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Preparation of pervaporation membranes by interfacial polymerization for acid wastewater purification



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ABSTRACT

A series of acid-resistant polysulfonamide/polyethersulfone composite pervaporation (PV) membranes were prepared by interfacial polymerization. The aqueous phase was a mixed solution containing m-phenylenediamine (MPD) and triethylenetetramine (TETA), and the organic phase was a 1,3-benzenedisulfonyl chloride (BDSC) n-hexane solution. Acid resistances of the composite membranes were assessed by attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR), energy dispersive spectrometer (EDS) and weight loss tests after being soaked in 20 wt% H₂SO₄ solution. The composite PV membrane exhibited a water flux of 10.1 kg/(m²·h) and NaCl rejection > 99.3 % when separating an aqueous solution with 3.5 wt% NaCl at 75 °. After soaked the membrane in 20 wt% H₂SO₄ solution for one week, the salt rejection did not decline. Moreover, water flux was stable over a 600 min PV test using a 10 wt% H₂SO₄ solution as feed at 75 °. To our best knowledge, this is the first report of acid-resistant PV desalination membrane.

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1. Introduction

With the development of human society, water pollution becomes a global issue (Shang et al., 2018; Li et al., 2018, 2013). Acidic wastewater is often produced in industry. For example, sulfuric acid is used as a catalyst or reagent in chemical industry such as the production of titanium dioxide (Li et al., 2016). Besides the chemical plants, steel factory, electroplating industry also produce a large amount of acidic wastewater (Kladnig, 2010; Li et al., 2015; Fu, 2006). Acidic wastewater is typically treated using methods including regeneration cycle, electro dialysis and acid-base neutralization et al. (Yao et al., 2011; Aguiar et al., 2018; Wang et al., 2019; Liang et al., 2014). All these methods, however, have problems. Regenerative cycle is costly (Zhang et al., 2019a,b). Electro dialysis requires tremendous pretreatment for raw water so that it is not recommended for treating large amount of acidic wastewater (Yu et al., 2000). Acid-base neutralization method not only consumes a lot of chemicals, but also causes secondary pollution (Xiao et al., 2018). It is therefore of great interest to develop suitable membrane technologies to recycle acidic wastewater in concern of the intrinsic merits of membrane separation such as low cost, environmental benignancy and high efficiency. (Shang et al., 2019; Xiao et al., 2018; Xue et al., 2019).

At present, there are many studies on the acid-resistant nanofiltration (NF) membranes. Dalwani et al. fabricated thin film composite NF membranes by spin coating a sulfonated polyetheretherketone solution on a polyethersulfone (PES) support (Dalwani et al., 2011). The membrane showed a long-term stable separation property at pH of 0–14. Hoseinpour et al. prepared an acid-resistant copolyamide composite membrane by interfacial polymerization (IP) with the aid of melamine (Karan et al., 2015). Zeng et al. developed an acid-resistant TPT-TMC/PSF NF membrane by IP (Zeng et al., 2018). The membrane exhibited better acid resistance than other NF membranes using polypiperazine amide as the selective layer. Yu et al. prepared a polysulfonamide NF membrane by IP between 1,3,6-naphthalene trisulfonyl chloride and trimesoyl chloride mixed with piperazine (Yu et al., 2013). The composite NF membrane showed excellent acid resistance compared to the polyamide composite membrane in both the dynamic acid test and the static acid soaking tests. Liu et al. prepared an acid-resistant nanofiltration composite membrane by reacting 1,3,6-naphthalenetrisulfonyl chloride with piperazine using IP technology (Liu et al., 2012). The membrane was used to recycle acidic wastewater produced from metal industry and showed good selectivity and long-term stability. Hoseinpour et al. produced three NF membranes based on polyamide, polyamide-sulfonamide and polysulfonamide by IP (Hoseinpour et al., 2016). The polysulfonamide NF membrane exhibited the best acid resistance (Jia et al., 2019). However, NF membranes typically show poor rejection to monovalent ions. Therefore, we aim to develop an acid-resistant pervaporation (PV) membrane for treating acidic wastewater containing monovalent ions such as NaCl.

PV have been studied for desalination applications and showed very good rejections to monovalent salts (Xue et al., 2019; Liang et al., 2018; Zhang et al., 2019a,b; Zhang et al., 2018a,b; Xu and Wang, 2015). However, acidic resistant PV desalination membranes have not been reported to our best knowledge. Conventional PV membrane materials such as polyvinyl alcohol are not stable in strong acids (Li

et al., 2019; Cao et al., 2014). Therefore, in this study we planned to prepare acid-resistant PV desalination membrane via interfacial polymerization. 1,5-naphthalene disulfonyl chloride and 1,3,6-naphthalene trisulfonyl chloride are commonly used chemicals to synthesize polysulfonamide, which have excellent acid resistance, due to their high reactivities during interfacial polymerization (Xiao et al., 2018). However, they are costly or commercially unavailable. Therefore, we chose 1,3-benzenedisulfonyl chloride (BDSC) in concern of its low price and commercial availability. Amines including *m*-phenylenediamine (MPD) and triethylenetetramine (TETA) were selected to tailor the crosslinking structure of polysulfonamide. Porous PES membrane was prepared as the substrate of polysulfonamide based composite membrane due to its excellent acid resistance. Parameters such as monomer compositions and IP time were optimized to obtain the best desalination property. Finally, the acid resistance of the PV composite membrane was evaluated by both static acid soaking tests and dynamic acid experiment.

2. Experimental

2.1. Materials and reagents

Polyethersulfone (PES, Udel P1700) was bought from Solvay S.A. Co. Ltd. *N*-methylpyrrolidone (NMP) was supplied by Tianjin Damao Chemical Reagent Factory (China). Polyvinylpyrrolidone (PVP K-30) was purchased from Gobekie Co. Ltd. PET non-woven fabric was got from Shanghai Poly Technology Co., Ltd. Sodium chloride (purity: 99.9%) was obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Deionized water (DI) was produced by a laboratory water purification system (Smart-Q15).

1,3-benzenedisulfonyl chloride (BDSC, purity: >98.0%) and 60 wt% triethylenetetramine (TETA) aqueous solution were purchased from TCI (China). *m*-phenylenediamine (MPD, purity: 99.5%) was supplied by Shanghai Macklin Biochemical Co. Ltd. The three chemical compounds were used for interfacial polymerization and hexane (purity: ≥95%, Beijing China) was used as the organic solvent.

2.2. Fabrication of the PES ultra-filtration membrane

The PES porous membrane was used as the substrate for the thin film composite membranes. A homogeneous PES dope solution containing 20 wt% PES, 4 wt% PVP (K-30) and 76 wt% NMP was prepared. The solution was then cast on a non-woven fabric using a 150 μm scraper at room temperature. The gel-like film was immediately immersed in water and solidified. After being soaked in water for 72 h to remove residual solvent, the water-wet membrane was air-dried before use.

Table 1 – The nomenclature of membranes, weight concentrations of the aqueous and hexane solutions and reaction durations of interfacial polymerization.

Membrane ID	TETA (w%)	MPD (w%)	BDSC (w%)	Reaction time (min)
M1	2	0.6	0.2	2
M2	2	0.6	0.5	2
M3	2	0.6	0.9	2
M4	2	0.6	1.4	2
M5	2	0.1	0.5	2
M6	2	0.9	0.5	2
M7	2	1.2	0.5	2
M8	3	0.6	0.5	2
M9	4	0.6	0.5	2
M10	5	0.6	0.5	2
M11	2	0.6	0.5	1
M12	2	0.6	0.5	5
M13	2	0.6	0.5	10
M14	2	0.6	0.5	30

2.3. Preparation and characterization of the self-standing polysulfonamide films

2.3.1. Fabrication of the self-standing polysulfonamide films

25 mL aqueous solution containing 0.6 w% MPD and 2 w% TETA was slowly poured into a glass beaker. After that, 25 mL of 0.5 wt% BDSC n-hexane solution was slowly added to the water surface to form a film at interface between the n-hexane and water phases, which was then taken out, rinsed with n-hexane, water, and dried in air.

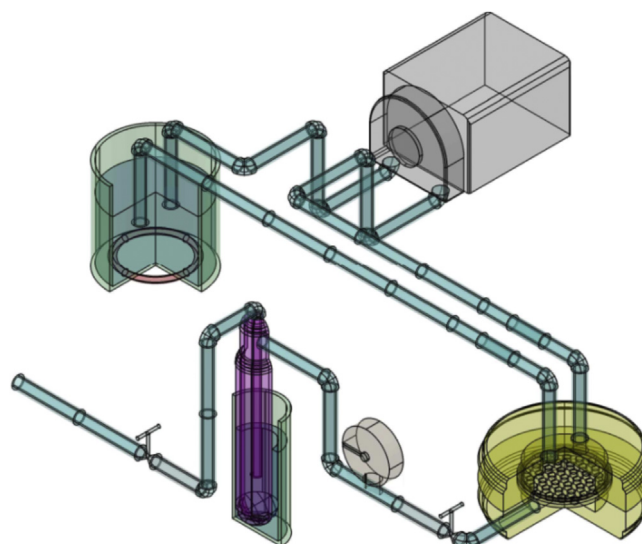
2.3.2. Characterization of the polysulfonamide film

To assess acid resistance, the polysulfonamide film was immersed in 20 wt% H₂SO₄ aqueous solution for 48 h at room temperature. After that, the film was taken out, rinsed with DI water before characterization. Fourier transform infrared (FTIR) spectra of the polysulfonamide films were measured using an infrared spectrophotometer (Nicolet IS5, Thermo Scientific, USA) to compare their chemical structures before and after acid treatment. Weights of the polysulfonamide films before and after soaking in acid were also compared using an analytical balance (Type AY 220, Shinadzu Corporation, Japan). Three samples were prepared and each sample was weighed three times to get the average value. The elemental composition of the polysulfonamide films before and after acid treatment was analyzed by an energy dispersive spectroscopy (EDS, HITACHI S-7800 Japan).

2.4. Preparation and characterization of composite pervaporation membranes

2.4.1. Preparation of thin film composite membranes

To optimize separation performance of the composite membranes, we tailored chemical structures of the IP layer by adjusting the chemical compositions in aqueous and organic solutions as well as the duration of IP reaction as listed in Table 1. To prepare a composite membrane, a piece of PES membrane (7.5 cm × 3.4 cm) was stuck to a PTFE plate (edges of the membrane were sealed using an organic solvent resistant tape). The PES membrane was soaked in an amine aqueous solution for 10 min and taken out. After wiped off excess solution on the membrane surface using a rubber roller, it was then immersed in a BDSC hexane solution for 1–30 min at ambi-

**Fig. 1 – Schematic diagram of pervaporation device.**

ent temperature to induce IP reaction. Finally, the composite membranes were cured for 5 min at 80 ° and stored in DI water.

2.4.2. Characterization of the thin film composite membranes

Surface morphologies of the composite membranes were characterized using a scanning electron microscope (SEM) (HITACHI S-7800 Japan). Samples were cracked in liquid nitrogen to obtain a smooth cross-section. Dense layer thicknesses of the composite membranes were analyzed using the Nano Measurer 1.2 software.

2.4.3. Pervaporation test of the thin film composite membranes

Desalination properties of the thin film composite films were measured using a bespoke equipment as illustrated in Fig. 1. The feed aqueous solution contained 35,000 ppm NaCl solution and was circulated at a flow rate of 0.1 m/s at 75 °C. The effective membrane area was 3.8 cm². Membrane permeate side was under vacuum at 100 Pa and water vapor was collected by a liquid nitrogen cold trap. Membrane flux (J , kg/(m²·h)) was calculated by Eq. (1).

$$J_1 = \frac{M_1}{A_1 t_1} \quad (1)$$

where M_1 was mass (kg) of the permeate; A_1 represented effective membrane area (m²); and t_1 was experimental time (h).

Conductivities of feed solution and permeate solution were measured using a conductivity meter (Oakton Con 110) to calculate salt concentrations. After each pervaporation test, back side of the film was rinsed by the collected permeate solution to dissolve any possibly crystallized NaCl. Salt rejection R was calculated using Eq. (2).

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

where C_f was the salt concentration of feed and C_p was the salt concentration of permeate.

2.5. Evaluation of the acid resistance of thin film composite membranes

2.5.1. Static acid soaking test

The static acid soaking tests were performed by soaking a composite membrane in a 20 wt% H₂SO₄ aqueous solution for one week. After that, the membrane was rinsed with DI water and tested its desalination properties. Water fluxes and salt rejections of the membrane before and after acid treatment were compared to evaluate the acid resistance.

2.5.2. Dynamic acid resistance test

A 10 wt% H₂SO₄ solution was used as the feed in a pervaporation test using a composite membrane at a feed temperature of 75 ° and a feed flow rate of 0.1 m/s. Water flux was monitored over 300 min to study the long-term operational stability.

3. Results and discussion

3.1. Optimizing the compositions of aqueous solutions

At the beginning of interfacial polymerization, amine monomers diffuse from aqueous phase to organic phase, and react with monomers in organic phase to form oligomers with varied molecular weights. After that, a layer forms on top of the porous substrate by nucleation and aggregation of oligomers and is densified over the reaction time (Karan et al., 2015). To tune crosslinking structures of the polysulfonamide film, both MPD which could form linear polymers with BDSC and TETA that would crosslink BDSC were selected as the chemicals in aqueous phase as shown in Fig. 2.

The interfacial polymerization was first carried out at the interface between the aqueous and organic solutions. When the water solution only had MPD, small and brittle films formed within 1 min. In contrast, an integral large film was produced at the interface between TETA and BDSC. However, the reaction rate was slow since it took 8 min to form a film. The high film formation speed of MPD/TETA system could be explained by the higher solubility in n-hexane and small size of MPD than TETA (Trushinski et al., 1998; Xu et al., 2017) resulting in faster diffusion rate of MPD to the organic phase. However, the low reactivity of BDSC (Hoseinpour et al., 2016) and less functional groups (–NH₂) of MPD decreased mechanical strength of the film and caused the large film broken into small pieces. On the other hand, the large polysulfonamide film formed by BDSC/TETA showed better mechanical strength due to the 4 functional groups of TETA significantly increased crosslinking density of the film as shown in Fig. 2. Therefore, to take advantages of the fast reaction rate of MPD and multiple functional groups of TETA, MPD/TETA mixed solutions were selected as the aqueous phase to prepare the composite membranes. Note that, we observed that solubility of MPD in n-hexane was roughly three folds to that of TETA. To maintain similar concentrations between these two chemicals in hexane solution, we prepared an aqueous solution containing 2 wt% MPD and 0.6 wt% TETA.

3.2. Acid resistance of the crosslinked polysulfonamide

Compared with other polyamides, backbone of polysulfonamide contains sulfonyl groups that have very strong electron-withdrawing effects. As a result, the ‘–NH’-group has less electron density and is difficult to be attacked by pro-

tons under acidic conditions (Pandith et al., 2017). To examine this theory, self-standing polysulfonamide films were soaked in 20 wt% H₂SO₄ solution to monitor any possible changes in their chemical structures.

According to Fig. 3a, peaks at 1410 cm⁻¹ and 1170 cm⁻¹ are attributed to the asymmetric stretching vibration and symmetric stretching vibration of sulfonamide groups (Zeng et al., 2018; Yu et al., 2013; Liu et al., 2012; Hoseinpour et al., 2016). This indicates the successful formation of polysulfonamide by interfacial polymerization. After being immersed in H₂SO₄ solution, no observable changes could be found on the FTIR spectra. Similarly, the EDS spectra in Fig. 3b show no difference before and after acid treatment. In addition, weight loss of the acid treated films were below 0.25%. All these results demonstrated the good acid resistance of the polysulfonamide.

3.3. Morphologies of the composite membranes

Fig. 4 shows surface morphologies of the composite membranes (M2, M11–14) prepared at different IP times. All membranes' surface showed no observable defects or pinholes. When IP reaction was 1 min (M11), a very thin polysulfonamide layer was formed with obvious ridge-valley structures. By increasing the reaction time, the ridge-valley structures gradually disappeared and some white nodules representing agglomerated polysulfonamide polymers formed. This indicated that the thickness of polysulfonamide layer increased. We hypothesized that in the initial stage of IP, amines diffused to organic phase and reacted with BDSC to form a thin layer. Due to the low reactivity of BDSC, some unreacted amines in the organic phase would continue to react with BDSC and form oligomers. These oligomers would agglomerate and deposit on surface of the dense layer, which appeared as nodules. On the other hand, more amines would diffuse to organic phase and react to BDSC. As a result, the dense layer became thicker and valleys were filled.

The cross-section images are shown in Fig. 5. Thicknesses of the dense layers were 56.46 ± 8.20 nm, 122.48 ± 10.84 nm, 159.02 ± 11.75 nm, 195.45 ± 8.94 nm, and 211.67 ± 9.07 nm, respectively, corresponding to the IP reaction times of 1 min, 2 min, 5 min, 10 min, and 30 min, respectively. Although it was difficult to distinguish the IP layer from the PES skin layer, the overall thicknesses of dense layers increased with the IP reaction time. When the IP reaction time was higher than 5 min, thicknesses of the dense layers were barely changed. This was due to the self-inhibition effect of IP (Karan et al., 2015).

3.4. Desalination performance

3.4.1. Effect of the BDSC concentration on desalination performance

Fig. 6a shows that the NaCl rejection is higher than 99.3% when the BDSC concentration is equal or greater than 0.5 wt%. Further increasing the BDSC concentration would only cause a decrement in water flux due to the formation of thicker and denser polysulfonamide layers. Fig. 6b shows that a high NaCl rejection over 99.4% can be obtained when the IP time is longer than 2 min.

In summary, the optimized aqueous solution should have 0.6 wt% MPD and 2 wt% TETA. The best organic phase should

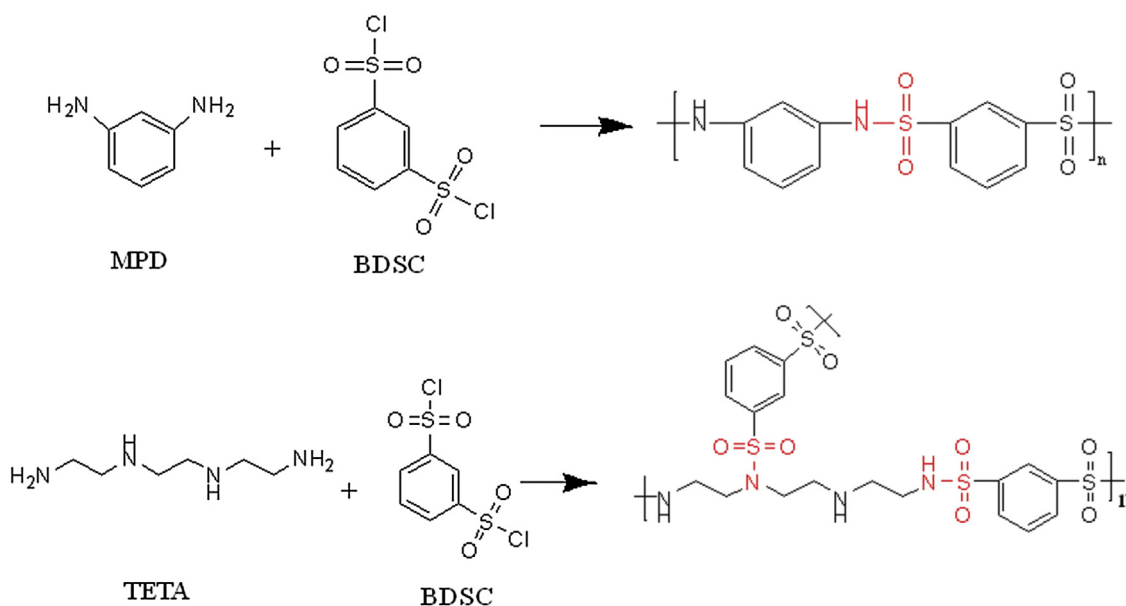


Fig. 2 – Chemical structures of the polymers formed by MPD/BDSC and TETA/BDSC via interfacial polymerization.

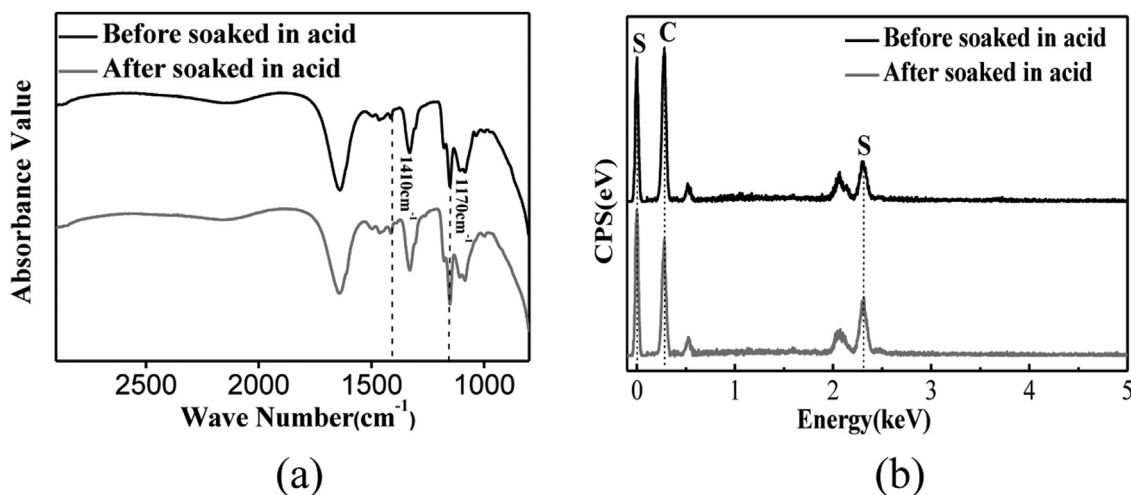


Fig. 3 – Infrared spectra of polysulfonamide films before and after acid treatment (a), EDS diagram before and after acid soaking (b).

contain 0.5 wt% BDSC. And the IP reaction time should be controlled at 2 min.

3.4.2. Effects of TETA and MPD concentrations on desalination properties

When fixed the concentrations of MPD and BDSC at 0.6 wt% and 0.5 wt%, respectively, and the IP reaction time at 2 min, water fluxes decreased from 10.1 kg/(m²·h) to 8.3 kg/(m²·h) with the increment in TETA concentration from 2 to 5 wt% as shown in Fig. 7a. And the NaCl rejections increased from 99.37%–99.9%. Clearly, a higher crosslinking density of the polysulfonamide layer was achieved at higher TETA loadings. Note that, as the TETA concentration increased to 3 wt%, increasing TETA content only resulted in the decrements in water fluxes. This was reasonable since salt rejection was close to 100%. Further increased the TETA loading would form thicker and denser polysulfonamide layer that should increase water transport resistance.

By fixed the concentrations of TETA and BDSC as well as the IP reaction time at 2 wt%, 0.5 wt%, and 2 min, respec-

tively, changes in water fluxes and NaCl rejections with the MPD concentrations were shown in Fig. 7b. The best MPD concentration was 0.6 wt%. When the MPD concentration was 0.1 wt%, the NaCl rejection was low, indicating that the IP layer had defects. At higher MPD concentrations, composite membranes with good NaCl rejections were obtained. However, as shown in Fig. 7(d–f), thicknesses of the dense layers increased from 122.48 ± 10.84 nm to 185.57 ± 15.45 nm. This resulted in the decrements in water fluxes.

3.5. Acid resistance of the composite membrane

Acid resistance of M2 was evaluated. As shown in Fig. 8, the membrane showed no observable changes after soaking in acid, such as color and surface topography. As shown in Fig. 9a, after immersed in 20 wt% H₂SO₄ for one week, water flux increased from 10.1 kg/(m²·h) to 13.5 kg/(m²·h). This might be due to that the acidic solution turned the unreacted amino groups and sulfonyl chloride groups in the polysulfonamide layer into more hydrophilic amino acids and sulfonic acids

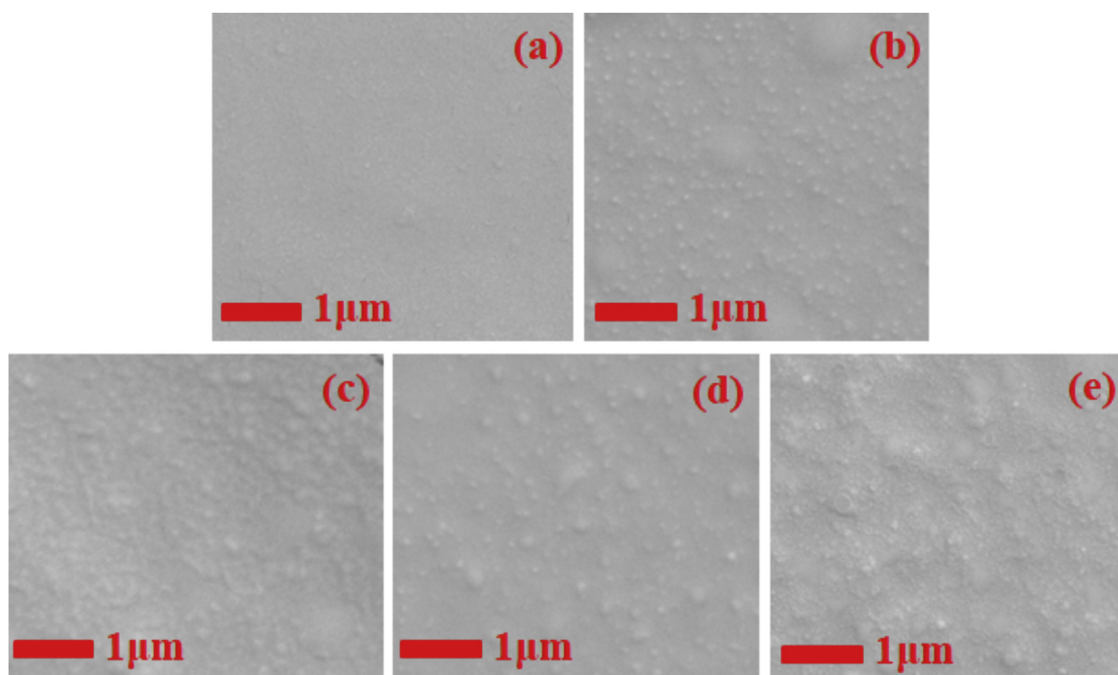


Fig. 4 – Surface images of the composite membranes prepared using different IP times: 1 min (a), 2 min (b), 5 min (c), 10 min (d), 30 min (e).

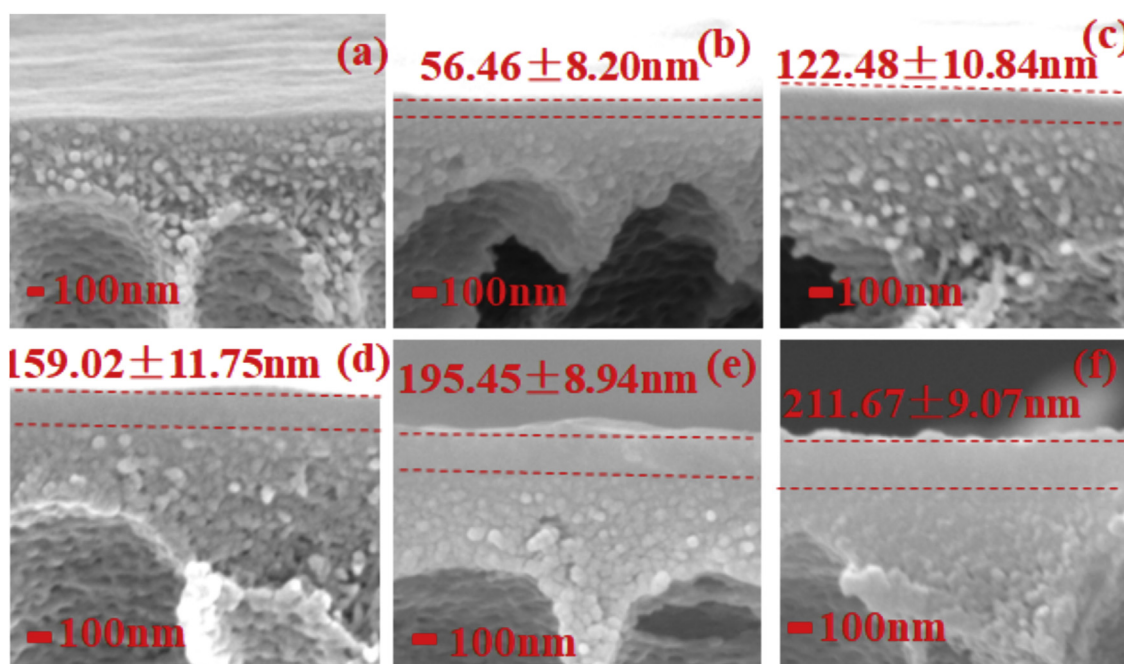


Fig. 5 – SEM images of the cross sections of support layer and thin film composite (TFC) at different IP times: Polyethersulfone support (a), 1 min (b), 2 min (c), 5 min (d), 10 min (e), 30 min (f).

that favored water transport. Note that, high salt rejections maintained that indicated good acid resistance of the polysulfonamide polymer. Due to the increased water flux of M2 membrane after soaked in 20 wt% H_2SO_4 solution, the long-term acid-resistance test of the M2 membrane was carried out for treating a relatively low concentrated H_2SO_4 solution (10 wt%) as shown in Fig. 9b. According to the results, the composite membrane showed very stable water flux for at least 600 min. The experiment result offered a very good proof of excellent acid resistance of the composite PV membrane.

To the end, we have listed recent reported membranes that can tolerate higher concentrations of sulfuric acid

(Table 2). The acid-resistant pervaporation membranes studied in literature are based on separation of mixtures with low acidity, and currently there are no reported membranes that can tolerate such high acid concentration as used in this study (20% H_2SO_4). Compared with other types of separation membranes, our PV membrane can be stable at a high temperature of 75 °C for a long time and maintain stable membrane performance. Moreover, the rejection to monovalent ions obtained by the pervaporation method is significantly higher than other acid-resistant membranes.

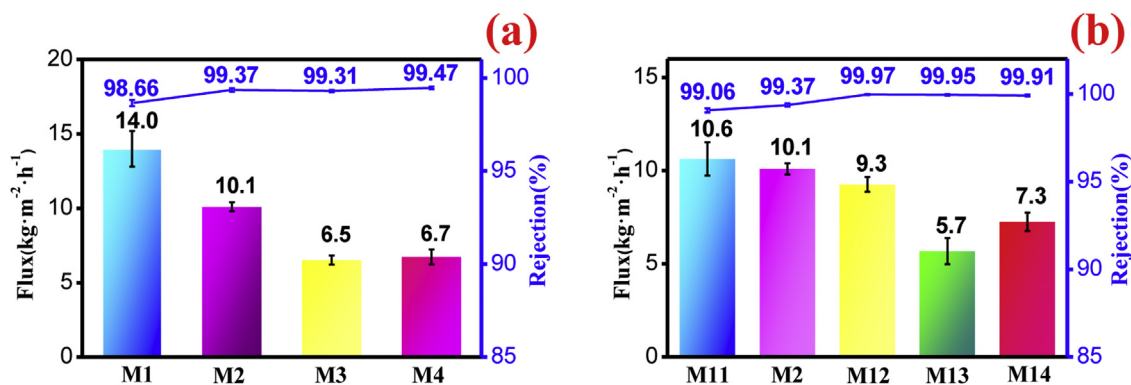


Fig. 6 – Effects of the BDSC concentrations on desalination performance (a), and effects of the IP reaction times on the desalination properties (b).

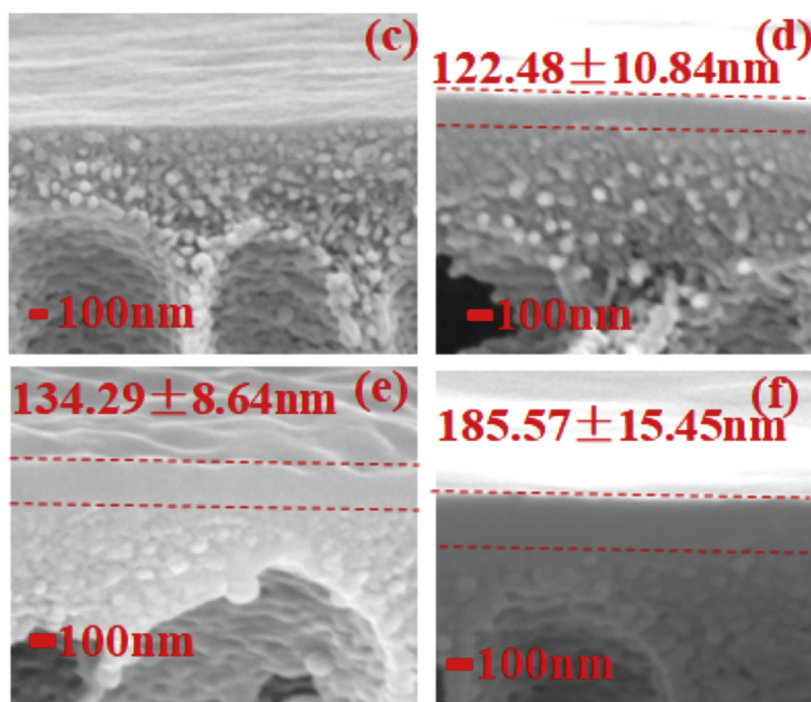
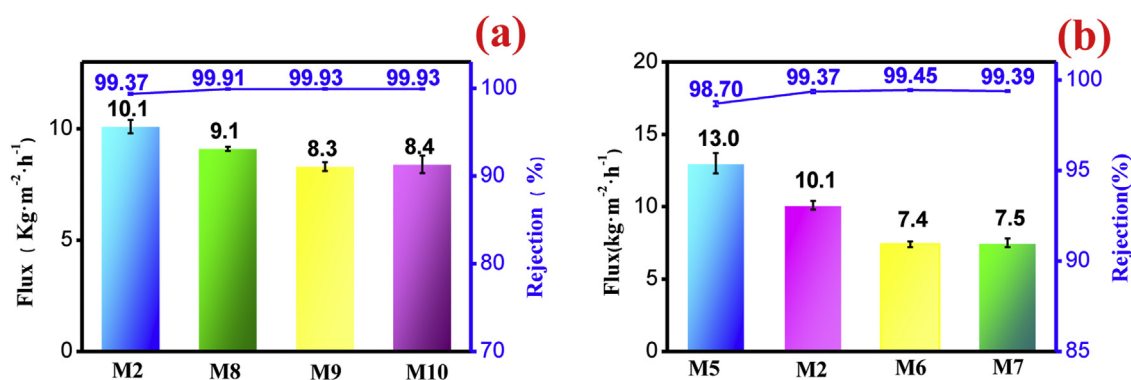


Fig. 7 – water fluxes and salt rejections of PV composite membranes prepared at different TETA concentrations (a), and MPD concentrations (b); the SEM images of support layer (c) and top regions at the cross-sections of composite membranes prepared at different MPD concentrations of 0.6 wt% (d), 0.9 wt% (e), 1.2 wt% (f).

4. Conclusions

We prepared polysulfonamide/PES composite PV membranes with excellent acid resistance. The polysulfonamide dense selective layer was prepared using the interfacial polymerization technology between an aqueous solution containing

MPD and TETA and an organic solution with BDSC. TETA had 4 functional groups would increase crosslinking density of the polysulfonamide polymer, while MPD would increase reaction rate of the IP polymerization. The optimized polysulfonamide/PES composite PV membrane showed water flux of 10.1 kg/(m²·h) at a feed solution (3.5 wt% NaCl aqueous solu-



Fig. 8 – Surface images of the membrane before and after it was soaked in acid.

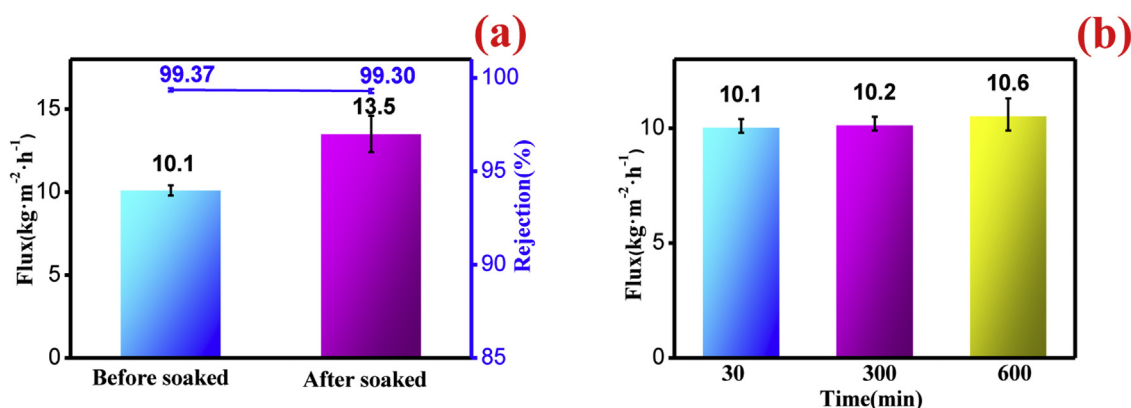


Fig. 9 – Comparison of the desalination properties of M2 before and after soaked in H₂SO₄ solution for one week (a), the long term water fluxes of M2 when using 10 wt% H₂SO₄ solution as feed at 75 °.

Table 2 – Separation properties of acid-resistant membranes.

Membrane type	Membrane material	Test conditions for acid resistance	Acid test method	Rejection (NaCl)
Reverse Osmosis (Shin et al., 2020)	DMSO-activated PE-TFC	15 wt% H ₂ SO ₄	Static	85.1
Nanofiltration (NF) (Zeng et al., 2018)	Poly (amide-s-triazine-amine)	0.05 M H ₂ SO ₄	Static	40.5
NF (Yu et al., 2013)	Poly (amide-sulfonamide)	8 wt% H ₂ SO ₄	Static	51.5–63.5
NF (Liu et al., 2012)	Polysulfonamide	20 wt% H ₂ SO ₄	Static	50
NF (Liu et al., 2012)	Polysulfonamide	4.9% (w/v) H ₂ SO ₄	Static	50
NF (Hoseinpour et al., 2016)	Poly (amide-sulfonamide)	10% (w/w) H ₂ SO ₄	Static	
NF (Hoseinpour et al., 2016)	Poly (amide-sulfonamide)	5% (w/w) H ₂ SO ₄	Dynamic 55(°)	
PV (This study)	Polysulfonamide	20 wt% H ₂ SO ₄	Static	99.37
PV (This study)	Polysulfonamide	10 wt% H ₂ SO ₄	Dynamic 75(°)	99.37

tion) temperature of 75 °. Although the water flux was not high, the membrane could maintain the desalination property at strong acid environment.

Competing financial interests

The authors declare no competing financial interests.

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References

- Aguilar, A., Andrade, L., Grossi, L., Pires, W., Amaral, M., 2018. Acid mine drainage treatment by nanofiltration: a study of membrane fouling, chemical cleaning, and membrane ageing. *Sep. Purif. Technol.* 192, 185–195.
- Cao, K., Jiang, Z., Zhao, J., Zhao, C., Gao, C., Pan, F., Wang, B., Cao, X., Yang, J., 2014. Enhanced water permeation through sodium alginate membranes by incorporating graphene oxides. *J. Membr. Sci.* 469, 272–283.
- Dalwani, M., Bargeman, G., Hosseiny, S.S., Boerrigter, M., Wessling, M., Benes, N.E., 2011. Sulfonated poly (ether ether ketone) based composite membranes for nanofiltration of acidic and alkaline media. *J. Membr. Sci.* 381, 81–89.

- Fu, Y.-P., 2006. Characterization of Ni–Cu–Zn ferrite prepared from steel pickling liquor and waste solutions of electroplating. *J. Am. Ceram. Soc.* 89, 3547–3549.
- Hoseinpour, H., Peyravi, M., Nozad, A., Jahanshahi, M., 2016. Static and dynamic assessments of polysulfonamide and poly (amide-sulfonamide) acid-stable membranes. *J. Taiwan Inst. Chem. E* 67, 453–466.
- Jia, T., Lu, J., Cheng, X., Xia, Q., Cao, X., Wang, Y., Xing, W., Sun, S., 2019. Surface enriched sulfonated polyarylene ether benzonitrile (SPEB) that enhances heavy metal removal from polyacrylonitrile (PAN) thin-film composite nanofiltration membranes. *J. Membr. Sci.* 580, 214–223.
- Karan, S., Jiang, Z., Livingston, A.G., 2015. Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation. *Science* 348, 1347–1351.
- Kladnig, W., 2010. Acid recycling in steel pickling plants: state-of-the-art and new developments in environmental protection. *Intern. J. Environ. Waste Manage.* 5, 368–378.
- Li, Y., He, G., Wang, S., Yu, S., Pan, F., Wu, H., Jiang, Z., 2013. Recent advances in the fabrication of advanced composite membranes. *J. Mater. Chem. A* 1, 10058–10077.
- Li, Z., Wang, Z., Ge, L., 2015. Preparation of nano-titanium dioxide from ilmenite using sulfuric acid-decomposition by liquid phase method. *Powder Technol.* 287, 256–263.
- Li, Z., Wang, Z., Li, G., 2016. Preparation of nano-titanium dioxide from ilmenite using sulfuric acid-decomposition by liquid phase method. *Powder Technol.* 287, 256–263.
- Li, Q., Cao, B., Li, P., 2018. Fabrication of high performance pervaporation desalination composite membranes by optimizing the support layer structures. *Ind. Eng. Chem. Res.* 57, 11178–11185.
- Li, J., Li, C., Li, X., Wang, N., Ji, S., An, Q.-F., 2019. 3D re-crosslinking of an acid-resistant layer on NaA tubular membrane for application in acidic feed. *J. Membr. Sci.* 589, 117259.
- Liang, C., Sun, S., Zhao, B., Li, F., Ong, Y., Chung, T., 2014. Treatment of highly concentrated synthetic multiple dyes wastewater by a combined process of coagulation/flocculation and nanofiltration. *J. Membr. Sci.* 469, 306–315.
- Liang, B., Li, Q., Cao, B., Li, P., 2018. Water permeance, permeability and desalination properties of the sulfonic acid functionalized composite pervaporation membranes. *Desalination* 433, 132–140.
- Liu, M., Yao, G., Cheng, Q., Ma, M., Yu, S., Gao, C., 2012. Acid stable thin-film composite membrane for nanofiltration prepared from naphthalene-1,3,6-trisulfonylchloride (NTSC) and piperazine (PIP). *J. Membr. Sci.* 415–416, 122–131.
- Pandith, A., Hazra, G., Kim, H.-S., 2017. A new fluorogenic sensing platform for salicylic acid derivatives based on π - π and NH- π interactions between electron-deficient and electron-rich aromatics. *Spectrochim. Acta, Part A* 178, 151–159.
- Shang, Y., Hei, P., Lu, S., Shang, L., Li, X., Wei, Y., Jia, D., Jiang, D., Ye, Y., Gong, J., Lei, X., Hao, M., Qiu, Y., Liu, J., Wang, H., 2018. China's energy-water nexus: assessing water conservation synergies of the total coal consumption cap strategy until 2050. *Appl. Energy* 210, 643–660.
- Shang, Q., Chen, J., Liu, C., Hu, Y., Hu, L., Yang, X., Zhou, Y., 2019. Facile fabrication of environmentally friendly bio-based superhydrophobic surfaces via UV-polymerization for self-cleaning and high efficient oil/water separation. *Prog. Org. Coat.* 137, 105346.
- Shin, M.G., Kwon, S.J., Park, H., Park, Y.-I., Lee, J.-H., 2020. High-performance and acid-resistant nanofiltration membranes prepared by solvent activation on polyamide reverse osmosis membranes. *J. Membr. Sci.* 595, 117590.
- Trushinski, B.J., Dickson, J.M., Smyth, T., Childs, R.F., Mccarry, B.E., 1998. Polysulfonamide thin-film composite reverse osmosis membranes. *J. Membr. Sci.* 143, 181–188.
- Wang, X., Yan, L., Ma, J., Bai, Y., Shao, L., 2019. Bioadhesion-inspired surface engineering constructing robust, hydrophilic membranes for highly-efficient wastewater remediation. *J. Membr. Sci.* 591, 117353.
- Xiao, D., Huang, H., Zhang, P., Gao, Z., Zhao, N., 2018. Utilizing the supernatant of waste sulfuric acid after dolomite neutralization to recover nutrients from swine wastewater. *Chem. Eng. J.* 337, 265–274.
- Xu, S., Wang, Y., 2015. Novel thermally cross-linked polyimide membranes for ethanol dehydration via pervaporation. *J. Membr. Sci.* 496, 142–155.
- Xu, S., Liu, L., Wang, Y., 2017. Network cross-linking of polyimide membranes for pervaporation dehydration. *Sep. Purif. Technol.* 185, 215–226.
- Xue, Y., Lau, C.H., Cao, B., Li, P., 2019. Elucidating the impact of polymer crosslinking and fixed carrier on enhanced water transport during desalination using pervaporation membranes. *J. Membr. Sci.* 575, 135–146.
- Yao, Y., Zeng, H., Lin, H., 2011. Reconstruction of high-concentration acid cleaning wastewater treatment project for steel factories. In: 2011 International Conference on Remote Sensing, Environment and Transportation Engineering, IEEE, pp. 577–580.
- Yu, L., Guo, Q., Hao, J., Jiang, W., 2000. Recovery of acetic acid from dilute wastewater by means of bipolar membrane electrodialysis. *Desalination* 129, 283–288.
- Yu, S., Zhou, Q., Shuai, S., Yao, G., Ma, M., Gao, C., 2013. Thin-film composite nanofiltration membranes with improved acid stability prepared from naphthalene-1,3,6-trisulfonylchloride (NTSC) and trimesoyl chloride (TMC). *Desalination* 315, 164–172.
- Zeng, Y., Wang, L., Zhang, L., Yu, J.Q., 2018. An acid resistant nanofiltration membrane prepared from a precursor of poly(s-triazine-amine) by interfacial polymerization. *J. Membr. Sci.* 546, 225–233.
- Zhang, R., Xu, X., Cao, B., Li, P., 2018a. Fabrication of high-performance PVA/PAN composite pervaporation membranes crosslinked by PMDA for wastewater desalination. *Petrol. Sci.* 15, 146–156.
- Zhang, R., Xue, J., Li, Y., Cao, B., Li, P., 2018b. A chemical imidization method to avoid pore collapsing and selective layer thickening of PMDA-ODA polyimide nanofiltration membranes. *Desalin. Water Treat.* 115, 33–44.
- Zhang, N., Liu, Y., Liu, R., She, Z., Tan, M., Mao, D., Fu, R., Zhang, Y., 2019a. Polymer inclusion membrane (PIM) containing ionic liquid as a proton blocker to improve waste acid recovery efficiency in electrodialysis process. *J. Membr. Sci.* 581, 18–27.
- Zhang, R., Liang, B., Qu, T., Cao, B., Li, P., 2019b. High-performance sulfosuccinic acid cross-linked PVA composite pervaporation membrane for desalination. *Environ. Technol.* 40, 312–320.