. Atomic force microscopy was performed in tapping mode with a drive frequency of 200–300 kHz. Silicon nitride oxide-sharpened tips (NCHR, Nanosensors, Germany) were used at room temperature.

### 2.4. Solvent transport and solute rejection tests of composite SRNF membranes

The permeance and flux of NF membranes were measured with a self-made filtration apparatus. Filtrations were performed in a stainless steel dead-end pressure cell with a 21.2 cm$^2$ membrane area. The feed solution was poured into the cell, which was pressurized with nitrogen to 5 bar at room temperature. During the filtration, the feed solution was stirred at 11.66 Hz (700 rpm) to minimize concentration polarization. The permeate samples were collected in cooled stainless steel dead-end pressure cell with a 21.2 cm$^2$ membrane area. The permeate samples were measured 0.5 h after the beginning of the filtration experiments.

The solute rejections of the NF membranes were calculated by the following equations [4]:

$$ F = \frac{V}{A t} $$

$$ P = \frac{F}{\Delta P} $$

(2)

where $F$ is the solvent flux (L m$^{-2}$ h$^{-1}$), $V$ (L) is the volume of the pure solvent (or solution) penetrating through the membrane, $A$ is the effective membrane area (m$^2$), $t$ is the operation time (h) and $\Delta P$ is trans-membrane pressure (bar). The volumes of permeate solvents were measured 0.5 h after the beginning of the filtration experiments.

The solute rejections of the NF membranes were calculated by

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

(3)

where $C_p$ and $C_f$ are the solute concentrations in the permeate and the feed solution, respectively. The concentrations of RB in IPA were measured by a UV–vis Cintra20-GBC apparatus ($\lambda_{\text{max}}$ of RB=548 nm). The feed concentration of RB in IPA was kept approximately 50 ppm.

The long term solvent permeance of the composite SRNF membranes was determined in IPA. The RB rejection data of the membranes were tested during this process. All data were obtained at 18 °C. The data exhibited deviations less than 5%, and every sample was tested three times to improve the reliability.

### 3. Results and discussion

#### 3.1. The performance of the PPy-based composite SRNF membranes

#### 3.1.1. The effects of oxidant types on membrane performance

The oxidation process is crucial for the synthesis of PPy. According to the polymerization mechanism shown in Fig. 1, cation radical species are first generated that can recombine to form a di-cation of a neutral bi-pyrrrole. After undergoing further oxidation, deprotonation and recombination steps, PPy is finally formed as the product of oxidative polymerization interlacing and tangling with the surface PAN-H molecules of the support. H$_2$O$_2$, (NH$_4$)$_2$S$_2$O$_8$, and FeCl$_3$ are the typical oxidants that have been used to initiate the polymerization of PPy [47]. H$_2$O$_2$, (NH$_4$)$_2$S$_2$O$_8$, and FeCl$_3$ were selected for this study, and the specific preparation conditions for the composite SRNF membranes are listed in Table 1. Table 2 reports the permeances and RB rejections (in IPA) of the support membrane (Mem-1) and the PPy-based composite SRNF membranes. The RB rejections of the composite SRNF membranes are much higher than those of the support membrane, indicating the formation of a dense selective layer. The selective layer of Mem-2 is sparser than those of Mem-3 and Mem-4, as indicated by its higher permeance and lower RB rejection. This phenomenon can be explained based on the process of PPy polymerization. The standard redox potentials of the oxidants used in this study are listed in Table 3. The oxidant activity determines the degree of pyrrole polymerization that occurs on the surface of the PAN support. A stronger oxidant activity makes it easier for the oxidant to receive electrons to form cation radical species. Therefore, Mem-4, prepared using (NH$_4$)$_2$S$_2$O$_8$ as the oxidant, has the highest RB rejection and the lowest permeance. The H$_2$O$_2$ oxidant can terminate cation radical polymerization interlacing and tangling with the surface PAN-H molecules of the support. H$_2$O$_2$, (NH$_4$)$_2$S$_2$O$_8$, and FeCl$_3$ were selected for this study, and the specific preparation conditions for the composite SRNF membranes are listed in Table 1. Table 2 reports the permeances and RB rejections (in IPA) of the support membrane (Mem-1) and the PPy-based composite SRNF membranes. The RB rejections of the composite SRNF membranes are much higher than those of the support membrane, indicating the formation of a dense selective layer. The selective layer of Mem-2 is sparser than those of Mem-3 and Mem-4, as indicated by its higher permeance and lower RB rejection. This phenomenon can be explained based on the process of PPy polymerization. The standard redox potentials of the oxidants used in this study are listed in Table 3. The oxidant activity determines the degree of pyrrole polymerization that occurs on the surface of the PAN support. A stronger oxidant activity makes it easier for the oxidant to receive electrons to form cation radical species. Therefore, Mem-4, prepared using (NH$_4$)$_2$S$_2$O$_8$ as the oxidant, has the highest RB rejection and the lowest permeance. The H$_2$O$_2$ oxidant can terminate cation radical species accompanying pyrrole oxidation, which may induce the formation of a PPy oligomer rather than the formation of an

### Table 1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Oxidant type</th>
<th>Oxidant concentration (mol L$^{-1}$)</th>
<th>Pyrrole concentration (wt%)</th>
<th>GO content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mem-1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mem-2</td>
<td>H$_2$O$_2$ (+1.78)</td>
<td>0.50</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-3</td>
<td>FeCl$_3$ (+0.77)</td>
<td>0.50</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-4</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-5</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.05</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-6</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-7</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>1.00</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-8</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-9</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-10</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>10.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-11</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>5.0</td>
<td>0.05</td>
</tr>
<tr>
<td>Mem-12</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.30</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-13</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.70</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>Mem-14</td>
<td>(NH$_4$)$_2$S$_2$O$_8$ (+2.05)</td>
<td>0.50</td>
<td>7.5</td>
<td>0</td>
</tr>
</tbody>
</table>
the (NH4)2S2O8 concentration increases from 0.05 to 0.5 mol L\(^{-1}\) the performance of PPy/PAN-H composite SRNF membranes. When membranes dramatically decrease from 11.36 to 1.46 L m\(^{-2}\) MeOH, EtOH and IPA permeances of PPy/PAN-H composite SRNF meances increase to 3.76, 2.31 and 1.24 L m\(^{-2}\) bar\(^{-1}\) respectively. With the goal of obtaining high RB rejection, the stronger oxidant (NH4)2S2O8 will be further investigated in this study.

Table 2
Effects of oxidant types on the performance of PPy based composite SRNF membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
<th>RB rejection in IPA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH ((%)) EtOH ((%)) IPA</td>
<td></td>
</tr>
<tr>
<td>Mem-1</td>
<td>150.94 (3.6) 59.43 (3.5) 30.56 (1.7)</td>
<td>29.8 (4.7)</td>
</tr>
<tr>
<td>Mem-2</td>
<td>38.72 (3.4) 12.47 (3.9) 7.44 (2.0)</td>
<td>66.7 (2.8)</td>
</tr>
<tr>
<td>Mem-3</td>
<td>7.07 (4.1) 6.45 (2.8) 3.97 (2.1)</td>
<td>93.5 (3.6)</td>
</tr>
<tr>
<td>Mem-4</td>
<td>1.46 (2.5) 1.30 (4.6) 0.79 (3.2)</td>
<td>99.1 (2.9)</td>
</tr>
</tbody>
</table>

\(\%\) is the deviation of the data.

Table 3
Basic properties of solvents used in this study.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Molecular weight (g mol(^{-1}))</th>
<th>Viscosity (mPa s)</th>
<th>Surface tension (mN m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>32.0</td>
<td>0.54</td>
<td>22.1</td>
</tr>
<tr>
<td>EtOH</td>
<td>46.1</td>
<td>1.08</td>
<td>22.0</td>
</tr>
<tr>
<td>IPA</td>
<td>60.1</td>
<td>2.06</td>
<td>21.0</td>
</tr>
</tbody>
</table>

integrated polymer layer. As a result, Mem-2 exhibits the lowest RB rejection and the highest permeance. In fact, the SEM results (discussed later) have verified the conclusions presented above. Table 2 indicates that the solvent permeance of all membranes is ordered as MeOH > EtOH > IPA. The solvent permeances of the SRNF membranes are reported to be related to molecular volume, viscosity and surface tension [48]. Based on the solvent properties listed in Table 3, the fact that MeOH has the lowest viscosity with a similar molecular volume and surface tension may account for the permeance performance of the composite SRNF membranes. Similar results have also been reported in other studies [49,50]. Among PPy/PAN-H composite SRNF membranes (Mem-2, Mem-3 and Mem-4) prepared using various oxidants, Mem-4 exhibits the highest RB rejection, with MeOH, EtOH and IPA permeances of 1.46, 1.30 and 0.79 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. With the goal of obtaining high RB rejection, the stronger oxidant (NH4)2S2O8 will be further investigated in this study.

3.1.2. The effects of oxidant ((NH4)\(_2\)S\(_2\)O\(_8\)) concentration on membrane performance

Fig. 2 shows the effects of oxidant ((NH4)\(_2\)S\(_2\)O\(_8\)) concentration on the performance of PPy/PAN-H composite SRNF membranes. When the (NH4)\(_2\)S\(_2\)O\(_8\) concentration increases from 0.05 to 0.5 mol L\(^{-1}\), the MeOH, EtOH and IPA permeances of PPy/PAN-H composite SRNF membranes dramatically decrease from 11.36 to 1.46 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), 4.90 to 1.30 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) and 1.31 to 0.79 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. When the oxidant concentration is further increased from 0.5 to 1.0 mol L\(^{-1}\), the MeOH, EtOH and IPA permeances increase to 3.76, 2.31 and 1.24 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. Correspondingly, the RB rejection exhibits its greatest value of 99.2% at the (NH4)\(_2\)S\(_2\)O\(_8\) concentration of 0.5 mol L\(^{-1}\). This phenomenon can be explained based on the pyrrole polymerization process. More radical species are available for the polymerization when more oxidants are used, leading to the formation of a shorter polymer chain at the same pyrrole concentration. At the initial stage of the polymerization with a low oxidant concentration, some pyrrole monomers spread into the solution, resulting in defects in the selective layer because too few radicals were generated to form a sufficiently integrated layer covering the PAN-H support. Under these circumstances, the RB rejection cannot reach a sufficiently high value, although the solvent permeance is dramatically lower than that of Mem-1. When the oxidant concentration is too high, generating an excess of radicals compared with the pyrrole monomers, shorter polymer chains will be formed, leading to defects in the selective layer. Therefore, an optimal oxidant content should exist. This is also consistent with the SEM results discussed later. In the remainder of this study, the (NH4)\(_2\)S\(_2\)O\(_8\) concentration is kept at 0.5 mol L\(^{-1}\), taken as the optimal concentration.

3.1.3. The effects of pyrrole concentration on the membrane performance

Fig. 3 shows the effect of pyrrole concentration on the performance of composite SRNF membranes. The variations in permeance and RB rejection with pyrrole concentrations are similar to the results of varying oxidant concentration. The permeances of MeOH, EtOH and IPA dramatically decrease with increasing pyrrole concentration from 1.0 wt% to 5.0 wt%. Further increasing the pyrrole concentration from 5.0 wt% to 10.0 wt% leads to a slight decline in the solvent permeance. The RB rejection shows an opposing trend. Under a pyrrole concentration of 1.0 wt%, the RB rejection was only 78.7% though the permeance was high, indicating that the selective layer cannot form integrally at this low monomer concentration. The monomer concentration increases to 2.0 wt%, resulting in an RB rejection over 96%, demonstrating the formation of a sufficiently dense selective layer. The membrane fabricated with a monomer concentration of 5.0 wt% exhibits the maximum RB rejection. Further increasing the monomer concentration to 10 wt% leads RB rejection to decline to 96.2% which may be due to the occurrence of defects because of the diffusion of
monomer at an extremely high concentration on the PAN-H surface into the oxidant solution. These results are also supported by the SEM examinations.

3.1.4. The effects of GO incorporation on the membrane performance

After optimizing polymerization conditions, GO is incorporated into PPy/PAN-H composite SRNF membranes. The performance of the GO-PPy/PAN-H composite SRNF membrane (Mem-11) is compared with that of Mem-4 in Table 4. Incorporation of GO significantly increases the MeOH, EtOH and IPA permeances of the SRNF membrane by approximately 94.5%, 63.5% and 37.7%, respectively. Interestingly, despite such a large increase in solvent permeance, the RB rejection only decreases slightly from 99.2% to 98.6%. These results demonstrate the significant improvement in membrane performance after GO incorporation. As reported in the literature, π–π interactions and electrostatic attractions occur between GO and pyrrole, leading to the absorption of pyrrole onto the GO surface [42,44,51]. The polymerization thus occurs around GO, enabling the formation of thinner selective layers on the surface of PAN-H. Therefore, fewer pyrrole oligomers are found in the pores of PAN-H, leading to a significant increase in solvent permeance without compromising RB rejection. Fig. 4 demonstrates the possible mechanism for the performance enhancement of PPy/PAN-H composite SRNF membranes after GO incorporation.

3.1.5. Long term performance of PPy composite SRNF membranes

Fig. 5 reports the long term performance of PPy/PAN-H and GO-PPy/PAN-H composite SRNF membranes. The IPA permeance of composite SRNF membranes decreases dramatically during the initial 20 hours. After that, the IPA permeance remains stable. The initial decreased permeance can be attributed to the compaction of membrane structures under applied pressure. The constant IPA permeances of Mem-4 and Mem-11 were 0.24 and 1.2 L m⁻² h⁻¹ bar⁻¹, respectively. The RB rejection fluctuated slightly approximately 99% under the experimental conditions. Moreover, the permeances of methanol and ethanol slightly fluctuated after 20 hours, showing a similar trend as IPA over time (shown in Fig. S-1). Therefore, both the composite membranes were stable in every solvent used in this study. For comparison, Table 5 summarizes the performance of different types of SRNF membranes reported in the literature. According to Table 5, the novel GO-PPy/PAN-H composite SRNF membrane developed in this study exhibits excellent performance. Therefore, this novel GO-PPy/PAN-H composite SRNF membrane may have great potential for the purification and separation of active molecules in many industrial fields.

3.2. Basic characterization

XRD of GO exhibits a peak centered at 11.6° corresponding to a 0.83 nm d-space (as shown in Fig. S-2). This d-space value is higher than that (0.34 nm) of pristine graphite, which is due to the oxygenation of the functional groups of GO [51,52]. Based on 0.83 nm per layer from the XRD results and the AFM image of GO shown in Fig. S-3, GO can be dispersed uniformly in ethanol with a thickness of 10 nm, representing the aggregation of approximately 12 layers of GO molecules (approximately). Besides, the uniform GO dispersion was stable after one week of aging, enabling the uniform incorporation of GO into PPy, possibly resulting in the good performance of the composite membranes containing GO. Further XPS results (Table 6) illustrate that the C/O ratio of GO is 70.5:29.5, which is consistent with the data reported in the literature [53,54]. Table 6 also reports the compositions of the typical composite SRNF membranes used in this study. Compared with Mem-I, both Mem-4 and Mem-11 have higher N and C contents, as PPy containing only C and N elements has formed on the top surface of the support membranes. The occurrence of

Table 4
Comparison of the performance of PPy/PAN-H and GO-PPy/PAN-H composite SRNF membranes.

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mem-4 (d%)</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.46 (2.5)</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.30 (4.6)</td>
</tr>
<tr>
<td>IPA</td>
<td>0.79 (3.2)</td>
</tr>
<tr>
<td>Rejection (%)</td>
<td>99.1(2.9)</td>
</tr>
</tbody>
</table>

%d is the deviation of the data.

Table 5
Performance comparison between the newly developed SRNF membrane in this work and other SRNF membranes reported in literatures.

<table>
<thead>
<tr>
<th>Membrane materials</th>
<th>Operated pressure (bar)</th>
<th>Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>RB rejection (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyelectrolytes</td>
<td>40</td>
<td>0.12–1.57</td>
<td>&gt;99</td>
<td>[20]</td>
</tr>
<tr>
<td>Polyimides</td>
<td>5</td>
<td>1.00</td>
<td>about 90</td>
<td>[15]</td>
</tr>
<tr>
<td>PPy based</td>
<td>10</td>
<td>0.74–1.42</td>
<td>99</td>
<td>[37]</td>
</tr>
<tr>
<td>PPy/PAN-H</td>
<td>5</td>
<td>0.79–1.03</td>
<td>96–98</td>
<td>This work</td>
</tr>
<tr>
<td>GO-PPy/PAN-H</td>
<td>5</td>
<td>3.17</td>
<td>98.5</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 5. Long term performance of PPy/PAN-H and GO-PPy/PAN-H composite SRNF membranes.

Fig. 4. Possible mechanism by which the incorporation of GO affects pyrrole polymerization.
The new peaks at 3300 cm\(^{-1}\) are due to the asymmetric stretching and symmetric vibrations of layer. This result is consistent with XPS results. The bands at 2934 cm\(^{-1}\) support the existence of nano-scaled pores in the selective layer formed readily after polymerization using oxidants. The incorporation of GO into PPy/PAN-H composite SRNF membranes can be deconvoluted into four fitting curves at 284.4, 285.3, 286.8 and 288.3 eV, and can be attributed to C–C, C–N, C–O and C=O, respectively, based on Fig. S-4. These results are similar to those found by Zhu and coworkers\(^{[51]}\), who have investigated graphene oxide/polymer nanocomposites for energy storage.

The FTIR-ATR results of the membranes are presented in Fig. 6. The peaks at 1446 and 2247 cm\(^{-1}\) are due to vibrations of the –CN moiety of the PAN membranes\(^{[55–57]}\). In fact, these two peaks also appear in Mem-4 and Mem-11, which are extremely weak because of the interlacing and entanglement between PPy molecular chains and PAN-H molecular chains on the surface of the support and the existence of nano-scaled pores in the selective layer. This result is consistent with XPS results. The bands at 2934 cm\(^{-1}\) are due to the asymmetric stretching and symmetric vibrations of CH\(_2\)\(^{[55,56]}\). The new peaks at 3300 cm\(^{-1}\), 1640 cm\(^{-1}\) and 1570 cm\(^{-1}\) are attributed to the stretching vibration of –OH, the stretching vibration of –C=O and the asymmetric stretching vibration of –COO\(^{-}\), respectively, revealing that the support membrane has been partially hydrolyzed\(^{[55,56]}\). For Mem-4 and Mem-11, the peaks at approximately 946 and 1612 cm\(^{-1}\) can be assigned to the out-of-plane vibration and the stretching vibration of C-H of the polymerized pyrrole, respectively\(^{[44]}\), indicating that the PPy selective layer formed readily after polymerization using oxidants. Compared with Mem-4, the intensities of the peaks of Mem-11 at 2247 and 2934 cm\(^{-1}\) became weaker when Mem-11 was covered with GO. The characteristic peak ascribed to the C–H stretching vibration of the pyrrole moiety shifts from 1612 cm\(^{-1}\) to 1603 cm\(^{-1}\) due to the π–π interactions between GO and PPy\(^{[42]}\). These results demonstrate that GO has been incorporated into the selective layer in Mem-11.

### Table 6

<table>
<thead>
<tr>
<th>Membrane</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
<th>O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>70.5</td>
<td>0</td>
<td>29.5</td>
</tr>
<tr>
<td>PAN-H (Mem-1)</td>
<td>68.9</td>
<td>9.7</td>
<td>21.5</td>
</tr>
<tr>
<td>PPy/PAN-H (Mem-4)</td>
<td>73.0</td>
<td>16.3</td>
<td>10.7</td>
</tr>
<tr>
<td>GO–PPy/PAN-H (Mem-11)</td>
<td>72.1</td>
<td>12.3</td>
<td>15.6</td>
</tr>
</tbody>
</table>

![Fig. 6. FTIR-ATR spectra of typical membranes.](image)

3.3. Morphological characterization of the composite SRNF membranes and the dispersion of GO

SEM images of the support membrane and the composite SRNF membranes are shown in Fig. 7. Fig. 7a depicts the morphology of the PAN-H support membrane. Small pores with a pore size of approximately 10 nm are present on the surface of Mem-1 (support membrane). Compared with the support membrane, all of the newly developed PPy-based composite SRNF membranes\(^{[42]}\) have a dense selective layer, and no visible pores can be observed on the surface, even at high magnification. Some small spots can also be observed on Mem-3 and Mem-4. Compared with Mem-3 and Mem-4, Mem-2 has some defects on the coating layer, indicating an imperfect selective layer, consistent with the solvent transport results. Mem-11 has some larger plates because of the uniform incorporation of GO into the selective layer. Furthermore, SEM images of the top surface morphologies of other composite SRNF membranes are shown in Fig. S-5. These SEM images indicate that when the pyrrole concentration increases from 0.5 to 5.0 wt%, the top surface of the membrane becomes denser, and small spots emerge, indicating the formation of the integrated selective layer. However, when the pyrrole concentration increases further from 5.0 to 10.0 wt%, the small spots disappear. The disappearance of these small spots illustrates that the defects happen again because of the spreading of extreme monomer content, which can also be inferred from the solvent transport results. Fig. 7f and g depict the morphologies of the cross-sections of Mem-4 and Mem-11. Both membranes with and without GO consist of a dense selective layer and finger-like pores. There is no apparent interfacial region between the selective layer and the support membrane, implying good compatibility. Compared with Mem-4, some GO plates were observed in Mem-11. In fact, SEM images of the cross-sectional morphologies of other representative composite SRNF membranes in this study are shown in Fig. S-5. All of the cross-sectional morphologies of membranes without GO exhibit similar structures.

4. Conclusions

The findings of this study can be summarized as follows:

1. The effects of oxidant type, oxidant concentration and pyrrole concentration on the performance of PPy-based composite SRNF membranes. Optimization of the polymerization enabled the formation of integral selective layers of SRNF membranes on PAN-H supports. The composite membrane fabricated under the optimal conditions exhibits 99.2% RB rejection in IPA, with MeOH, EtOH and IPA permeances of 1.46, 1.30, and 0.79 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. The solvent permeances can be ordered as MeOH > EtOH > IPA, indicating that the solvent viscosity may dominate the solvent mass transfer process of PPy-based composite SRNF membranes.

2. The incorporation of GO into PPy/PAN-H composite SRNF membranes significantly enhanced the solvent permeance without compromising RB rejection. The IPA permeance of the GO–PPy/PAN-H composite SRNF membrane under 5 bar remained steady at 1.21 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) after the long term test. The newly developed GO–PPy/PAN-H composite SRNF membrane has great potential applications in the purification and separation of active molecules.
(3) FTIR-ATR and XPS can prove pyrrole polymerization and the incorporation of GO into the composite SRNF membrane. The morphological observations made by SEM illustrate the formation of an integral selective layer on the surface of PAN-H via the polymerization of pyrrole under the optimal conditions.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2013.10.021.

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