Optimization, characterization and nanofiltration properties test of MWNTs/polyester thin film nanocomposite membrane

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Abstract

MWNTs/polyester thin film nanocomposite (TFN) membranes were prepared through an improved process by interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC) on the polysulfone (PSf) supporting membrane in the presence of multi-walled carbon nanotubes (MWNTs). The effect of MWNTs concentration and surfactant species in the aqueous phase as well as the reaction time of interfacial polymerization on the membrane properties were investigated. The water permeability increased as the MWNTs concentration in aqueous phase increased up to 0.5 mg/mL, reaching a maximum which was nearly double that of the thin film membrane without MWNTs, while the membrane rejection kept increasing dramatically. Compared with cationic (CTAB) and non-ionic (Triton X-100) surfactants, anionic (SDS) surfactant was more suitable for the preparation of TFN membrane. The reaction time determined the extent of interfacial polymerization and the integrality of surface skin layer. Furthermore, the nanofiltration properties of the MWNTs/polyester TFN membrane were tested by examining the separation performance of different feed solutions, feed concentrations, feed pHs at 0.6 MPa operating pressure. Additionally, the MWNTs/polyester TFN membrane exhibited a good long-term stability.

1. Introduction

Water is perhaps the most important natural resource for human survival. The quality and availability of water resource are essential for food production, industrial productivity, energy production, domestic consumption and the global economy [1]. With the continuous decline of available freshwater supplies, recycling of municipal, industrial, and commercial wastewaters is gaining popularity in recent environmental policy. Membrane-based separation has emerged as an attractive process for water desalination, ultra pure water production, and waste water treatment. Especially, process based on nanofiltration (NF) membrane is increasingly recognized as one of the best processes for water treatment and production of portable water [2]. It exhibits favorable properties including high permeation flux, high reten tion of multi-valent ion salts, low operation pressure, and low maintenance cost. Most of the NF membranes are thin film composite membranes which are characterized by an ultra-thin separation selective layer supported on a porous substrate. A large number of NF membranes have been successfully developed from different polymers such as polyamide, polyester, etc [3,4]. However, the existing polymeric membrane materials seemingly reach a limit where the membrane structure and preparation processes are inadequate to meet the current expectations on both selectivity and permeability. Developing a new class of membrane materials that exhibit excellent separation performance has been proved to be a challenge following traditional polymer chemistry approaches.

An important recent discovery in the membrane technology is the nano-material/polymer mixed matrix membrane or nanocomposite membrane, where an inorganic filler material is dispersed throughout a continuous polymeric matrix. Nanoparticles such as zeolite, titanium dioxide, silica have been used to improve the performance of polymeric membranes [5,6]. Mixed matrix/nanocomposite membranes may exhibit improved mechanical, chemical, and thermal stability, as well as separation, reaction, and sorption capacity [7–12]. Carbon nanotubes (CNTs) now is one of the world hotspots of research due to its excellent mechanical, electrical, thermal properties and rapid mass transport behavior especially [13–17]. A great deal of impressive work related to CNTs/polymer mixed matrix membranes have been reported in virtue of many researchers’ hard efforts [18–25]. These mixed matrix membranes based on CNTs dispersed inside
a polymer matrix are mostly prepared by phase inversion method and for ultrafiltration separation. But the attention paid to the application of CNTs in the thin film composite membrane especially NF membrane is limited. Park et al. developed MWNTs/PA nanocomposite reverse osmosis (RO) membrane through a conventional process by interfacial polymerization of m-phenylene diamine (MPDA) and trimesoyl chloride (TMC) on the PSf support membrane. When a reasonable amount of MWNTs was used, chlorine resistance of MWNTs/PA nanocomposite RO membrane was measurably improved compared to the pure PA membrane [26]. Roy et al. prepared solvent-resistant nanofiltration membranes using conventional interfacial polymerization technique wherein MWCNTs were dispersed in either the organic phase or the aqueous phase after the outside surfaces of the MWCNTs were appropriately functionalized [27].

An improved process of interfacial polymerization was initiated to prepare MWNTs/polyester thin film nanocomposite (TFN) membrane in our previous study [28]. The improved process is facilely done by immersing the support membrane into the organic phase before the conventional process of interfacial polymerization. The procedure before the conventional process plays a positive role in the membrane properties which is realized by introducing a large amount of hydrophilic and negatively charged carboxyl groups on the membrane surface as well as being favorable for the incorporation of MWNTs in the thin film layer. The obtained TFN membrane exhibits improved permeability and excellent selectivity. As a continuation, the influences of MWNTs concentration and the kind of surfactants in the aqueous phase as well as the reaction time of interfacial polymerization on the nanocomposite membrane performance and morphologies were investigated in the present study. Furthermore, the nanofiltration properties of the TFN membrane were tested by examining the separation performance of different electrolyte solutions, feed concentrations and feed pHs. Additionally, the stability of the TFN membrane in long-time running was also tested.

2. Experimental

2.1. Materials

The microporous polysulphone supporting film was supplied by the Development Center of Water Treatment Technology (Hangzhou, China). Triethanolamine (TEOA, analytical grade), cetyltrimethylammonium bromide (CTAB, analytical grade) and Triton X-100 (chemical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trimesoyl chloride (TMC, 99%) was purchased from Chengdu Organic Chemicals Co., Ltd (Chinese Academy of Sciences), Na2CO3, NaOH, Na2SO4 and NaCl were analytical grade and used without further purification.

2.2. Membrane preparation

The MWNTs/polyester thin film nanocomposite membranes were prepared through an improved process. TEOA (60 mg/mL), a certain kind of surfactant (CTAB, SDS, Triton X-100, 3 mg/mL) and a certain amount of MWNTs (0.2, 0.4, 0.5, 06, 0.8, 1.0, 1.5 and 2.0 mg/mL) were placed in deionized water with the pH adjusted by a mixture of NaOH and Na2CO3, blended in 1:2 proportion, and then were sonicated to obtain the aqueous phase solution; TMC (6 mg/mL) was placed in n-hexane to obtain the organic phase solution. Therefore, the improved process for preparing MWNTs/polyester thin film nanocomposite membrane proceeded as follows and is shown in Scheme 1. First, the microporous PSf support membrane was immersed into the organic phase for 30 min. Then, the TMC-saturated support membrane was immersed into the aqueous phase for 35 min (step-1). After draining excess solution on the surface, the membrane was put into the organic phase again for a certain time (step-2). And then the membrane was post-treated in a 60 °C oven at atmospheric pressure for 30 min for further polymerization and formation of a skin layer. The membrane was washed in deionized water repeatedly to remove the excess trimesoyl chloride left on the membrane surface. The final membrane was stored in deionized water. The above-mentioned operation proceeded in a 35 °C water bath. The thickness of thin film layer formed upon the polysulphone supporting membrane is approximately 500 nm.

It should be noted that the TFC membrane is meant to represent the thin film composite membrane without the presence of MWNTs, while the TFN membrane denotes the MWNTs/polyester thin film nanocomposite membrane.

2.3. Membrane characterization

2.3.1. Flux and separation experiments

The measurements of pure water flux and salt rejection were performed using a cross-flow membrane module as shown in our previous paper [4]. The experimental setup is shown in Scheme 2, which can offer a membrane area of 27 cm². Before the measurement, all the membranes were pretreated at 0.8 MPa operation pressure for about 20 min and then the pure water flux and salt rejection were measured at an operation pressure of 0.6 MPa at room temperature. The water flux was calculated in Eq. (1):

\[ F = \frac{V}{At} \]

where \( V \) is the total volume of permeated pure water, \( A \) is the membrane area, and \( t \) is the operation time. Deionized water was
used for this measurement. The rejection was measured with 5 mmol/L Na$_2$SO$_4$ solution at an operation pressure of 0.6 MPa. The concentrations of the permeation and feed solutions were determined by electrical conductivity HANA-EC215 (Italy). The rejection $R$ was calculated in Eq. (2):

\[
R = 1 - \frac{C_p}{C_f}
\]

where $C_p$ and $C_f$ are the concentrations of the permeation and feed solutions, respectively.

### 2.3.2. Contact angle measurement

Water was used as the probe liquid for determination of the hydrophilicity at the membrane surface. The static contact angle of water on the surface of a polymer membrane was measured by using OCA15 (Dataphysics Co., Germany) and following the sessile drop method at 25 °C and a relative humidity of 65%. Drops were formed using a 10-μl Hamilton positive displacement syringe. The volume of each drop was 2.00 μL. The average value of the contact angle on each polymer membrane was calculated using at least five different locations on each membrane.

### 2.3.3. Streaming potential

Reversible Ag/AgCl electrodes were used to measure the resulting electrical potential difference ($\Delta E$) as the pressure difference across the membrane ($\Delta P$) changed through a digital electrometer (VC 890D, Shenzhen Victor Hi-tech Co., Ltd.). Then the streaming potential was calculated in Eq. (3):

\[
SP = \frac{\Delta E}{\Delta P}
\]

The pressure difference ranged from 0 to 4 × 10$^5$ Pa. The 5 mmol/L KCl solution was put in the unit by N$_2$ pressure controlled by a gauge.

### 2.3.4. Membrane morphology and observation

The morphologies of the surface of obtained membranes were observed with a scanning electron microscopy (TESCAN 5136MM) after being coated with conductive layer of sputtered gold. Quantitative surface roughness analysis of the composite membranes was measured using AFM imaging and analysis (NanoScope IV). Membrane samples were fixed on a specimen holder and 2 × 2 μm areas were scanned by tapping mode in air. The surface roughness was reported in terms of the average plane roughness ($R_a$) and root mean square roughness ($R_{rms}$).

### 2.3.5. Testing long-term stability of the MWNTs/polyester thin film nanocomposite membrane

Long-term test was conducted at an operation pressure of 0.6 MPa with 5 mmol/L Na$_2$SO$_4$ solution to investigate the mechanical property and performance stability of the MWNTs/polyester thin film nanocomposite membrane. Periodical measurements were carried out to check the permeability and rejection of the membrane.

### 3. Results and discussion

#### 3.1. Effect of MWNTs on the TFN membrane performance and morphologies

To investigate the influence of MWNTs content on the performance and morphology of the TFN membrane, MWNTs with concentrations of 0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 1.5 and 2.0 mg/mL were respectively added into aqueous phase to prepare TFN membrane. The TFC membrane was also prepared for comparison. Both the reaction time of step 1 and step 2 were fixed at 35 min, SDS was used as surfactant.

Fig. 1 is a plot of pure water flux and rejection to Na$_2$SO$_4$ vs. MWNTs concentration in aqueous phase. As MWNTs concentration increases, the pure water flux of the membranes continuously increases from the initial lower value of 10.8 L/m$^2$h when aqueous phase is without the presence of MWNTs, quickly to a maximum of 21.2 L/m$^2$h, when MWNTs concentration in aqueous phase is 0.5 mg/mL. Very interestingly, the salt rejection of membranes does not decrease but increase as the pure water flux improves. However, when MWNTs concentration increases further, especially past 0.5 mg/mL, the pure water flux of the membranes goes down with a slight decrease in the salt rejection.

When the concentration of MWNTs in aqueous phase is low enough (<0.5 mg/mL), carboxyl MWNTs can disperse well in the water solution with surfactant (SDS) through ultrasonication, contributing to TFN membrane with well dispersed MWNTs as validated in our previous paper [28]. The hydrophilic groups (–COOH and –OH) on the surface of MWNTs can improve the hydrophilicity of membrane surface, alleviate the membrane fouling, and enhance the pure water flux as a result. Fig. 2 shows the water contact angles of the TFN membranes with different concentrations of MWNTs. As the amount of MWNTs added into aqueous phase increases, the contact angle of membrane decreases and correspondingly the membrane hydrophilicity increases until it reaches an inflexion. The incorporated MWNTs can also hinder the formation of densely-crosslinked polyester film structure, contributing to the enhancement of water flux.
However, when the amount of MWNTs in aqueous phase is high enough (> 0.5 mg/mL), the distribution of MWNTs becomes worse, leading to non-uniform dispersion, agglomeration and cluster forming of MWNTs in the solution. MWNTs bundles have smaller specific surface area and lower adsorption activity with membrane surface. Consequently, over high concentration of MWNTs in the aqueous phase may result in a decrease in the TFN membrane hydrophilicity and water permeate rate.

Fig. 3 shows the streaming potentials of TFN membranes prepared with different concentrations of MWNTs. The streaming potential of TFN membrane with both improved water permeability and salt rejection is prepared through the improved process, which is done by immersing the support membrane into organic phase followed with step-1 and step-2, as shown in Scheme 1. In our previous study, it is found that the process of step-1 plays a positive role in the performance and the morphology of the TFN membrane. To further reveal the role of the step-2 of the improved process in the TFN membrane formation, the influence of surfactant on the TFN membrane performance, different kinds of anionic (SDS), cationic (CTAB), and non-ionic (Triton X-100) surfactants were added into the aqueous phase respectively, and the concentration of MWNTs in the aqueous phase was 0.5 mg/mL. Seen from Fig. 3, surfactants play a distinctive role on the TFN membrane properties. Membrane prepared with cationic surfactant CTAB exhibits the highest water flux and the most serious declined salt rejection. It can be attributed to the non-uniform distribution, severe aggregation and precipitation of MWNTs in the aqueous phase using CTAB as surfactant even after ultrasonic, which could be observed during the experiment (Fig. 5 inset). The agglomeration and cluster formation of MWNTs bring about poor interfacial compatibility of MWNTs and polymer, leading to nonselective voids formed in the thin film layer. Thus the permeability increases and the selectivity deteriorates. MWNTs can disperse well in the aqueous phase solution with Triton X-100 and SDS respectively. The negative charge of SDS may increase the charge density of thin layer, contributing to a higher rejection to Na₂SO₄ of TFN membrane, in comparison with membrane with non-ionic surfactant Triton X-100 [30]. Therefore, SDS is considered to be more suitable for the preparation of MWNTs/polyester TFN membrane.

3.2. Effect of surfactant on the TFN membrane performance

It has been reported that surfactant has a significant effect on the TFC membrane property and morphology [30]. To investigate the effect of surfactant on the TFN membrane performance, the TFC membrane property and morphology [30]. To investigate the effect of surfactant on the TFN membrane performance, the effect of surfactant on the TFN membrane performance, the effect of surfactant on the TFN membrane performance, the concentration of MWNTs in the aqueous phase was 0.5 mg/mL. Seen from Fig. 5, surfactants play a distinctive role on the TFN membrane properties. Membrane prepared with cationic surfactant CTAB exhibits the highest water flux and the most serious declined salt rejection. It can be attributed to the non-uniform distribution, severe aggregation and precipitation of MWNTs in the aqueous phase using CTAB as surfactant even after ultrasonic, which could be observed during the experiment (Fig. 5 inset). The agglomeration and cluster formation of MWNTs bring about poor interfacial compatibility of MWNTs and polymer, leading to nonselective voids formed in the thin film layer. Thus the permeability increases and the selectivity deteriorates. MWNTs can disperse well in the aqueous phase solution with Triton X-100 and SDS respectively. The negative charge of SDS may increase the charge density of thin layer, contributing to a higher rejection to Na₂SO₄ of TFN membrane, in comparison with membrane with non-ionic surfactant Triton X-100 [30]. Therefore, SDS is considered to be more suitable for the preparation of MWNTs/polyester TFN membrane.

The TFN membrane with both improved water permeability and salt rejection is prepared through the improved process, which is done by immersing the support membrane into organic phase followed with step-1 and step-2, as shown in Scheme 1. In our previous study, it is found that the process of step-1 plays a positive role in the performance and the morphology of the TFN membrane. To further reveal the role of the step-2 of the improved process in the TFN membrane formation, the influence of reaction time of step-2 ranging from 0 to 40 min on the TFN membrane properties was investigated. The concentration of MWNTs in the aqueous phase was 0.5 mg/mL. Seen from Fig. 5, surfactants play a distinctive role on the TFN membrane properties. Membrane prepared with cationic surfactant CTAB exhibits the highest water flux and the most serious declined salt rejection. It can be attributed to the non-uniform distribution, severe aggregation and precipitation of MWNTs in the aqueous phase using CTAB as surfactant even after ultrasonic, which could be observed during the experiment (Fig. 5 inset). The agglomeration and cluster formation of MWNTs bring about poor interfacial compatibility of MWNTs and polymer, leading to nonselective voids formed in the thin film layer. Thus the permeability increases and the selectivity deteriorates. MWNTs can disperse well in the aqueous phase solution with Triton X-100 and SDS respectively. The negative charge of SDS may increase the charge density of thin layer, contributing to a higher rejection to Na₂SO₄ of TFN membrane, in comparison with membrane with non-ionic surfactant Triton X-100 [30]. Therefore, SDS is considered to be more suitable for the preparation of MWNTs/polyester TFN membrane.

3.3. Effect of reaction time of step-2 on the TFN membrane performance and morphologies

The TFN membrane with both improved water permeability and salt rejection is prepared through the improved process, which is done by immersing the support membrane into organic phase followed with step-1 and step-2, as shown in Scheme 1. In our previous study, it is found that the process of step-1 plays a positive role in the performance and the morphology of the TFN membrane. To further reveal the role of the step-2 of the improved process in the TFN membrane formation, the influence of reaction time of step-2 ranging from 0 to 40 min on the TFN membrane properties was investigated. The concentration of MWNTs in the aqueous phase was 0.5 mg/mL. SDS was used as surfactant, and the reaction time of step 1 was fixed at 35 min. A plot of pure water flux and rejection to Na₂SO₄ vs. reaction time of step-2 is shown in Fig. 6. There is a significant decrease in the pure water flux of the TFN membrane when the reaction time of step-2 is up to 15 min, and then the water permeate flux is almost unaffected by the reaction time of step-2 from 15 to 40 min. Besides, the result also demonstrates that the membrane has only little retention to Na₂SO₄ solution when reaction time is less than 15 min. However, the salt rejection increases from 64.7% to 79.5% when the reaction time of step-2 is prolonged from 15 min to 40 min. As is well known, interfacial polymerization is diffusion-controlled and exists in a self-limiting phenomenon. Thus, the reaction time of interfacial polymerization plays an
important role in determining the extent of reaction [31–33]. The top skin layer thickness of the composite membrane increases as the polymerization time prolongs. When thin layer is thick enough to prevent the monomer diffusing from one phase into the other phase, the top layer thickness may stop growing. In the case of the aqueous phase containing MWNTs in the study, the role of reaction time of step-2 is mainly considered to increase the top layer thickness and anchor MWNTs in the top layer. Thus, with a short reaction time of step-2, the extent of cross-linking of polymerization is low, leading to a high permeability of the membrane. After a certain period of reaction, the pure water flux will almost stay constant because the thickness of selective layer is almost fixed [34]. However, the poor morphology of the membrane surface layer will be improved with the increase of reaction time and the membrane may gradually become integrate. Thus, the salt rejection still increases although the top layer thickness stops growing.

Furthermore, the other role of reaction time of step-2 is speculated to anchor MWNTs in the top layer, bringing about an increase in the hydrophilicity of membrane surface. Fig. 7 is a plot of water contact angle of the TFN membrane vs. reaction time of step-2. As the reaction time of step-2 increases, the contact angle of membrane surface rapidly decreases. It is likely caused by the increased amount of hydrophilic groups from polymer and MWNTs on the surfaces of the membrane.

Fig. 8 presents the SEM images of the surfaces of TFN membranes with various reaction times of step-2. The TFN membrane possesses a rough and nodular surface structure. Besides, the surfaces of TFN membranes become rougher and finally more compact as the reaction time increases. The roughness of the
membrane surface can be quantified from the AFM results as presented in Fig. 9 and Table 1. Clearly, the surface of the TFN membrane becomes rougher as the reaction time of step-2 increases.

3.4. Separation properties of the TFN nanocomposite membrane

The TFN membranes to be studied were constructed under the optimized preparation parameters: the concentration of MWNTs added into aqueous phase was 0.5 mg/mL, SDS was used as surfactant, and the reaction time of step-1 and step-2 were both fixed at 35 min.

3.4.1. Effect of feed concentration on the membrane performance

The effect of feed concentration on the rejection for solute NaCl and Na$_2$SO$_4$ is shown in Fig. 10. For NaCl solution, the rejection decreases rapidly as the feed concentration increases and reaches a low value about 12% when the NaCl concentration is larger than 15 mmol/L. For Na$_2$SO$_4$ solution, the rejection decreases relative slightly as the feed concentration increases and still remains more than 54% even when the Na$_2$SO$_4$ concentration is larger than 20 mmol/L. The reason that rejection declines as feed concentration increases is related to concentration polarization. The negative charges on the TFN membranes and the mobility of the ions across the membrane jointly result in the retention difference between NaCl and Na$_2$SO$_4$ [35–37]. Donnan exclusion of the solute co-ions occurs at the interface of a membrane with fixed charges which cannot freely 'move out' of the membrane matrix, thus the membrane will absorb solute counter ions and repel solute co-ions. For negatively charged TFN membranes, Na$_2$SO$_4$ has stronger repel force and lower diffusion coefficient than NaCl, leading to higher rejection of Na$_2$SO$_4$ [38]. Based on the experimental results for different solute, it is possible for TFN membranes to be applied in the treatment of concentrated sodium chloride aqueous with sodium sulfate for that high rejection selectivity of SO$_4^{2-}$/C$_0$/Cl$_0$/C$_0$.

3.4.2. Effect of pH in feed on the TFN membrane performance

The effect of pH in feed on the flux and salt rejection for Na$_2$SO$_4$ solution is shown in Fig. 11 (To avoid the influence of unwanted ions on separation performance, pH in the Na$_2$SO$_4$ solution was adjusted from 5 to 9 using H$_2$SO$_4$ and NaOH; the pressure applied was fixed at 0.6 MPa; the solute concentration of the feed was 5 mmol/L). The flux for Na$_2$SO$_4$ solution is found to decrease at first and then increase when the pH value in feed increases from 5 to 9. This is perhaps due to the presence of tertiary amino groups on the surface of MWNTs/polyester nanocomposite membranes. At a lower pH value of the feed, amino groups on the membrane surface change into R$_3$HN$^+$, which results in an increase in the hydrophilicity of the membrane and correspondingly the higher permeate flux [4].
Whereas, with the increasing pH in the feed, tertiary amino groups on the surface of the TFN membranes cannot be transferred into R₃HN⁺, and the negatively charged groups (−COO⁻/C₀O⁻) of the membrane surface increase, possibly resulting in more repulsion between the polymer segments and thus an increase of the free volume in the membrane matrix \[39\]. Therefore, the flux increases and rejection decreases in a higher pH feed. Although the electrostatic repulsion between the negatively charged groups (−COO⁻) on the membrane surface and SO₄²⁻ in the feed solution also increases with an increase in pH of feed, leading to an increase in the rejection, the effect of free volume has a greater impact on the rejection property of TFN membrane.

Table 1

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Ra (nm)</th>
<th>Rms (nm)</th>
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<tbody>
<tr>
<td>0</td>
<td>5.93</td>
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<tr>
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<tr>
<td>40</td>
<td>42.3</td>
<td>53.4</td>
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</tbody>
</table>

Fig. 9. AFM images of the surfaces of the TFN membranes with different reaction times of step-2: (a) 0 min and (b) 35 min.

Fig. 10. Salt rejections as a function of the feed concentrations of Na₂SO₄ and NaCl solutions for TFN membrane at 0.6 MPa.

Fig. 11. Rejection and flux of Na₂SO₄ solution as a function of the pH value of Na₂SO₄ solutions for TFN membrane at 0.6 MPa.
3.5. Stability of the TFN membrane in long-time running

The mechanical property and performance stability are very important for membrane application. Thus, a long-term test was carried out at an operation pressure of 0.6 MPa with 5 mmol/L Na$_2$SO$_4$ aqueous solution. The fluxes and rejections of the studied TFN membrane were examined during 70 h of filtration running as shown in Fig. 12. It can be seen that the MWNTs/polyester thin film nanocomposite membrane exhibits a good long-term stability.

4. Conclusions

Multi-walled carbon nanotubes (MWNTs)/polyester thin film nanocomposite (TFN) membranes were prepared through an improved process by interfacial polymerization of MWNTs-dispersed triethanolamine (TEOA) aqueous solution and trimesoyl chloride (TMC) organic solution. The membrane performance and morphologies are remarkably influenced by MWNTs concentration and surfactant in the aqueous phase as well as the reaction time of interfacial polymerization. The results suggest that it is feasible to construct MWNTs/polyester nanocomposite membrane with both high permeation flux and excellent selectivity, using an adequate amount of MWNTs, an appropriate kind of surfactant and a proper reaction time. Furthermore, the experiment of membrane separation properties suggests it is possible for the TFN membrane to be applied in the removal of sodium sulfate from the concentrated brine of chloralkali industry due to high rejection selectivity of SO$_4^{2-}$ from Cl$^-$. The effect of pH on the flux and salt rejection for Na$_2$SO$_4$ solution was also investigated, and the results indicates the TFN membrane is relatively suitable for neutral and alkali feed. Additionally, the TFN membrane exhibits a good long-term stability.

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