



Study on a novel polyester composite nanofiltration membrane by interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC)

I. Preparation, characterization and nanofiltration properties test of membrane

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ABSTRACT

A novel thin-film composite (TFC) membrane for nanofiltration (NF) was developed by the interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC) on the polysulfone (PSF) supporting membrane. The active surface of the membrane was characterized by using FT-IR, XPS and SEM. The performance of TFC membrane was optimized by studying the preparation parameters, such as the reaction time of polymerization, pH of aqueous phase and the concentration of reactive monomers. It is found that the membrane performance is related to the changes of the monomer content in the aqueous phase rather than in the organic phase. Furthermore, the nanofiltration properties of the TFC membrane were tested by examining the separating performance of various salts at 0.6 MPa operating pressure. The rejection to different salt solutions decreased as per the order of Na_2SO_4 (82.2%), MgSO_4 (76.5%), NaCl (42.2%) and MgCl_2 (23%). Also, streaming potential tests indicated that isoelectric point of the TFC membrane is between pH 4 and 5. Moreover, the investigation of the flux for NaCl solution at different pH showed that the polyester NF composite membrane is also particularly suitable for treating acidic feeds: the flux increased from 8.4 to 11.5 L/m² h when pH of the feed decreased from 9 to 3. Additionally, the TFC membrane exhibits good long-term stability.

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1. Introduction

Nanofiltration (NF) membrane separation plays an important role in various industrial fields, such as water treatment, pharmaceutical, biochemical industries and so on thanks to its advantages including low operation pressure, high permeate flux and high retention of multi-valent ion salts [1–3]. The current worldwide expansion and diverse applications of NF technology result from the introduction of thin-film composite (TFC) membranes by interfacial polymerization in 1972 [4–6]. The TFC composite membrane is characterized by an ultra-thin separating selective layer supported on a porous substrate. Moreover, the top selective layer and bottom porous substrate of the composite membrane can be independently selected, studied and modified to maximize the overall membrane performance [7,8]. A large number of TFC membranes have been successfully developed from different polymers such as polyurea [9], polyamides [10], polyurea-amides [4,11,12], polyimide [13], polyester [14,15], polysulfonamide [16], etc. In recent

years, studies have been focused on choosing or synthesizing of new monomers with special functional groups to prepare the TFC membrane. For instance, a novel nanofiltration membrane was prepared with poly (amidoamine) (PAMAM) dendrimer and trimesoyl chloride (TMC) by *in situ* interfacial polymerization on ultrafiltration membrane [17]. The membrane surface charge can be adjusted according to the amino groups and tertiary amino groups on the membrane. Reddy prepared poly (amide-imide) composite membrane containing poly (amide-amic acid) ultrathin barrier layer by the interfacial polymerization of diamine amic acids (DAAs) and isophthaloyl chloride (IPC) [18]. The membrane displayed high water permeation due to the fact that the membrane contained less compact and highly hydrophilic PAA barrier layer.

However, it is particularly important to prepare TFC membrane for the purpose of practicality and easy realization. Thus, it is natural to seek an inexpensive monomer to manufacture a new membrane whose property spectrum has the optimum cost-performance balance for application. In our primary experiment, it is found that triethanolamine (TEOA) is an active monomer which is environment-friendly, economical and easy to be obtained. And it can react with multifunctional acid chloride to form cross-linked network structure due to the existence of multi-hydroxyl in its

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molecule. Furthermore, the tertiary amino group in its molecule can be transferred into quaternary ammonium group to improve the membrane performance by adjusting pH of the feed solution or reacting with alkyl halides. Thus, in the present work, a novel polyester composite nanofiltration membrane was prepared by interfacial polymerization of TEOA and TMC on the polysulfone supporting membrane. The performance of TFC membrane was optimized by studying the preparation parameters, such as the reaction time of polymerization, pH of aqueous phase and the concentration of reactive monomers. And the nanofiltration properties of the TFC membrane were also tested by examining separating performance of various salts. It is found that the novel polyester composite nanofiltration membrane can be efficiently applied in separating multi-valent anion from mono-valent anion in neutral electrolyte solution because the TFC membrane presents negative charge at pH higher than the isoelectric point of the membrane (between pH 4 and 5). Additionally, the result that the flux for NaCl solution increased with the decrease of the pH in the feed shows that the TFC polyester membrane is also particularly suitable for treating acidic feed.

2. Experimental

2.1. Materials

The microporous polysulphone supporting film was supplied by the Development Center of Water Treatment Technology, SOA, Hangzhou, China. Triethanolamine (TEOA) purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) was used as an active monomer of aqueous phase. Trimesoyl chloride (TMC) used as an active monomer of organic phase was obtained from Qindao Sanli Chemical Engineering Technology Co., Ltd. *n*-hexane was used as the organic phase solvent, which was obtained from Shanghai Feida Industry & Trade Co. Ltd. Sodium dodecyl sulphate (SDS) was achieved from Wenmin Biochemistry Science and Technology Co. Ltd. Na₂SO₄, MgSO₄, NaCl and MgCl₂ were analytical grade and used without further purification.

2.2. Membrane preparation

The composite membranes were prepared by conventional interfacial polymerization technology. The typical, simple process used in this study was as follows. Firstly, the aqueous phase solution was prepared: TEOA and SDS (0.3%, w/v) were placed in deionized water with pH adjusted by the mixture of NaOH and Na₂CO₃, which was blended in the proportion of 1:2, whereas the organic phase solution was composed of TMC in the *n*-hexane. Then, the microporous PSf supporting membrane was immersed into the aqueous phase for about 30 min at 35 °C. The surface was rolled with a soft rubber roller to eliminate any little bubbles during soaking procedure. The excess solution was drained from the membrane surface and air-dried at room temperature until no remaining liquids. Afterwards, we placed the membrane into the organic phase for a certain time. And then the membrane was post-treated in a 60 °C oven for about 30 min for further polymerization, leading to the formation of a skin layer. The final membranes were washed in deionized water repeatedly and stored in deionized water.

2.3. Membrane characterization

2.3.1. ATR-FT-IR

Chemical characterization of the membrane surface was accomplished by attenuated total reflectance infrared (ATR-FT-IR) spectroscopy instrument with Nicolet Nexus Smart ARK Fourier transform infrared spectrometer. Dry specimens of the membrane

samples were cut to ATR crystal size and mounted in an ATR cell. The reactive monomers such as TEOA and TMC were characterized with transmission FT-IR. The spectra were collected at spectral resolution of 4 cm⁻¹ by accumulating 128 scans. The measured wavenumber range was 4000–650 cm⁻¹. All original spectra were baseline corrected using the Omnic 5.1 software.

2.3.2. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using a RBD upgraded PHI-5000C ESCA system (PerkinElmer) with Mg K α radiation ($h\nu = 1253.6$ eV). The X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The base pressure of the analyzer chamber was about 5×10^{-8} Pa. Binding energies were calibrated by using the containment carbon (C 1s = 284.6 eV).

2.3.3. SEM observation

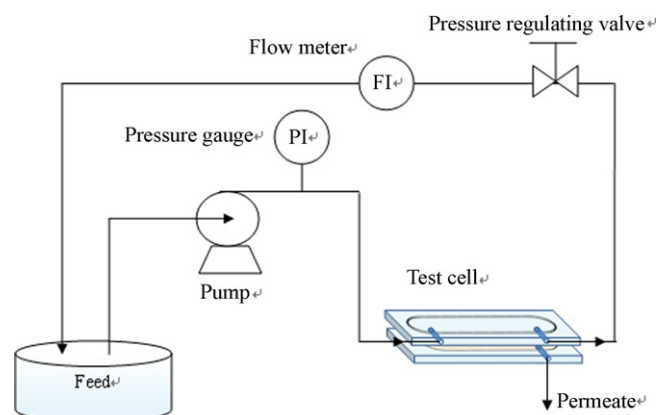
The morphologies of the surface of the TFC membrane and PSf supporting membrane were observed with a scanning electron microscopy (XL 30 Philips). The membrane samples were coated with gold before observation.

2.3.4. Pure water flux and rejection

Pure water flux and salt rejection test were conducted with a cross-flow membrane module (the experimental setup is shown in Scheme 1), which can offer a membrane area of 60 cm². Before measurement, all the membranes were pretreated with high pressure drop (0.6 MPa) for about 20 min and then the pure water flux and salt rejection were measured at 0.6 MPa operation pressure difference. Water flux was achieved by measuring the volume of permeate that penetrated the unit area membrane per unit time and calculated as $F = V/At$, where V is the total volume of pure permeated during the experiment, A represents the membrane area and t denotes the operation time. The rejection of the membrane was measured at 0.6 MPa with 5 mmol/L MgSO₄ solution. Rejection, R , is defined by the following equation: $R = 1 - (C_p/C_f)$. Where C_p and C_f are the concentration of the permeate and the feed, which was determined by electrical conductivity HANA-EC215 (Italy).

2.3.5. Streaming potential

The setup to determine streaming potentials was almost similar to that described by our previous paper [19]. Reversible Ag/AgCl electrodes, placed on both sides of the membrane, were used to measure the resulting electrical potential difference (ΔE) as the pressure difference across the membrane (ΔP) changed through a digital electrometer (VC 890D, Shenzhen Victor Hi-tech Co. Ltd.). Then the streaming potential was calculated as $SP = \Delta E/\Delta P$. The pressure difference ranged from 0 to 4×10^5 Pa. The 5 mol/m³ KCl



Scheme 1. Schematic representation of membrane property test apparatus.

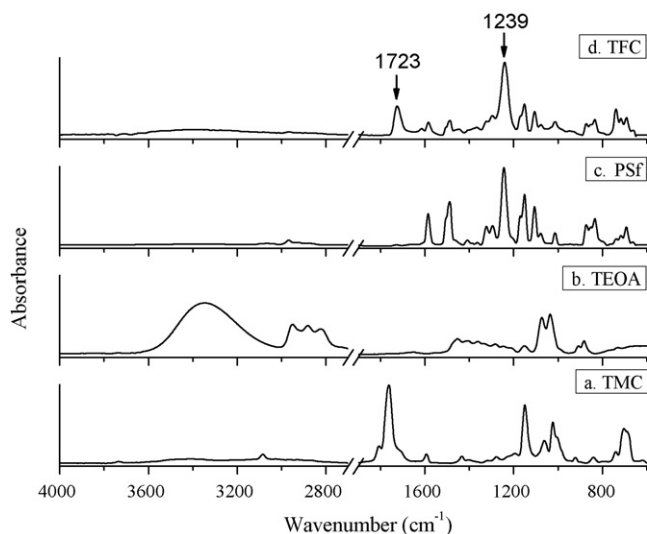


Fig. 1. FT-IR spectra of (a) TMC; (b) TEOA; (c) PSf support membrane and (d) TFC membrane.

solution with pH 3–6 adjusted by hydrochloric acid aqueous solution and 7–11 by potassium hydroxide aqueous solution, was put in the unit by N_2 pressure controlled by a gauge.

2.4. Testing long-term stability of the composite membrane

Long-term test was conducted at operating pressure of 0.6 MPa with 5 mmol/L Na_2SO_4 solution to investigate the mechanical property and performance stability of the composite membrane. Periodical measurements were carried out to check the permeability and rejection of the membrane.

3. Results and discussion

3.1. Characterization of surface layer

Samples of the thin-film composite membrane were characterized by using ATR-FT-IR for surface analysis. As a comparison, the FT-IR spectra of PSf supporting membrane and the reactive monomers (TEOA and TMC) are also displayed. The results are demonstrated in Fig. 1, which indicate that the interfacial polymerization has occurred since the acid chloride band at 1760 cm^{-1} (Fig. 1(a)) is absent and two strong bands at 1723 and 1239 cm^{-1} (Fig. 1(d)) are present, which are characteristic of $\nu C=O$ and $\nu C-O-C$ of ester compound, respectively. Furthermore, the TFC membrane was analyzed for the chemical composition of skin layer through XPS analysis. The XPS survey scan for the investigated sample is shown in Fig. 2 and the elemental compositions are summarized in Table 1. When polymerizing on the surface of PSf supporting membrane, it was assumed that three possible ideal categories of cross-linked polymer chains had been formed, including totally

Table 1
Relative surface atomic concentration of the cross-linked polymer chain and their concentration ratios

Unit	C (%)	O (%)	N (%)	O/N
Calculated data from three ideal structures				
Totally cross-linked (A)	68.18	27.27	4.55	6
Polymer chain with pendant $-COOH$ (B)	65.22	30.43	4.35	7
Polymer chain with pendant $-CH_2CH_2OH$ (C)	65.63	28.13	6.25	4.5
Actual data of XPS analysis	63.29	31.09	5.62	5.53

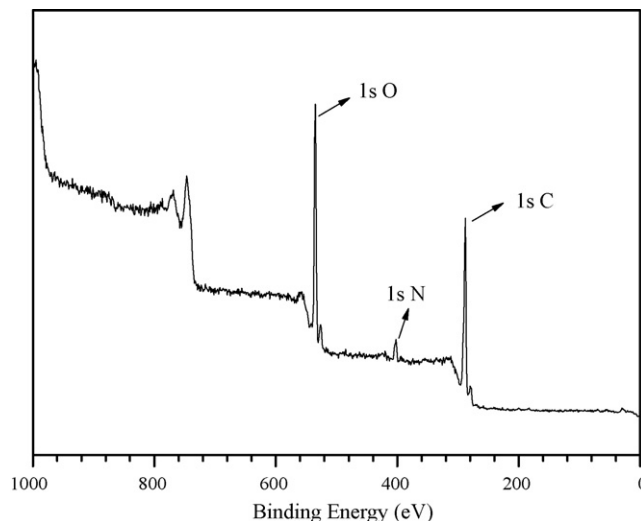


Fig. 2. XPS survey spectra for TFC membrane.

cross-linked chain (A), chain with pendant $-COOH$ (B) and chain with pendant $-CH_2CH_2OH$ (C) (as shown in Scheme 2). According to the three chemical structures, the relative atomic concentrations were calculated (Table 1). As shown in Table 1, the atomic concentrations of C and O in TFC membrane, measured by XPS, are very close to them in the unit B. Whereas, the atomic ratio O/N of 5.53 is between 4.5 determined from unit C and 6 from unit A. These results clearly evidence the existence of all three polymer chains in the surface layer of TFC membrane, correspondingly exhibits larger polymer chain with pendant $-COOH$ as compared to polymer chain with pendant $-CH_2CH_2OH$ and a small amount of totally cross-linked polymer chain.

The changes of the surface morphologies between PSf supporting membrane and the TFC membrane can be observed distinctly from Fig. 3, which shows the surface SEM images of PSf supporting membrane and the TFC membrane at different magnification. Comparing with Fig. 3(a), one can see that the interfacial polymerization technique generates a rough active layer on the PSf supporting membrane (as shown in Fig. 3(b)). Upon further observation of TFC membrane, it is found that the surface of the skin layer is also dense (Fig. 3(c)).

3.2. The performance optimization of the TFC membrane

In general, the performance of the composite membrane is determined by the chemistry and the preparation conditions of the ultra-thin selective layer. The former is an inherent property of the reactants taken to form the selective layer while the latter plays an important role in determining the structure of the interfacially polymerized film and subsequently the membrane performance [8]. For any given pair of reactants taken to form the ultra-thin film selective layer, the preparation conditions have to be optimized to obtain a membrane with optimal performance characteristics. Thus, in the following section, the preparation conditions such as the reaction time of polymerization, the pH of aqueous phase solution as well as the concentration of the reactants including the monomer in the aqueous phase and the organic phase were investigated to optimize the membrane performance.

3.2.1. Reaction time

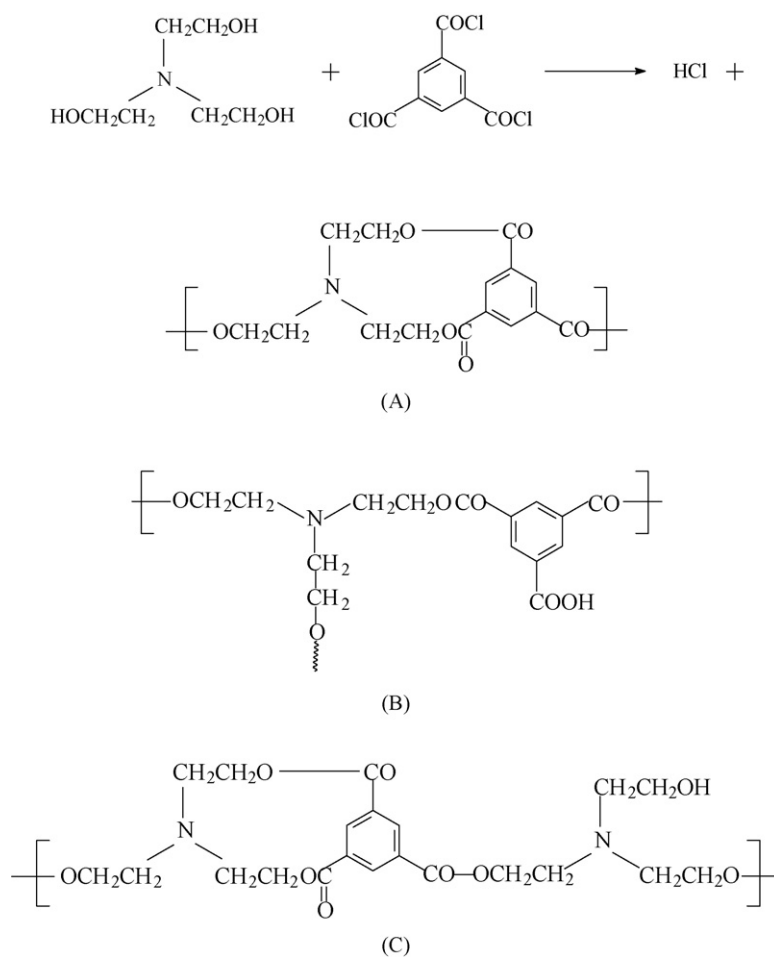
The reaction time of polymerization from 1 to 35 min was investigated firstly under the following membrane preparation

condition: 4.0% (w/v) TEOA and 0.3% (w/v) NaOH/Na₂CO₃ in H₂O; 0.5% (w/v) TMC in *n*-hexane at 35 °C. The results of the pure water flux and rejection to MgSO₄ solution are presented in Fig. 4 (at 0.6 MPa operating pressure). One can see that, there is a significant decrease in the pure water flux of the membrane when the reaction time is up to 6 min, and then the permeate flux is almost unaffected by the reaction time from 6 to 35 min. On the other hand, the result of the salt rejection of the membrane demonstrates that there is nearly no retention of the membrane to MgSO₄ solution when reaction time is less than 6 min. However, the salt rejection increases slightly from 12.1% to 22.1% when the reaction time is prolonged from 6 to 35 min. It is well known that the interfacial polymerization is diffusion-controlled and exists in a self-limiting phenomenon. Thus, the reaction time plays an important role in determining the extent of reaction [8,10,20]. The top skin layer thickness of the composite membrane increases with increasing polymerization time. When the thickness of the thin layer is enough to prevent the monomer diffusing from one phase into the other phase, the top layer thickness will stop growing. Thus, for a short reaction time, the extent of cross-linking is low; as a result, the permeability of the membrane is high. After a certain period of reaction, the pure water flux will almost stay constant because the thickness of selective layer is almost fixed [21]. However, the poor morphology of the membrane surface layer will be improved with the increase of reaction time and the membrane will gradually become integrated. Thus, the salt rejection increases slightly although the top layer thickness stops growing. In the study, 35 min

is considered as an optimal reaction time, which shows relatively high retention and proper water flux.

3.2.2. The pH of aqueous phase solution

To further increase the separation performance of the composite membrane, other factors enhancing the top skin layer morphology are considered. Among them, one factor that affects the top layer formation is the pH of the aqueous phase solution. In the study, the pH of aqueous phase solution was adjusted by the mixture of NaOH and Na₂CO₃, which was blended in the proportion of 1:2. Thus, for easy calculation, the effect of the pH on the membrane performance is demonstrated by direct investigation of the influence of mass fraction of NaOH/Na₂CO₃ in the aqueous phase solution on the membrane performance. Fig. 5 is the experimental results of the pure water flux and MgSO₄ rejection of the membranes which were prepared under different concentration of NaOH/Na₂CO₃ in the aqueous phase at reaction time about 35 min and the other preparation parameters were same as the former. It is found that the flux decreases drastically when the concentration of NaOH/Na₂CO₃ increases from 0.1% (w/v) (the pH is about 10) to 0.6% (w/v) (the pH is about 12), which corresponds to an increase in the salt rejection of the membrane. However, the membrane performance has a break if the concentration of NaOH/Na₂CO₃ is increased to 0.7% (w/v) (the pH is about 12.2). It is known that the hydrogen chloride is formed during the interfacial polymerization as presented in Scheme 2. The mixture of NaOH/Na₂CO₃ in the aqueous solution is an acid acceptor and can absorb hydrogen chloride. This is



Scheme 2. Possible polymerization reaction between TEOA and TMC to form (A) totally cross-linked polymer chain, (B) polymer chain with pendant -COOH and (C) polymer chain with pendant -CH₂CH₂OH.

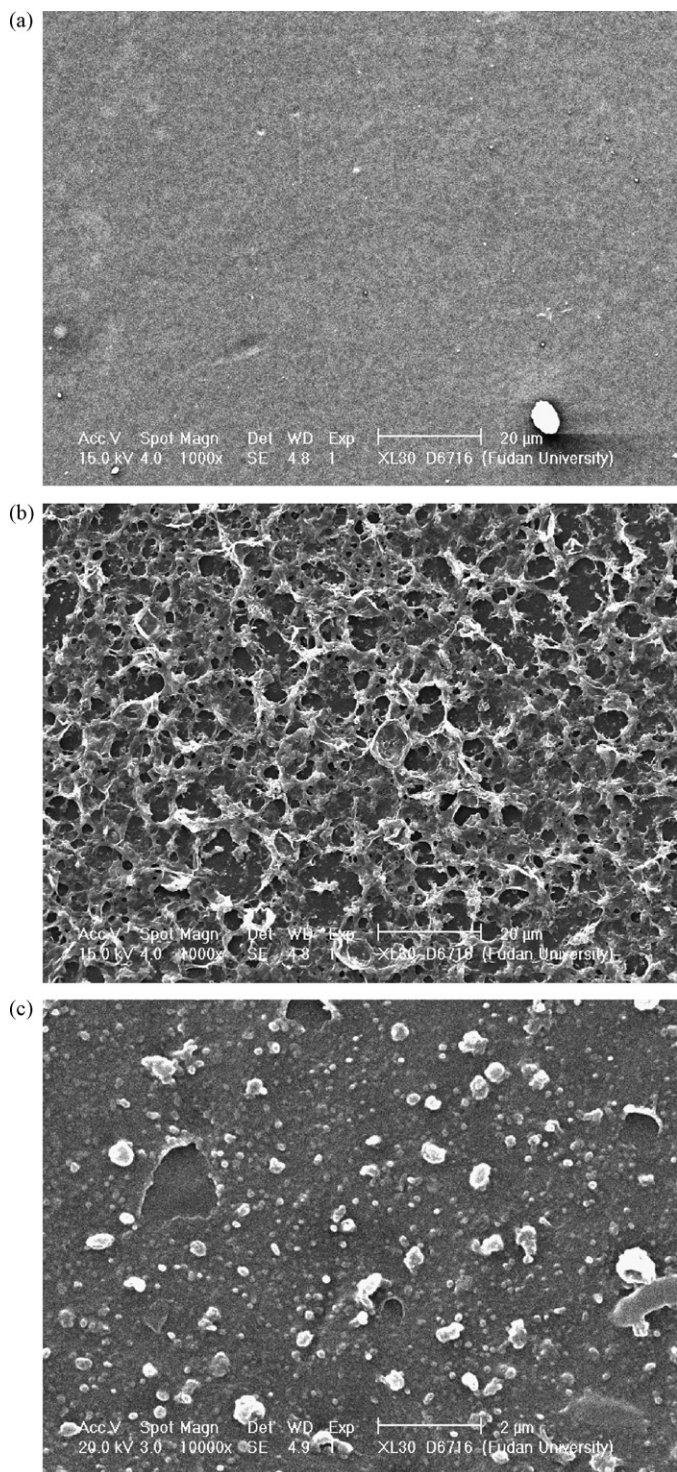


Fig. 3. SEM images of surface morphologies of (a) PSf supporting membrane, (b) TFC-PSf membrane (1000 \times magnification) and (c) TFC-PSf membrane (10,000 \times magnification).

beneficial to the processing of the positive reaction of the chemical equilibrium. Then the polymer with high molecular weight will form gradually and result in a dense skin layer on the membrane surface. Therefore, the membrane shows a high salt rejection and low water permeability at high pH of the aqueous phase solution. However, when the concentration of NaOH/Na₂CO₃ is increased to 0.7% (w/v), the membrane performance has a break due to the for-

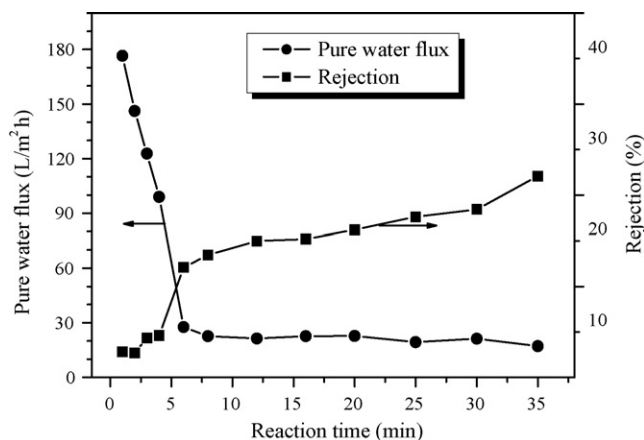


Fig. 4. Effect of reaction time on the pure water flux (—●—) and MgSO₄ rejection (—■—) of polyester composite NF membrane at 0.6MPa operating pressure.

mation of defect under the condition of strong alkali. Considering both good salt rejection and higher water permeability, a concentration of 0.6% (w/v) was chosen as the optimum for NaOH/Na₂CO₃ concentration.

3.2.3. The concentration of the monomers

It is known from the literature that the concentration of the monomer in the organic phase plays an important role in the preparation of TFC membrane by interfacial polymerization; however, the concentration of the monomer in the aqueous phase is not the dominant factor for polymerization [10]. To optimize the membrane performance, the influences of these parameters by changing the concentration of TEOA and TMC (which corresponds to the monomer in the aqueous phase and the organic phase) were respectively investigated on the premise of keeping another monomer concentration constant. It is surprisingly found that the law is opposite in our study. Fig. 6 displays the pure water flux and salt rejection of the TFC membrane when the concentration of TEOA increases from 2 to 7% (w/v). Inconsistent with the report in the literature, the membrane performance is affected significantly by the concentration of monomer in the aqueous phase. Increasing the amount of TEOA in the aqueous phase results in an almost linear increase in the MgSO₄ separation except the concentration of TEOA at the lowest (2%, w/v) and the highest (7%, w/v) within the range of investigation. Correspondingly, the pure water flux decreases approximately

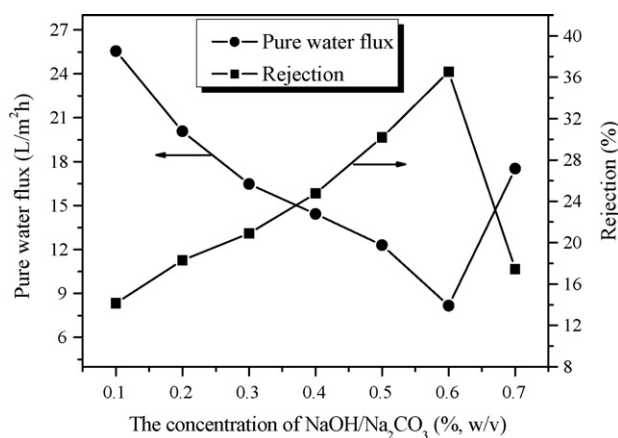


Fig. 5. Effect of NaOH/Na₂CO₃ concentration on the pure water flux (—●—) and MgSO₄ rejection (—■—) of polyester composite NF membrane at 0.6MPa operating pressure.

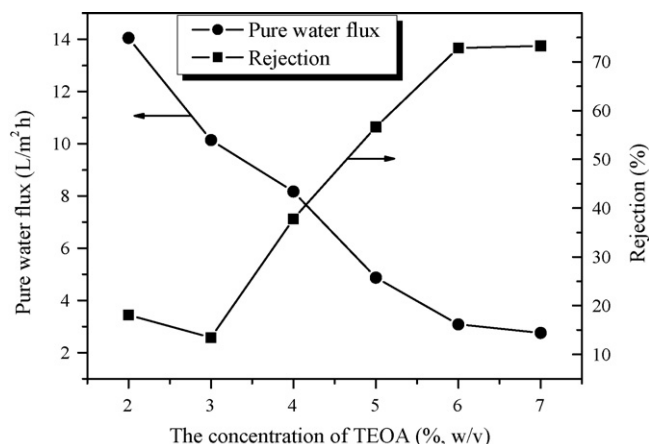


Fig. 6. Effect of concentration of TEOA on the pure water flux (—●—) and MgSO_4 rejection (—■—) of polyester composite NF membrane at 0.6 MPa operating pressure.

exponentially as the amount of TEOA is increased. The separation and flux behavior may be interpreted in terms of both the chemical and structural changes occurring within the composite coating. It has been reported that the content of monomer determines the rate of reaction in the preparation of TFC membrane by the interfacial polymerization [8]. Furthermore, the monomer that can predominate the reaction rate must be the one that has low reaction activity from our viewpoint. In our study, TEOA is considered as the monomer that determines the rate of reaction of the interfacial polymerization because the reaction between TEOA and TMC is much slower than that between TMC and other monomers such as multi-amine, which can be deduced from the reaction time of polymerization. Therefore, at low TEOA content, the rate of reaction is very low, which produces polymer aggregating with low molecular weight. The small polymer aggregates are closely packed to give a dense surface structure. However, the existence of the poor morphology on the surface of the TFC membrane may result in a decrease in rejection at low TEOA content (from 2 to 3%, w/v). With an increase in the amount of TEOA in the aqueous phase, an apparently denser, higher molecular weight coating is produced resulting in a distinct decrease in flux and enhanced separation. But excessive high content of TEOA is likely to be sterically hindered from cross-linking and therefore does not increase the molecular weight or density of the coating polymer. Thus, the water flux and rejection nearly keep constant when the concentration of TEOA is higher than 6% (w/v).

On the other hand, it can be seen from Fig. 7 that the membrane performance is almost independent of the TMC concentration in the organic phase (the concentration of TEOA is 5% (w/v)). The reason is the same as the above analysis because the monomer TMC does not predominate the reaction rate of the polymerization. Therefore, it can be concluded that the concentration in the aqueous phase plays a dominant factor in affecting the membrane performance, and the content of TEOA provides a control of the relative separation and flux obtained.

3.3. Membrane nanofiltration properties test

The TFC membranes were tested through various feed solutions, such as 5 mmol/L aqueous solutions of NaCl, MgCl_2 , Na_2SO_4 and MgSO_4 , to determine the nanofiltration properties of the membrane. It should be pointed out that the TMC concentration about 0.2% (w/v) in *n*-hexane was chosen in the membrane preparation because the membrane performance is almost independent of TMC concentration as mentioned above. And the two membranes, which

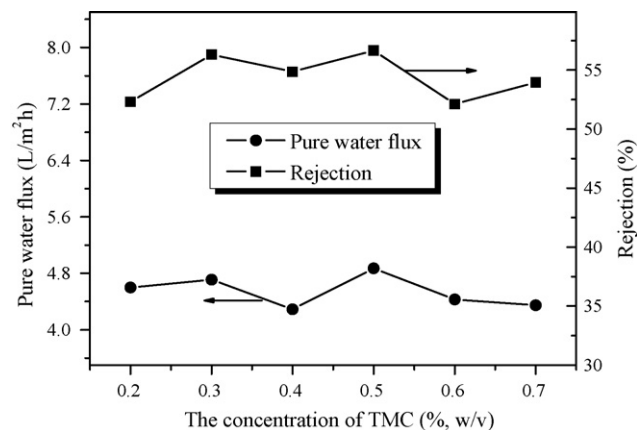


Fig. 7. Effect of concentration of TMC on the pure water flux (—●—) and MgSO_4 rejection (—■—) of polyester composite NF membrane at 0.6 MPa operating pressure.

were prepared at 5 and 6% (w/v) concentration of TEOA, were examined. The experimental results are presented in Fig. 8. The rejection of two membranes for Na_2SO_4 , MgSO_4 , NaCl and MgCl_2 were 54.9%, 52.3%, 28.1%, 22.8% and 82.2%, 76.5%, 42.2% and 23%, respectively. It can be seen that the salt rejection of the membrane decreases as per the order of Na_2SO_4 , MgSO_4 , NaCl and MgCl_2 for two membranes. The result is similar to the sequence developed by Dai et al. [22] and Zhang et al. [23], where the negatively charged NF membrane was used. As well known, the rejection to salt for a charged NF membrane is not only related with the pore size of the membrane, but also largely depends on the electrostatic action between the membrane and the ions in solution [24,25]. Thus, the surface charge character of the TFC membrane was examined. Fig. 9 shows the streaming potential of the TFC membrane at different pH. The sign of the streaming potential indicates the sign of the electrical charges of the membranes and the magnitude can qualitatively reflect these relative magnitudes. As can be observed from Fig. 9, the streaming potential of the TFC membrane is positive at pH less than 4, and negative at pH higher than 5, showing that the membrane has the amphoteric surface and its isoelectric point is between pH 4

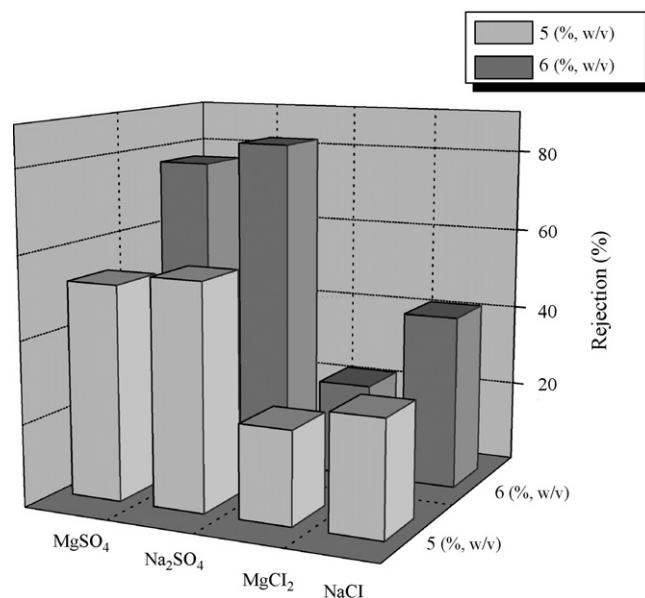


Fig. 8. Different salt rejections of the membrane prepared from TEOA concentration: 5% (w/v) and 6% (w/v).

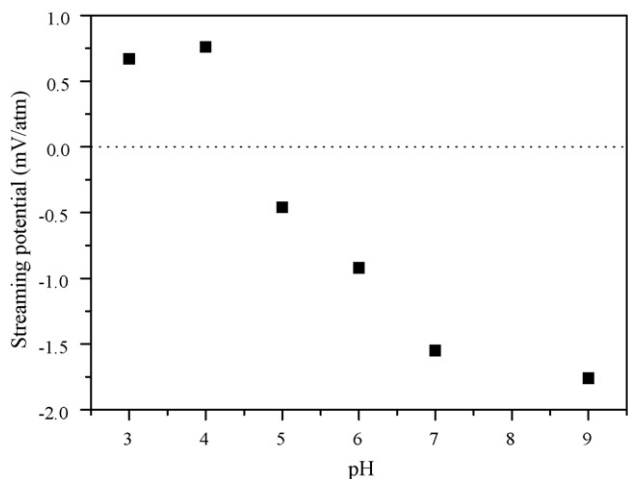


Fig. 9. Streaming potentials of the TFC membrane at different pH.

and 5. This is mainly due to the co-existence of $-\text{COOH}$ groups and tertiary amino groups (as the reactive formula shown in Scheme 2). So, the TFC membrane presents negative charge at pH higher than the isoelectric point of the membrane. The negative charge on the membrane surface will attract high-valent cation and repulse high-valent anion, which results in a high rejection to salt with high-valent anion and low rejection to salt with high-valent cation.

3.4. Effect of pH in feed on the TFC membrane flux for NaCl solution

Fig. 10 shows the effect of pH in the feed on NaCl solution flux (pH in the solution was adjusted from 2 to 9 using hydrochloric acid and sodium hydroxide; the pressure applied was fixed at 0.6 MPa; the feed solution was 5 mmol/L NaCl solution). Interestingly, it is found that the flux for NaCl solution increases with a decrease in pH value in feed except pH 2. This implies that tertiary amino groups on the membrane surface interact with ions in the feed. As the pH in the feed is decreased, amino group on the membrane surface changes into R_3HN^+ , which results in an increase in the hydrophilicity of the membrane. Therefore, the flux of the membrane is improved at low pH value of the feed. However, if the pH of the feed is too low (at pH 2), the electrostatic repulsion between the positively charged group (R_3HN^+) on the membrane surface and

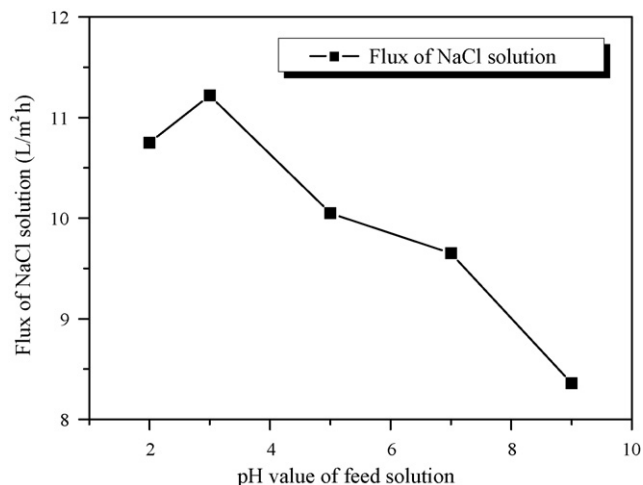


Fig. 10. Effect of pH in feed on the flux of NaCl solution.

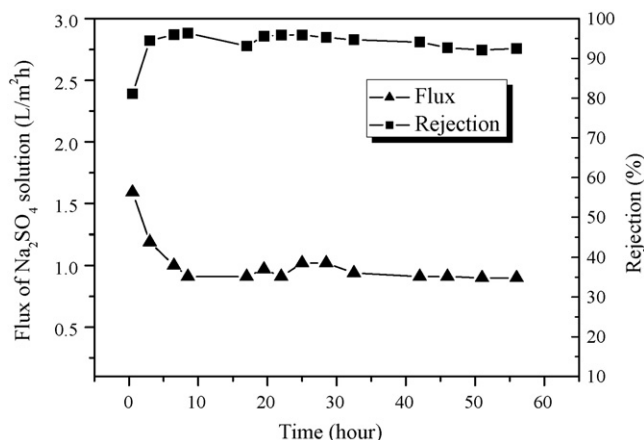


Fig. 11. Long-term stability of the TFC membrane. Tested at 0.6 MPa, room temperature with 5 mmol/L Na_2SO_4 aqueous solution.

H^+ in the feed increases, resulting in the shrinkage of pore size. So, there is a decrease in the flux for NaCl solution at pH 2 in the feed. Whereas, increasing the pH in the feed, tertiary amino groups on the surface of the membrane cannot be transferred into R_3HN^+ , and the electrostatic repulsion between the negatively charged group ($-\text{COO}^-$) of the membrane surface and OH^- in the feed solution increases, resulting in the shrinkage of pore size of the membrane surface. Thus, the flux of the membrane decreases with the increase of the pH value in the feed. The results are similar to NF membrane reported by Li et al. [17] and Zwijnenburg et al. [26]. Therefore, the polyester NF membrane prepared with TEOA and TMC by the interfacial polymerization is particularly suitable for treating acidic feeds.

3.5. Stability of the composite membrane in long-time running

The mechanical property and performance stability are very important for a membrane. Thus, a long-term test was carried out at operating pressure of 0.6 MPa with 5 mmol/L Na_2SO_4 aqueous solution. The fluxes and rejections of the studied TFC membrane during 70 h of filtration are shown in Fig. 11. It can be seen that the TFC membrane exhibits good long-term stability. Furthermore, the rejection of the membrane can reach about 95% after a stable running period.

4. Conclusions

A novel composite membrane for nanofiltration was prepared by the interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC) on the polysulfone supporting membrane. The characterization by using FT-IR, XPS and SEM showed that a rough and dense polyester selective layer was formed on the surface of the PSf supporting membrane. The performance of TFC membrane was optimized by studying the preparation parameters, such as the reaction time of polymerization, pH of aqueous phase and the concentration of reactive monomers.

As a result, with an increase in reaction time, there is a significant decrease in the pure water flux of the membrane and then the permeate flux is almost unaffected by the time. However, the salt rejection gradually increases all the time. The flux decreases drastically when the concentration of $\text{NaOH}/\text{Na}_2\text{CO}_3$ in the aqueous phase is increased from 0.1 to 0.6% (w/v), which corresponds to an increase in the salt rejection of the membrane. However, the membrane performance has a break if the concentration of $\text{NaOH}/\text{Na}_2\text{CO}_3$ is increased to 0.7% (w/v), which is due

to the formation of defect under the condition of strong alkali. The separation performance of TFC membrane is mainly related to the change of monomer content in the aqueous phase rather than in the organic phase, because TEOA which has low reaction activity is the monomer that predominates the rate of reaction in our study.

The rejection to different salt solutions of the TFC membrane decreases as per the order of Na₂SO₄, MgSO₄, NaCl and MgCl₂, which reveals that the membrane carries negative charge on the surface of the membrane at neutral solution. Also, streaming potential tests indicate that isoelectric point of the TFC membrane is between pH 4 and 5. This is mainly due to the co-existence of –COOH groups and tertiary amino groups. The result that the flux for NaCl solution increasing with the decrease of pH in the feed shows that TFC polyester membrane is also particularly suitable for treating acidic feed. And the TFC membrane exhibits good long-term stability.

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