



## High-performance nanofiltration membrane prepared by dopamine-assisted interfacial polymerization on PES nanofibrous scaffolds

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### ABSTRACT

Thin-film nanofiltration composite (TFNC) membrane with high performance was demonstrated in this work. The membrane consisted of dopamine-modified polyethersulfone (PES) nanofibrous supporting layer and interfacially polymerized polyamide selective barrier layer. PES nanofibrous scaffold was modified with dopamine through self-polymerization. Here, dopamine was introduced to facilitate the formation of ultra-thin TFNC membrane on PES substrate with high performance and enhance the interfacial compatibility and structural stability of the composite membrane. An ultra-thin selective layer was generated by interfacial polymerization reaction between solutions of piperazine and trimesoyl chloride on the dopamine-modified porous PES membrane. Various parameters in interfacial polymerization, including monomer concentration, curing temperature, and curing time, were discussed and optimized to achieve high-performance composite nanofiltration membrane. The resulting TFNC membrane possessed relative high salt rejection (~99.4%) and high flux (~63.0 L/m<sup>2</sup> h) to Na<sub>2</sub>SO<sub>4</sub> solutions at a low pressure of 0.6 MPa, doubling the flux of TFNC membranes prepared at the same conditions, but without dopamine modification. It is believed that dopamine modification offers an efficient route for the fabrication of composite nanofiltration membranes with high filtration performance.

*Keywords:* Dopamine-modified PES nanofibrous substrate; Interfacial polymerization; Thin film nanofiltration composite membrane

### 1. Introduction

Nanofiltration (NF) has gained much attention all over the world in recent years due to its excellent advantages such as high rejection of multivalent ion salts, relative high permeate flux, and low operating pressure [1–3]. High rejection and high flux are the major targets in preparing NF membranes. Generally, NF membranes are prepared as composite membranes with a hierarchical structure to increase the NF

efficiency. The composite membrane usually consists of a porous low resistant substrate offering mechanical support and a thin top layer offering filtration function [4,5].

Nanofibrous membranes obtained from electrospinning are promising candidates as porous substrate for composite membranes due to their unique properties of large porosity, high surface-to-volume ratio, and interconnected pore structures [6–8], which may enable them to have high permeability and low energy cost in water filtration applications [4]. The

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polyethersulfone (PES) ultrafiltration membranes are generally used as support in making thin-film composite NF membrane for its excellent thermal resistance, chemical stability, and mechanical strength [9,10]. However, its relatively hydrophobic nature greatly limits its application in water filtration due to low water permeation and easy fouling. Therefore, measures should be taken to improve its hydrophilicity to enable high rates of water transport while retaining the excellent physical properties of PES.

Interfacial polymerization is a very common and effective method to prepare the thin barrier layer [11]. Generally, the porous substrate is firstly immersed into aqueous phase containing amine monomer, then into the organic phase containing organic monomer; thus, the top active layer is formed at the interface on the substrate. High monomer concentration is often required to achieve the active layer with high rejection, only leading to low permeate flux due to the thick active layer [12]. Although thinner active layer and higher flux can be achieved by decreasing the monomer concentration, the rejection may decline significantly because of structural defects. Besides, the top active layer is easily detached from underneath porous supporting layer, especially during the thermal treatment, since there is usually no strong inter-linkage between two different materials. To solve these problems, many efforts have been devoted to preparing thin but dense active layer with good stability. Oh et al. [13] successfully prepared polyamide (PA) composite membranes with good structural stability via the formation of ionic bonds. Microporous polyacrylonitrile (PAN) supports were treated with NaOH solution to create carboxylic groups on their surface, and ionic bonds were formed between PA active layers and supporting layers when piperazine (PIP) was interfacially polymerized with trimesoyl chloride (TMC). Jiang et al. [12] also prepared composite NF membranes by interfacial polymerization on hydrolyzed PAN substrate activated by 1-ethyl-(3-(3-dimethylaminopropyl) carbodiimide hydrochloride/N-hydroxysuccinimide to enhance the reactivity with amine groups, and the resulting membrane showed very high flux and structural stability. However, these modification methods usually destroyed the substrate partially, thus resulting in low pressure resistance of the composite membrane. It is crucial to find a simple, yet effective, method to prepare composite membranes with good structural stability and high flux.

Recently, mussel adhesive proteins (MAPs) have been considered for their ability to form strong adhesive interaction with various materials, which depended on the existence of 3,4-dihydroxyphenylalanine (DA) in MAPs [14,15]. DA can self-polymerize to

form poly(dopamine) (PDA) and PDA coatings show many excellent properties [16,17], such as robust interfacial binding force, ultra-thin and controllable coating thickness, no damage to substrate, high hydrophilicity, and many active groups for further modification. Thus, they have been used for surface modification of various materials [14,18–20], intermediate layer [17,21], and filtration [16,22].

In this paper, we devoted efforts to fabricating integrated ultra-thin NF membrane with high performance (both high permeation flux and high salt rejection). The nanofiltration membrane was prepared by interfacial polymerization on PDA-modified PES electrospun nanofibrous scaffold. Here, dopamine as one derivative functional element of MAPs is used not only to improve the hydrophilicity of the substrate membrane, but also to increase the interfacial compatibility between the top active layer and the substrate, thereafter the structural integral and stability of the composite membrane.

## 2. Experimental

### 2.1. Materials

PES powder (CAS.: 9002-88-4, Mw = 64,000) was purchased from Shanghai Solvay Co., Ltd. N, N-Dimethylacetamide (CAS.: 127-19-5, DMAc) was supplied by Shanghai Boer Chemical Reagent Co., Ltd. Dopamine (CAS.: 51-61-6) was purchased from Acros Organics. Tris (hydroxymethyl) aminomethane (CAS.: 77-86-1, Tris), hydrochloric acid (CAS.: 7647-01-0), n-hexane (CAS.: 110-54-3), PIP (CAS.: 110-85-0, PIP), TMC (CAS.: 4422-95-1, TMC), sodium sulfate (CAS.: 7757-82-6, Na<sub>2</sub>SO<sub>4</sub>), magnesium sulfate (CAS.: 7487-88-9, MgSO<sub>4</sub>), magnesium chloride (CAS.: 7786-30-3, MgCl<sub>2</sub>), and sodium chloride (CAS.: 7647-14-5, NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

### 2.2. Preparation of PES nanofibrous membrane by electrospinning

PES was dissolved in DMAc until it became a homogeneous solution with concentration of 26 wt% for electrospinning. Typical parameters for electrospinning experiments were as following: the applied electric voltage was 22 kV, the solution feed rate was 15  $\mu$ L/min, and the distance between the spinneret and the collector was 15 cm. A grounded rotating metallic drum was utilized to collect the deposited electrospun nanofibers.

### 2.3. Dopamine modification of PES nanofibrous membrane

One gram per liter dopamine solution was prepared by dissolving dopamine in Tris–HCl buffer solution (10 mM, pH 8.0). PES nanofibrous membrane was immersed into the dopamine solution and vibrated at 30°C for a designed time. Then, the PES membrane was taken out and washed with deionized water. Thus, the surface of PES nanofibers was modified with poly(dopamine). Finally, the membranes were dried in the air for further use.

### 2.4. Interfacial polymerization for water filtration

The nanofiltration membranes were prepared by interfacial polymerization on dopamine-modified PES membrane using PIP and TMC solution. First, the PDA/PES membrane was immersed into PIP solution with different concentrations for 1 min, and then immersed into the TMC organic solution after excess PIP solution was drained off. The reaction time was set at 60 s and the excess TMC solution was removed off the membrane; thus, a thin film poly(piperazine-amide) was formed on the top of the PDA/PES support membrane. Finally, the composite membrane was treated at different temperature for certain time. The resulting poly(piperazine-amide) (PAM) membranes prepared with and without PDA-assisted interfacial polymerization hereinafter are referred to as PAM/PDA–PES and PAM/PES, respectively.

### 2.5. Characterization

The surface morphology and cross-sectional morphology of the composite membrane were observed using scanning electron microscope (SEM, JEM-5600LV, Jeol, Japan), at an accelerating voltage of 15 kV. Prior to scanning, samples were sputter-coated with platinum for analysis.

The dynamic water contact angle was measured using dynamic contact angle testing instrument (OCA40, German) to analyze the surface hydrophilicity of PES membrane before and after dopamine modification. A droplet of 0.5  $\mu$ L of distilled water was adhered on the surface of a membrane sample and the nanofibrous membrane was pulled away from the water drop at a speed of 1 mm/s after 10 s. The water contact angle was measured visually.

### 2.6. NF membrane performance evaluation

A cross-flow filtration cell was used to evaluate the filtration performance of the composite membranes.

The area of tested membrane was 3.8 cm<sup>2</sup>. Before testing, each membrane was placed in the filtration cell and compacted under 0.8 MPa for 0.5 h to make sure the membrane remained in a steady state. After the compacting process, the measurement pressure was lowered to 0.6 MPa. Membrane salt rejection performances were determined by Na<sub>2</sub>SO<sub>4</sub> solution and MgSO<sub>4</sub> solution at the concentration of 1,000 mg/L (pH 6). The water flux was determined by direct measurement of the permeate flux in terms of liter per square meter per hour (L/m<sup>2</sup> h). The salt concentrations were determined by measuring the conductivity using a conductivity detector (FE30, Mettler Toledo). The permeation flux ( $J$ ) and salt rejection ( $R$ ) of the membranes were calculated using Eqs. (1) and (2)

$$J = \frac{V}{A \cdot \Delta t} \quad (1)$$

$$R = \left(1 - \frac{C_f}{C_p}\right) \times 100\% \quad (2)$$

where  $V$  is the volume of permeate solution during the test time,  $A$  is the effective membrane area,  $\Delta t$  is the test time,  $C_p$  and  $C_f$  are the salt concentration of permeate solution and feed solution, respectively. All the samples for the determination of water flux and solute rejection were collected after at least 30 min of filtration and the results presented are average data with standard deviation from at least three samples.

## 3. Results and discussion

### 3.1. PDA-modified PES nanofibrous membrane

Dopamine can be self-polymerized to form a surface-adherent film and adhered firmly onto the surface of both hydrophilic and hydrophobic substrates in aqueous solutions [16,21]; thus, it can be used to improve the hydrophilicity and interfacial properties of various materials. Here, electrospun PES membrane was dipped into the DA solution for different time to endow the membrane adherence and many hydrophilic groups (catechol and imino groups, etc.) in PDA. Fig. 1 shows the influence of dipping time on water contact angle and pure water flux (the applied pressure: 0.2 MPa) of the PDA/PES nanofibrous membrane to select an optimum modification time. As can be seen from Fig. 1(a), the contact angle of the nanofibrous membrane decreased dramatically from 81.6° to 26.8° after 3 h dopamine modification and then kept at a constant. At the same time, the pure water flux increased significantly with the increase of

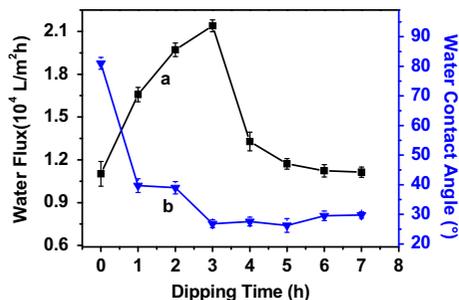


Fig. 1. Dipping time dependencies of pure water flux (a) and contact angle (b) for dopamine-modified PES nanofibrous membrane at a pressure of 0.2 MPa.

modification time and reached the maximum ( $2.1 \times 10^4$  L/m<sup>2</sup> h) at the dipping time of 3 h, then decreased to level off ( $1.1 \times 10^4$  L/m<sup>2</sup> h). It can be ascribed that more and more dopamine was deposited on the surface of PES nanofibers, the hydrophilicity of PES membrane increased with increasing dipping time, but after 3 h there are so many PDAs adhered on PES that they may block the pore of PES electrospun membrane to decrease the water flux. Therefore, the optimized modification time of PES membrane by dopamine was set at 3 h.

### 3.2. Optimization of Interfacial polymerization on PDA-modified PES substrate

For TMC and PIP or any given pair of reactants taken to form the ultra-thin film barrier layer on dopamine-modified PES substrate, the preparation conditions have to be optimized to obtain a membrane with optimal performance characteristics. Generally speaking, preparation conditions play an important role in determining the structure of the interfacial polymerized membrane and subsequently the membrane performance [1,2,5]. Many preparation conditions can affect the performance of the membrane prepared by interfacial polymerization, mainly including the concentration of the reactants in the aqueous phase and organic phase, reaction time of polymerization, as well as thermal treatment. Thus, in the following section, the above preparation parameters were investigated to optimize the membrane performance.

It is well known that the concentrations of the monomer in organic phase play an important role in the preparation of Thin-film nanofiltration composite (TFNC) membranes by interfacial polymerization [1]. To ensure enough PIP could be adsorbed by the PDA/PES membrane for the following interfacial polymerization, the concentration of PIP in aqueous phase was fixed at 1 wt% [11,23].

To fix the organic phase (TMC) concentration, the relationship between TMC concentration and filtration performance for the composite membranes was investigated and the results were shown in Fig. 2. The reaction time was fixed at 60 s, and the curing time was set for 30 min at 60 °C. As shown in Fig. 2, the salt rejection to both Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> increased significantly while permeate flux decreased when changing TMC concentration from 0.2 to 0.6 wt%; then, the rejection increased slightly after TMC concentration of 0.6 wt% while the permeate flux further decreases rapidly (62.0–53.4 L/m<sup>2</sup> h) with further increase of TMC concentration from 0.6 to 1.0 wt%. This can be explained by the change of both the thickness and morphology of the as-prepared TFNC membrane. As is known to all, the interfacial polymerization between an acid chloride and a diamine takes place on the organic side of the two phase interface [23,24]; thus, TMC concentration has a great effect on the rate of polymerization, consequently affecting the morphology and thickness of the resulting skin layer during polymerization [23]. It is expected to be low for the rate of interfacial polymerization when the TMC concentration is low because of insufficient triacyl chloride groups at the reaction zone [2,25]. As a result, the as-prepared thin barrier layer

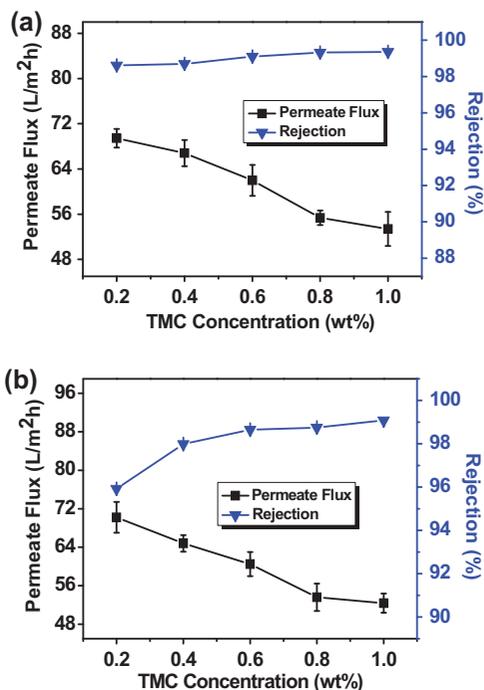


Fig. 2. TMC concentration dependencies of permeate flux and rejection ratio for PAM/PDA-PES nanofibrous membranes toward 1,000 ppm Na<sub>2</sub>SO<sub>4</sub> (a) and MgSO<sub>4</sub> (b) solution at operation pressure 0.6 MPa (under the conditions: 1 wt% PIP in aqueous phase; curing at 60 °C for 30 min).

was very thin and loose, so that the resulting TFNC membrane showed lower rejection to  $\text{Na}_2\text{SO}_4$ , but higher permeate flux. With TMC concentration increase, the obtained PA skin layer becomes thicker and compacter due to the faster rate of reaction, resulting in a higher rejection and lower permeate flux. It nearly tends to have no impact on the salt rejection when TMC concentration exceeds 0.6 wt%, but the permeate flux further decreases. By considering that the rejection and flux are the two key parameters to evaluate the performance of filtration membrane, the TMC concentration will be set at 0.6 wt%.

Thermal treatment is always applied for further polymerization and to facilitate the removal of residual organic solvent from nascent thin film [2], which has profound influences on the membrane performance [24]. The curing parameters including temperature and time were also investigated to improve the filtration performance of the composite membranes.

Fig. 3(a) and (b) showed the performance of composite membranes cured at different temperatures for 30 min. It is obvious that the curing temperature has a great effect on the rejection and the permeate flux of the as-prepared membranes to  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  solution. The rejection of both  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  increased while their permeate flux decreased all the time as the curing temperature varies from 20 to 100°C. For the TFNC membrane without thermal treatment, i.e. at 20°C, it has a high flux of about

91.5  $\text{L}/\text{m}^2\text{h}$  to  $\text{Na}_2\text{SO}_4$  and 83.1  $\text{L}/\text{m}^2\text{h}$  to  $\text{MgSO}_4$ , but the rejections are not high (~86.2% for  $\text{Na}_2\text{SO}_4$  and 81.3% for  $\text{MgSO}_4$ ). There are significant changes for both permeate flux and rejection when the curing temperature increases: the permeate flux decreases fast and rejection increases rapidly. Denser top active layer was achieved at higher temperature due to rapid diffusion rate of amino groups with higher degree of polymerization. The membrane prepared from curing at 60°C has a rejection of ~99.3% for  $\text{Na}_2\text{SO}_4$  and 98.9% for  $\text{MgSO}_4$ , and has a flux of 61.2  $\text{L}/\text{m}^2\text{h}$  for  $\text{Na}_2\text{SO}_4$  and 60.5  $\text{L}/\text{m}^2\text{h}$  for  $\text{MgSO}_4$ . The rejection keeps steady and does not change much when the temperature is higher than 60°C; however, the permeate flux will decrease continuously, so the membrane was cured at 60°C to achieve a better performance.

To study the effect of curing time, a series of TFNC membranes were prepared with different time in the range of 10–50 min at 60°C, and the results were shown in Fig. 3(c) and (d). It was clearly seen that the salt rejection increased and flux decreased all the time with the increase of curing time. The longer curing time led to a higher degree of interfacial polymerization on the substrate, resulting in a compacter structure of the skin layer with lower permeate flux. But when the curing time was prolonged over 30 min, the salt rejection was almost constant (99.3% for  $\text{Na}_2\text{SO}_4$  and 99.1% for  $\text{MgSO}_4$ ), while the permeate flux still decreased markedly. It was concluded that 30 min

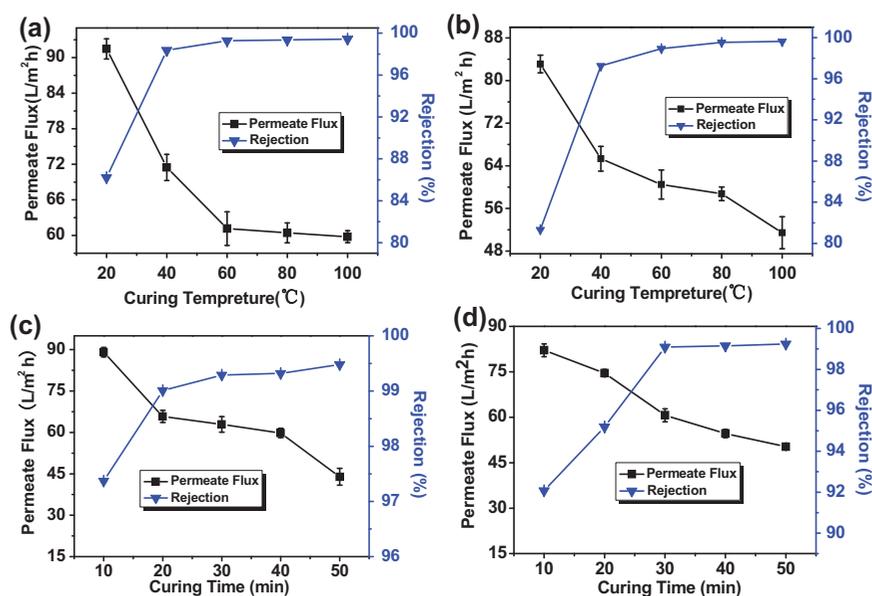


Fig. 3. Curing temperature (a, b) and curing time (c, d) dependencies of permeate flux and rejection ratio for PAM/PDA-PES nanofibrous membranes toward 1,000 ppm  $\text{Na}_2\text{SO}_4$  (a, c) and  $\text{MgSO}_4$  solution (b, d) at operation pressure 0.6 MPa (under the conditions: 1.0 wt% PIP in aqueous phase; 0.6 wt% TMC in organic phase (n-hexane)).

was enough for thermal treatment of the resultant TFNC membrane with high salt rejection (99.3% for  $\text{Na}_2\text{SO}_4$  and 99.1% for  $\text{MgSO}_4$ ) and high permeate flux (63.0  $\text{L}/\text{m}^2 \text{ h}$  for  $\text{Na}_2\text{SO}_4$  and 60.7  $\text{L}/\text{m}^2 \text{ h}$  for  $\text{MgSO}_4$ ).

Based on the above results, the preparation parameters of the TFNC membranes were set as following: 1 wt% PIP in aqueous phase; 0.6 wt% TMC in organic phase (n-hexane); curing at  $60^\circ\text{C}$  for 30 min. A series of the membranes were prepared under the above conditions to further analyze their properties and NF performance in the following part.

### 3.3. Characterization of the composite membrane

Typical SEM images of the PES nanofibrous membrane before (a) and after (b) PDA modification were shown in Fig. 4. As can be seen from Fig. 4(a) and (b), the as-prepared PES nanofibrous mat is well fabricated with uniform fiber size, and very tiny particles appear on the PES fibers after PDA modification and the fiber size does not change much.

The typical surface and cross-sectional morphologies of the resultant PAM/PDA–PES TFNC membranes prepared by interfacial polymerization were shown in Fig. 4(c) and (d). An ultra-thin film could be clearly observed on the substrate and the film was so thin that the surface contour of the PDA/PES nanofibrous substrate was also clearly seen in Fig. 4(c). Besides, the top active layer is closely combined with the substrate without any stripping as shown in cross-sectional image from Fig. 4(d). Many hydrophilic

groups (amine and phenol groups in dopamine, catechol groups of polydopamine) were introduced onto the surface of the substrate by PDA modification, which will facilitate the porous substrate to be saturated with PIP through covalent bond and non-covalent bonds. Besides, both the PIP and PDA can react with TMC [26], resulting in an integrated TFNC membrane formation. The thickness of the uniform barrier layer was 133 nm as seen in the cross-sectional image from Fig. 4(d).

The PAM/PDA–PES TFNC membranes were tested by filtering four different feeding solutions ( $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{MgSO}_4$  solutions with the same concentration of 1,000 ppm) to further determine their NF properties. As can be seen from Fig. 5, the rejections for divalent anions are clearly higher than that of monovalent anions which were typical characteristics for negatively charged membranes. It was confirmed that PIP/TMC active layers were negatively charged because of the carboxylic group due to the partial hydrolysis of acyl chloride units of TMC during the interfacial polymerization [27,28]. Divalent cation  $\text{Mg}^{2+}$  with an opposite charge to the resultant membrane has strong binding force to the membrane, which will reduce the negative charge on the membrane surface and lead to the rejection of  $\text{MgCl}_2$  less than that of  $\text{NaCl}$ .

The mechanical property, durability, and performance stability are very important for the application of thin-film composite nanofiltration membranes. Therefore, pressure resistance test and long-term

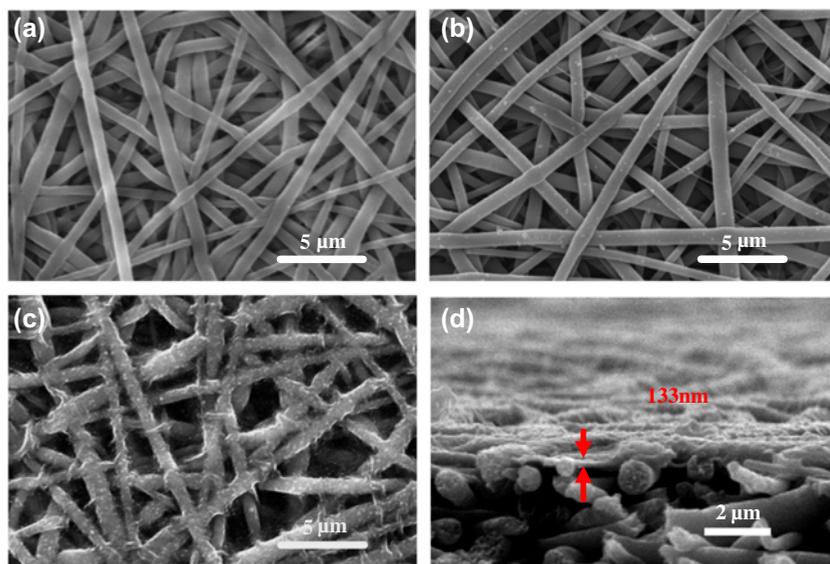


Fig. 4. Typical SEM images of electrospun PES nanofibrous membrane before (a) and after (b) PDA modification, surface (c) and cross-sectional (d) SEM images of PAM/PDA–PES composite NF membrane.

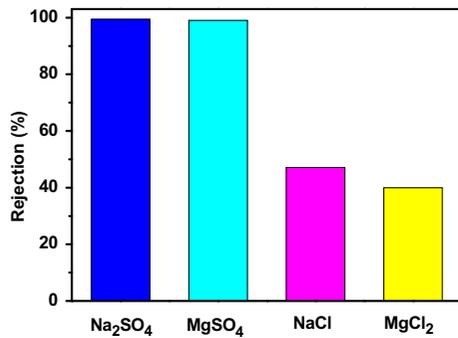


Fig. 5. Rejection ratio of PAM/PDA-PES membrane toward different salt solutions at operation pressure 0.6 MPa.

permeate test were carried out with 1,000 ppm Na<sub>2</sub>SO<sub>4</sub> aqueous solution. For comparison, TFNC membranes (called PAM/PES in the following), prepared at the same conditions as those of PAM/PDA-PES membrane but without PDA modification, were also evaluated.

Operating pressure has great effect on permeate flux and salt rejection as well as the energy consumption of the filtration process; therefore, the effect of operating pressure on the PAM/PDA-PES and PAM/PES NF performance were investigated and the results were shown in Fig. 6. It was observed in Fig. 6(a) that the rejection of PAM/PDA-PES membrane increases with operating pressure increase and appears to reach a constant rejection, while the permeate flux increases linearly with increasing operating pressure. This linear relationship between the permeate flux and operating pressure could be ascribed to the good mechanical strength and structural integrity of the PAM/PDA-PES membrane over the investigated pressure range (0.2–1.0 MPa).

However, as for PAM/PES membranes in Fig. 6(b), it showed a slow increase for rejection to Na<sub>2</sub>SO<sub>4</sub> as the operating pressure increased till 0.6 MPa, then the rejection decreased slightly with further operating pressure increase. Meanwhile, although the permeate flux increased with increasing operating pressure, the relationship between permeate flux and operating pressure is non-linear. This may be attributed to the compactness of the PAM/PES membranes after high pressure was exerted, indicating that PAM/PES membranes exhibit relatively weak pressure resistance. Besides, the salt rejection and permeate flux of PAM/PDA-PES membrane were obviously much higher than those of the PAM/PES membrane, which indirectly proved that the PDA played an important role in the fabrication of the integrated TFNC membrane by interfacial polymerization. The PAM/PDA-PES

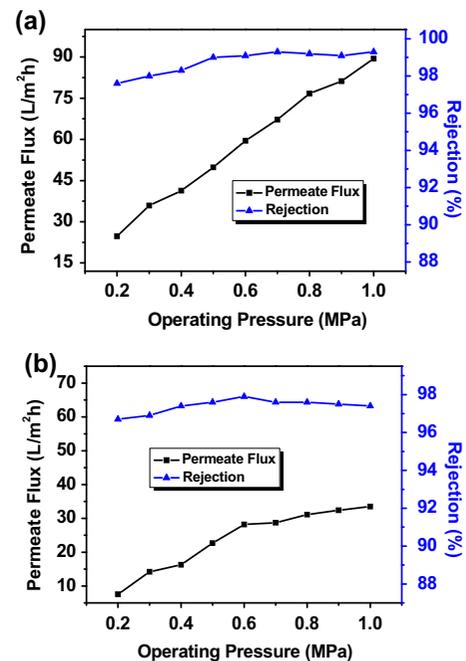


Fig. 6. Pressure dependencies of the composite nanofibrous membranes interfacially polymerized on PDA/PES nanofibrous membrane (a) and pure PES nanofibrous membrane (b) toward 1,000 ppm Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

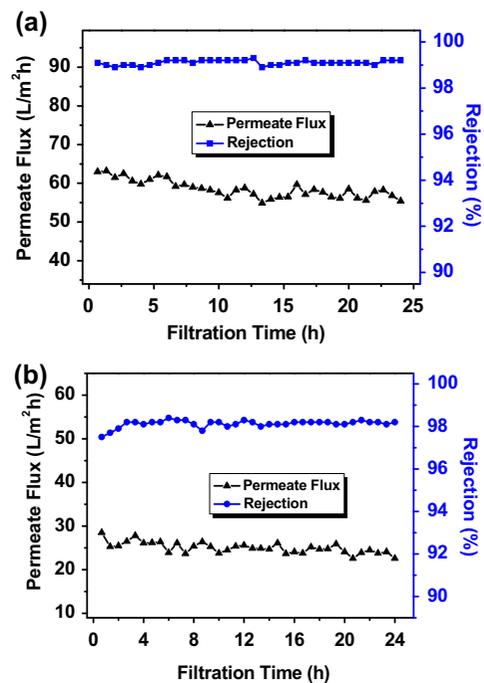


Fig. 7. Filtration time dependency of rejection and flux for composite nanofibrous membrane interfacially polymerized on PDA/PES nanofibrous membrane (a) and pure PES nanofibrous membrane (b) toward 1,000 ppm Na<sub>2</sub>SO<sub>4</sub> aqueous solution at operation pressure of 0.6 MPa.

Table 1  
Permeate flux and salt rejection ratio for different types of NF membranes

Barrier layer/scaffold	Salt	Applied pressure (MPa)	Flux (L/m <sup>2</sup> h)	Rejection (%)
TEOA–TMC/PSF [1]	600 ppm Na <sub>2</sub> SO <sub>4</sub>	0.6	11.5	82.2
PVAm–IPC/polyamide [5]	1000 ppm MgSO <sub>4</sub>	0.6	26.5	93.8
PIP–AEPPS/PSF [29]	1000 ppm Ka <sub>2</sub> SO <sub>4</sub>	0.6	43.1	97
PVAm–TMC/PS [30]	500 ppm Na <sub>2</sub> SO <sub>4</sub>	0.6	51.2	94.8
PEI–TMC/PES [31]	500 ppm MgSO <sub>4</sub>	0.8	24.5	94.4
PAM/PDA/PES (This work)	1000 ppm Na <sub>2</sub> SO <sub>4</sub>	0.6	63.0	99.2
PAM/PES (This work)	1000 ppm Na <sub>2</sub> SO <sub>4</sub>	0.6	28.5	98.2

membranes possess good mechanical integrity under the operation pressure in the range of 0.2–1.0 MPa.

Long-time NF tests were carried out to evaluate the NF performance at operating pressure of 0.6 MPa with 1,000 ppm Na<sub>2</sub>SO<sub>4</sub> aqueous solution during 24 h filtration and the results were shown in Fig. 7. It was clearly seen that the salt rejection of both membranes remained stable (99.2% for PAM/PDA–PES and 98.2% for PAM/PES membranes) during the whole filtration process, while the flux decreased slightly from 63.0 to 58.3 L/m<sup>2</sup> h (declined by 7.5%) for PAM/PDA–PES and from 28.5 to 22.6 L/m<sup>2</sup> h (declined by 20.7%) for PAM/PES membranes after 24 h. Besides, the permeate flux of PAM/PDA–PES was more than twice that of PAM/PES membrane and much higher than many other membranes (prepared by interfacial polymerization) reported in literatures (shown in Table 1) [1,5,29–31]. Obviously, the performances of PAM/PDA–PES membrane are much better than that of PAM/PES membrane both in rejection and permeate flux. Thus, it can be concluded that the PAM/PDA–PES membrane possessed excellent antifouling property: the flux declined less than 8% while salt rejection stayed constant to some extent during the testing period.

#### 4. Conclusion

TFNC membrane with high performance was successfully prepared by PDA-assisted interfacial polymerization. PES nanofibrous scaffold was modified by dopamine through self-polymerization for 3 h, followed by an interfacial polymerization at optimized conditions below: 1 wt% PIP in aqueous phase; 0.6 wt % TMC in organic phase (n-hexane); curing at 60 °C for 30 min. The PAM/PDA–PES TFNC membrane prepared at the optimized conditions showed relatively high permeate flux (~63.0 L/m<sup>2</sup> h) and high salt rejection (~99.4%) to divalent anion solutions (1,000 mg/L, Na<sub>2</sub>SO<sub>4</sub>) at a pressure of 0.6 MPa, doubling the flux of the TFNC membranes prepared at the same conditions but without dopamine modification (PAM/PES). The rejection order of the

resulting membrane for different salts is as following: Na<sub>2</sub>SO<sub>4</sub> ≈ MgSO<sub>4</sub> > NaCl > MgCl<sub>2</sub>. Besides, the PAM/PDA–PES membranes possessed excellent interfacial compatibility, pressure resistance, and antifouling property due to the PDA modification. The bioadhesion of PDA plays an important role in linking the active layer to the substrate. It was believed that dopamine modification was very efficient to fabricate integrated composite membranes with high filtration performance.

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