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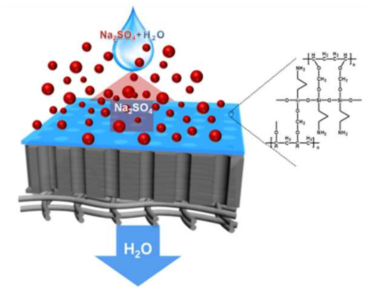

Novel NF membranes have been fabricated by a simple and environmentally friendly process for treating wastewater with extreme pH values.

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Novel organic-inorganic hybrid composite membranes for nanofiltration of acid and alkaline media

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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This study focuses on the development of novel organic-inorganic hybrid composite nanofiltration membranes based on poly(vinyl alcohol)-aminopropyl triethoxysilane (PVA-APES), which exhibit a rejection of 98.5% and a water flux of 13.5 L m^{-2} h^{-1} for a feed containing 2000 ppm Na_2SO_4 at 2.0 MPa at best-optimized aminopropyl triethoxysilane ratio and thermal cross-linking time. No irreversible changes in membrane performance have been observed after prolonged exposure (up to several weeks) of PVA-APES-1.0 membrane to the solutions with a pH in the range of 0-14. Moreover, after exposure to different acid solutions for 150 days, the Na_2SO_4 rejection of the composite membrane could still maintain above 98%, and with an appropriate water flux. Notably, non-toxic solvent is used during the membrane preparation, showing enough green chemistry technology for environmental protection. A combination of high salt rejection, appropriate water flux, improved acid/alkali stability and environmentally friendly producing route indicates that these PVA-APES-xx membranes may be good candidate materials for nanofiltration in treating industrial wastewater at extreme pH values.

Introduction

Nanofiltration (NF) has attracted more and more attention in industrial separation field during the past few decades, due to the attainable high retention of divalent salts and neutral molecules of low molecular weight (200-1000 g mol^{-1}).[1,2] Up to now, most commercially available NF membranes are in composite form and mostly known as thin-film composite (TFC) membranes. These TFC NF membranes are typically made from polyamide (PA), which exhibit high retention and water flux at a relatively low pressure.[3] However, the moderate stability of the commercial PA membranes limits their use to aqueous streams with a pH in the range of 2-11, thus excluding many potential industrial applications involving more extreme pH condition.[4] For example, production of sodium sulfate crystals from mother liquor obtained from salt production,[5] sugar industry,[6] treatment of effluents from pulp and paper[7] and textile industry,[1] usually require the NF membranes to tolerate high pH condition during the application. On the other hand, the applications involving very low pH conditions include purification of acids,[8,9] recovery of phosphorus from sewage sludge,[10] removal of sulfate ions from effluents in the mining industry,[11] as well as metal industry.[12] To date, only several commercial NF membranes including SelRO series fabricated by Koch Membrane Systems, D-series by Desal/Osmonics and HYDRACoRe series by Hydranautics/Nitto Denko have been reported to be suitable for application at the extreme pH conditions.[13,14] However, these membrane products are costly and their compositions are not completely open, which stimulates many efforts in the development of alternative NF membranes with outstanding acid/alkali resistance associated with appropriate separation properties and relatively low cost.

In recent years, more and more researchers have focused their attention on the development of novel materials for the pH-stable NF membrane. Gao and coworkers reported a series of polysulfonamide thin-film composite membrane by in-situ interfacial polymerization, and the resulting NF membranes exhibited improved acid resistance ability even after exposure to 4.9% (w/v) H_2SO_4 solution for two months.[15] Benes et al. fabricated several TFC nanofiltration membranes by spin coating a sulfonated poly(ether ether ketone) solution on a poly(ether sulfone) support, which exhibited no irreversible changes in membrane performances after prolonged exposure (up to several weeks) to the solutions with a pH in the range of 0-14.[16] Livingston et al. developed a new class of NF membranes based on cross-linked polybenzimidazole, which showed good tolerance towards extreme pH conditions and superior chemical stability.[17] Unfortunately, most of these membranes suffer from a relatively complex preparation process or fall in the nanofiltration membrane category with a relatively low salts rejection, which limit their practical application in large scale.

The objective of this study is to prepare novel NF composite membranes with improved acid/alkali stability, and to explore the optimized production engineering. In this article, we developed a series of novel TFC membranes by brush-coating the poly(vinyl alcohol)-aminopropyl triethoxysilane solution prepared by a sol-gel process in acidic condition on porous polysulfone support, followed by thermal cross-linking treatment. The intrinsic hydrophilicity of poly(vinyl alcohol) (PVA) along with its remarkable chemical, thermal, mechanical, as well as appropriate acid/alkali stability, makes it a suitable polymer for fabricating water treatment membranes.[18-20] Moreover, the hydroxyl groups in PVA can react with multifunctional compounds, such as dialdehydes, dicarboxylic acids, and dianhydrides, and form cross-linked network structure.[21-24] Thus, various types of NF and reverse osmosis membranes based on PVA have been fabricated.[25,26] However, most of the NF membranes made from PVA suffer from relatively poor rejection to divalent salts (<95%) in comparison with the commercial NF membranes.[27,28] Herein, it is expected that the introduction of aminopropyl triethoxysilane as a cross-linker into the PVA system could not only increase the cross-linking degree, which may result in high ions rejection, but also improve the acid/alkali stability of the membranes. On the other hand, the $-NH_2$ in the TFC membranes is a very active group, which can react with $-COOH$, $-COCl$ as well as sultones under a mild condition.[29,30] As a result, secondary cross-linking and hydrophilic modifying can be achieved to improve the rejection or permeation properties. The resulting TFC membranes and their properties related to NF performance for applications were also evaluated thoroughly.

Experimental

Materials

Poly(vinyl alcohol) (PVA) (95% hydrolysed, M_w: 95000) and aminopropyl triethoxysilane (APES) were obtained from Aldrich Chemicals. Polysulfone porous support (molecular weight cut-off: 50000 Da) was obtained from MEY Membrane Technology Co., China. Other chemical reagents were purchased from Beijing Chemical Company and used without further purification.

TFC membrane preparation

For the TFC membrane preparations, 1.0 g PVA was dissolved in 100 g hot deionized water in a beaker to obtain a homogeneous solution, followed by adding the desired quantity of APES to the solution to maintain the pre-decided organic-inorganic ratio. Then a certain amount of 0.1 M HCl was introduced into the above solution to keep the pH between 2 and 3, resulting in an acid catalyzed gel. The obtained gel was brush-coated onto the dry polysulfone porous support, which was subsequently dried at 60 °C for 30 min to obtain the pristine TFC membranes. These membranes were then immersed in a solution containing formaldehyde (54.1 g), sodium sulfate (150.0 g), sulfuric acid (125.0 g) and deionized water (470.0 g) at 60 °C for a desired time for effective cross-linking in the membrane by formal reaction.[31-34] Finally, the resulting TFC membranes were washed with deionized water for several times to remove the excess acid on the surface of the membranes, and the obtained samples were designated as PVA-APES-xx, where xx refers to the quantity ratio of APES to PVA in the coating solution.

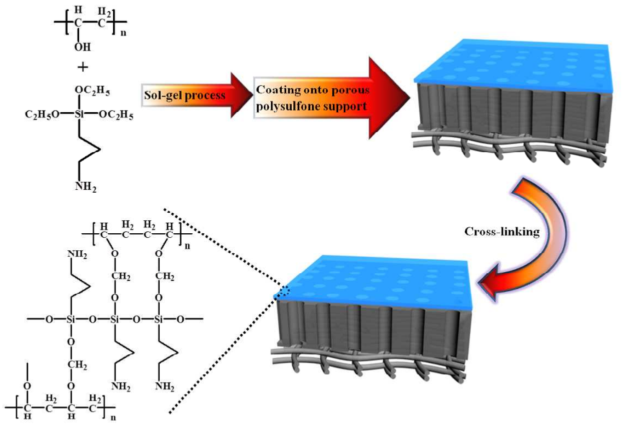

Fig. 1 Reaction scheme for the TFC membrane preparation: representative polymer structure of functional layer.

Instrumentation and testing

Attenuated Total Reflectance Infrared (ATR-IR) spectra were acquired using a Nicolet 6700 spectrophotometer. The surface and cross-section morphologies were visually examined using a scanning electron microscope (SEM, Hitachi S-4800, Japan). Quantitative surface roughness analysis of the TFC sample was measured using AFM imaging and analysis (Park Instrument Auto Probe CT). Air-dried TFC membranes were fixed on a specimen holder and 10 µm × 10 µm areas were scanned using tapping mode in air. The permeation and separation performance tests of the PVA-APES-xx membranes were conducted at 2.0 MPa using a 2000 ppm salt solution, such as Na_2SO_4、$MgSO_4$、NaCl, at room temperature in dead-end cells (HP4750, Sterlitech). The membranes were initially subjected to a pure water pressure of 2.0 MPa for 2 h prior to performing the NF test experiments, and the effective membrane area (for each cell) was 13.85 cm^2. The water flux was determined by direct measurement of permeate flow (L m^{-2} h^{-1}). The rejection was measured by the salt concentration in the permeate obtained through measurements of the permeate and the feed using a conductance meter (DDS-11A, China). The salts rejection was calculated according to the following equation: $R\ (\%) = (1 - C_p/C_f) \times 100$, where C_p (mg L^{-1}) and C_f (mg L^{-1}) are the permeate and feed concentration, respectively. All membrane samples were prepared and tested in at least three measurements, results of which have been averaged. In order to investigate the acid/alkali-tolerance properties of the PVA-APES-xx membranes, the samples were exposed to the corresponding acid or alkali aqueous solution for a desired time. The acid/alkali stability of the TFC membrane was evaluated by measuring the change of water flux and salt rejection under a pressure of 2.0 MPa using 2000 ppm Na_2SO_4 solution.

Results and discussions

Fabrication of TFC membranes

The TFC films were prepared by coating dilute polymer solutions based on PVA and APES onto the porous polysulfone support. Prior to that, the membrane forming material was formed by condensation polymerization of the silica precursor

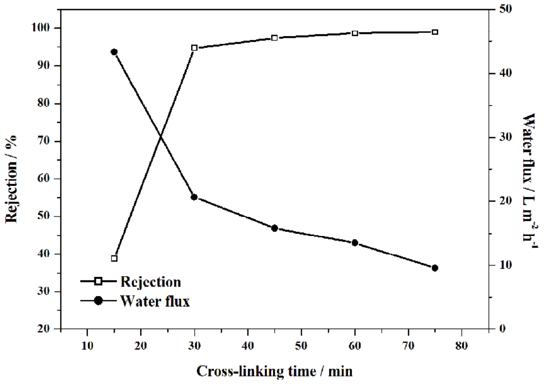

Fig. 2 Effect of cross-linking time on the performance of PVA-APES-1.0 TFC membrane tested with 2000 ppm Na_2SO_4 solution at 2.0 MPa.

(aminopropyltriethoxysilane) in aqueous media in the presence of PVA with acid catalyst at room temperature for 24 h. After brush-coating, the resulting membranes were cross-linked with formaldehyde for different time periods. The representative reaction scheme is presented in Fig. 1. Non-toxic solvent has been involved during the membranes preparation process, providing a green and environmentally friendly route for fabricating TFC NF membranes.

The permeation and separation properties

The water flux and salt rejection of the PVA-APES-xx TFC membranes were tested in a dead-end test cell, and the results are presented in Table 1. The water flux of the PVA-APES-xx TFC membranes decreases from 45.5±1.8 L m^{-2} h^{-1} to 7.8±0.2 L m^{-2} h^{-1}, and the corresponding Na_2SO_4 rejection increases from 84.3±0.8% to 98.5±1.1% with increasing the APES content in the coating solution. In this system, APES can serve as a macromolecule cross-linker formed by condensation polymerization during sol-gel process. With the increase of the APES content, the cross-linking degree of the TFC membranes increases, resulting in much denser functional layer. However, when the APES content is more than 1.0% (w/v) in the coating solution, the Na_2SO_4 rejection decreases obviously. This is because the dense cross-linking structure hinders not only salt ions but also water molecules permeating through the membrane, and the relatively low water flux (7.8±0.2 L m^{-2} h^{-1}) for PVA-APES-1.2 increases the ions concentration in the permeate water indirectly.

The influence of cross-linking time on the permeation properties of the TFC membranes was also investigated, and the results are shown in Fig. 2. The PVA-APES-1.0 sample without cross-linking shows no rejection ability to Na_2SO_4, due to the water solubility of the functional layer. With the increase of the cross-linking time, the water flux decreases to 9.6 L m^{-2} h^{-1}, and the Na_2SO_4 rejection increases to 98.9%. These results indicate the cross-linking degree of the functional layer can also be controlled by varying cross-linking time. With the increase of cross-linking time, much denser cross-linked net-work structure can be obtained, which could prevent water molecules and salt ions from permeating through the membranes.

Table 1 Permeation and separation performance of the PVA-APES-xx TFC membranes.

Samples[a]	Rejection (%)	Water flux (L m^{-2} h^{-1})
PVA	84.3±0.8	45.5±1.8
PVA-APES-0.2	88.1±0.6	32.6±1.4
PVA-APES-0.4	90.2±1.5	23.4±0.8
PVA-APES-0.6	93.5±0.7	17.9±1.0
PVA-APES-0.8	95.7±1.2	14.7±0.6
PVA-APES-1.0	98.5±1.1	13.5±0.3
PVA-APES-1.2	94.9±0.9	7.8±0.2

[a] Test conditions: feed Na_2SO_4 concentration = 2000 ppm, operating pressure = 2.0 MPa.

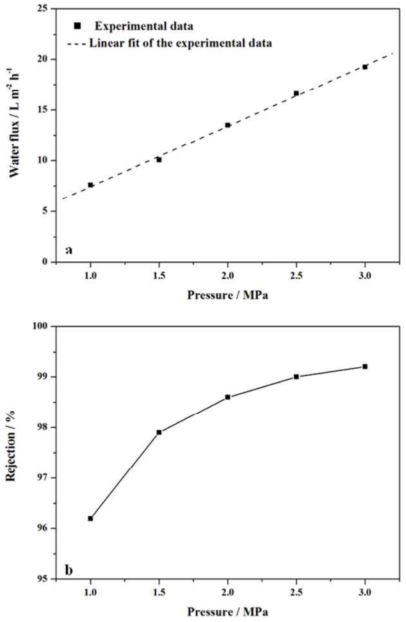

Fig. 3 (a) Pure water flux and (b) rejection as a function of operating pressure for PVA-APES-1.0 membrane tested with deionized water and 2000 ppm Na_2SO_4 solution, respectively.

To sum up, the performance of the resulting PVA-APES-xx TFC membranes can be modulated by varying the cross-linker content and cross-linking time. Considering of the balance between the rejection and water flux, the APES content in coating solution and cross-linking time are optimized for 1% (w/v) and 1h, respectively. The following discussion related to the NF performance and structure characterization is based on the sample prepared using the optimized conditions above.

The permeation and separation properties of the PVA-APES-1.0 sample at different operating pressures are shown in Fig. 3. It is observed that there is an almost linear proportional relationship between the pure water flux of PVA-APES-1.0 membrane and the operating pressure (Fig. 3(a)), which is in accordance with the Spiegler-Kedem model.[35] Moreover, the Na_2SO_4 rejection of the PVA-APES-1.0 membrane can run up to 99.2% with increasing the operating pressure (Fig. 3(b)). This is because the permeability rate of water molecular is much higher than that of salt ions with the increase of operating pressure, resulting in high

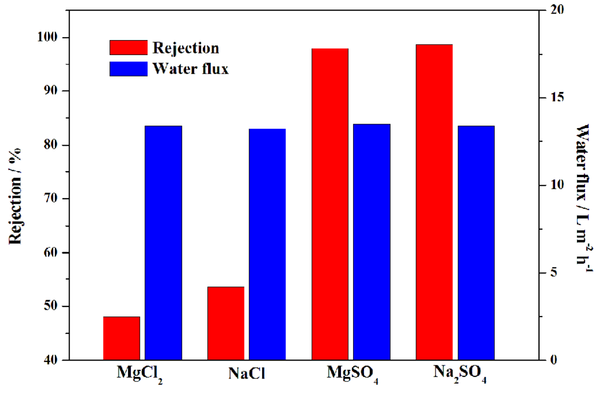

Fig. 4 Water flux and rejection to different salt ions for the PVA-APES-1.0 TFC membrane tested with 2000 ppm salt solution at 2.0 MPa.

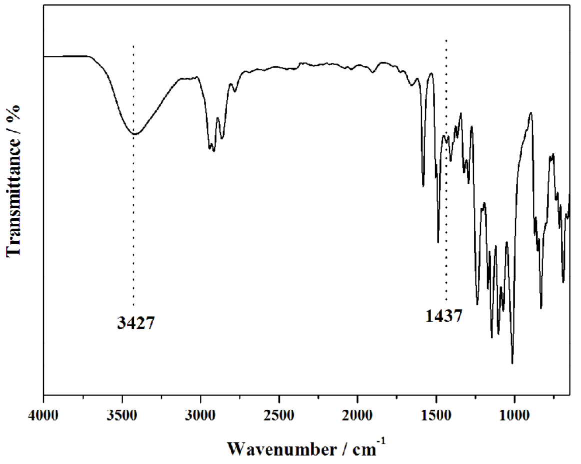

Fig. 5 The ATR-IR spectrum of the PVA-APES-1.0 membrane.

ions rejection finally. These results also indicate the PVA-APES-xx TFC membranes possess excellent mechanical properties, which can be operated with the pressure increasing even up to 3.0 MPa.

The salt rejection characteristics of the PVA-APES-1.0 sample in terms of other different salts, $MgCl_2$, NaCl and $MgSO_4$ were also studied, and the results are presented in Fig. 4. The rejections of the membrane to different salts follow the order of $MgCl_2$ (48.1%) < NaCl (53.6%) < $MgSO_4$ (97.9%) < Na_2SO_4 (98.5%), due to different ions size.

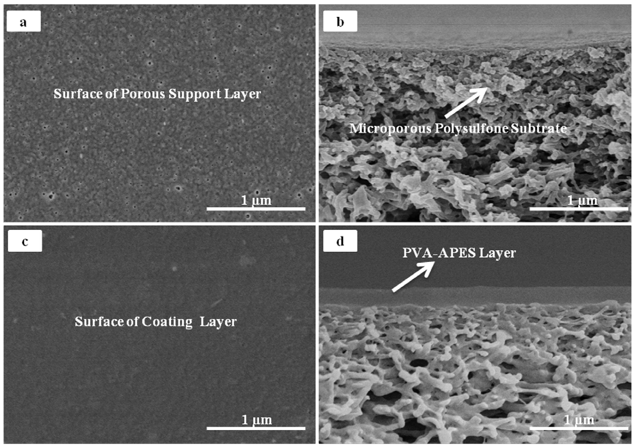

Fig. 6 SEM micrographs of (a) the surface of porous polysulfone support, (b) the cross-section of porous polysulfone support, (c) the surface of PVA-APES-1.0 TFC membrane and (d) the cross-section of PVA-APES-1.0 TFC membrane.

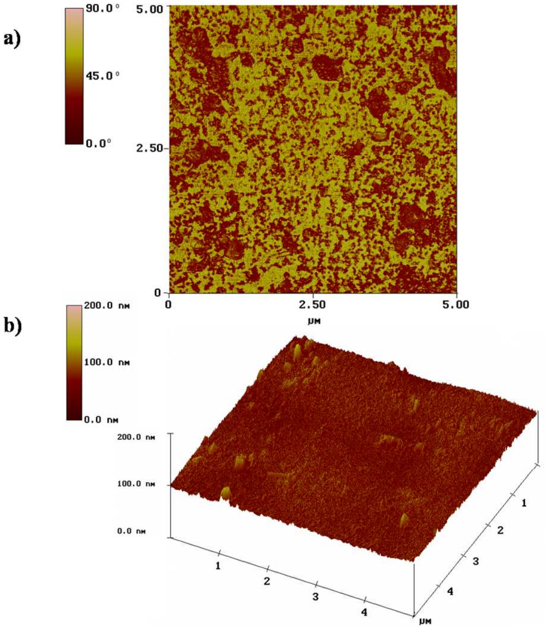

Fig. 7 AFM images of the PVA-APES-1.0 TFC membrane: (a) phase image and (b) height image.

TFC membrane characterizations

Fig. 5 shows the ATR-IR spectrum of the PVA-APES-1.0 membrane. The sample shows a broad band in the range of 3300-3400 cm^{-1}, indicating that there is a significant number of –OH due to the noncondensed SiOH and/or unreacted –OH in PVA, which is responsible for the hydrophilicity of the TFC membranes. Generally, the asymmetric and symmetric absorptions of $-NH_2$ can be observed around 3300 cm^{-1}, which may be overlapped by the broad absorption band of –OH in this study.[36] However, the characteristic band at 1437 cm^{-1} can also be ascribed to $-NH_2$ presented in APES. The absorption band around 1103 cm^{-1} corresponds to Si–O–Si formed during the sol-gel process of APES.

SEM was employed to characterize the morphology of the TFC membrane surface and cross-section, and the images are exhibited in Fig. 6. In comparison with the surface of the porous polysulfone support (Fig. 6(a)), the surface of PVA-APES-1.0 film is relatively smooth and no defect is observed (Fig. 6(c)). From the micrographs of the cross-section of PVA-APES-1.0 film and porous polysulfone support (Fig. 6(b) and (Fig. 6(d)), a dense and thin layer can be distinguished from the support layer, with a thickness of about 200 nm. The dense and thin cross-linking layer can play an important role in achieving high ions rejection and

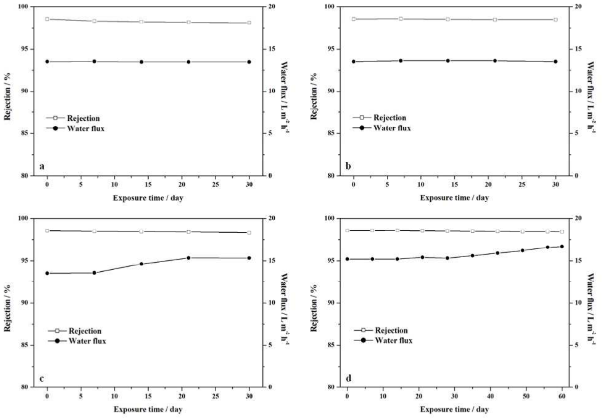

Fig. 8 Effect of exposure to different acid aqueous solutions on the performance of PVA-APES-1.0 TFC membrane: (a) 5% H_2SO_4 (w/v), (b) 5% HCl (w/v), (c) 20% H_3PO_4 (w/v) and (d) 15% H_2SO_4 (w/v), tested with 2000 ppm Na_2SO_4 solution at 2.0 MPa.

appropriate water flux. Combined with the ATR-IR results, we confirm that the TFC NF membranes based on PVA and APES have been fabricated by brush-coating, followed by the cross-linking.

The dispersion and morphology of the silica formed by sol-gel process in the composite membranes may affect the performance of the TFC membranes. AFM was employed to investigate the morphology and surface properties of the TFC membranes. As shown in Fig. 7(a), the bright areas corresponding to continuous phase represent PVA, and the dark areas corresponding to dispersed phase represent silica. Fig. 7(b) shows the height image of the corresponding TFC sample. The colorific intensity shows the vertical profile of the membrane surface with the light regions representing the highest points and the dark regions representing the depressions. In addition, the PVA-APES-1.0 membrane exhibits a smooth surface with a root-mean-square of 6.58 nm, which may improve the anti-fouling properties of the NF membranes during the practical application.[37,38]

The acid/alkali-tolerance performance

Acid/alkali-tolerance studies were performed on PVA-APES-1.0 TFC membranes. In these studies, the membranes were immersed in different acid or alkali aqueous solution for 30 days at least, and magnetic stirring was used to ensure uniformity. Fig. 8 gives the Na_2SO_4 rejection and water flux of the PVA-APES-1.0 TFC membrane immersed in 5% (w/v) H_2SO_4, 5% (w/v) HCl, 20% (w/v) H_3PO_4, as well as 15% (w/v) H_2SO_4 aqueous solution successively for different times. It should be noted that the TFC membrane tested for acid-tolerance is the same sample. As observed, there are no obvious changes in membrane performance, after soaking in 5% (w/v) H_2SO_4 and 5% (w/v) HCl aqueous solution for 30 days. Furthermore, after soaking in 20% (w/v) H_3PO_4 for 30 days, only the water flux increases slightly from 13.5 L m^{-2} h^{-1} to 15.2 L m^{-2} h^{-1}, while the Na_2SO_4 rejection of the soaked sample is nearly the same as that of the virgin sample. The same change trend of the membrane performance can also be observed, after soaking the corresponding sample in 15% (w/v) H_2SO_4 aqueous solution for 60 days, with water flux increasing from 15.2 L m^{-2} h^{-1} to 16.6 L m^{-2} h^{-1} and Na_2SO_4 rejection no obvious change. The functional layer in TFC based on cross-linked PVA with APES may swell in acid aqueous solution with relatively high concentrations. Thus, the large free volume among the polymer molecular chains allows water and salt molecules passing through the TFC membrane relatively easily, resulting in the increasing of water flux and slightly decreasing of salt rejection. However, even though the PVA-APES-1.0 TFC sample has been exposed to extreme pH condition for about 150 days successively, the Na_2SO_4 rejection is still maintained above 98%. For one reason, the intrinsic acid-tolerance and the cross-linking structure of the functional layer materials can contribute to the excellent separation property of the TFC membrane during long-term measurement with extreme pH condition. On the other hand, the hydrogen bond can be formed between the $-NH_2$ in the functional layer and the sulfone groups in the support layer, as reported by Jiang et al., which can increase the interaction between the two layers in TFC membranes and avoid separating during long-term measurement.[39] As a result, the TFC membranes prepared from PVA and APES in this study possess good acid stability and long-term stability, which may be applied as NF membranes in treating industrial wastewater with extreme low pH values.

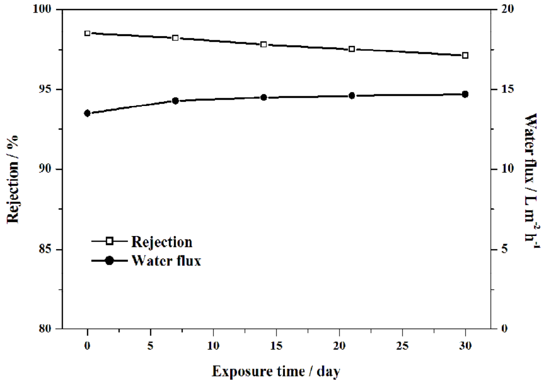

Fig. 9 Effect of exposure to 4% (w/v) NaOH aqueous solution on the PVA-APES-1.0 TFC membrane performance tested with 2000 ppm Na_2SO_4 solution at 2.0 MPa.

Fig. 9 shows the permeation and separation properties of the PVA-APES-1.0 TFC membrane exposed to 4% (w/v) NaOH aqueous solution for different time. After exposure to 4% (w/v) NaOH aqueous solution for 30 days, the Na_2SO_4 rejection of the sample decreases from 98.5% to 97.1%, and the water flux increases from 13.5 L m^{-2} h^{-1} to 14.7 L m^{-2} h^{-1}. These results indicate the PVA-APES-1.0 TFC membrane possesses appropriate alkali stability. The decrease of the rejection with increasing exposure time may result from the swelling of the membrane in NaOH aqueous solution. Furthermore, the non-woven polyester paper acted as a backing layer in TFC membrane may degrade under alkali condition, resulting in the deterioration of the mechanical properties of the membrane. Thus, in order to

Table 2 The acid/alkali-tolerance properties of PVA-APES-1.0, conventional PPA and commercial pH-stable NF membranes.

Samples	Rejection (%)	Water flux ($L\ m^{-2}\ h^{-1}$)	After acid-exposure for 30 days[a]		After alkali-exposure for 30 days[b]	
			Rejection (%)	Water flux ($L\ m^{-2}\ h^{-1}$)	Rejection (%)	Water flux ($L\ m^{-2}\ h^{-1}$)
PVA-APES-1.0[c]	98.5±1.1	13.5±0.3	98.4±1.6	13.8±0.6	97.1±1.9	14.7±1.3
PPA[d]	98.6±1.8	59.3±2.6	31.0±2.7	378.8±9.5	0	466.7±17.6
HYDRACoRe70[d]	97.6±0.7	34.7±1.4	97.4±0.9	34.7±1.7	78.0±2.1	43.3±3.3

[a] 15% (w/v) H_2SO_4 aqueous solution.

[b] 4% (w/v) NaOH aqueous solution.

[c] Test conditions: feed Na_2SO_4 concentration = 2000 ppm, operating pressure = 2.0 MPa.

[d] Test conditions: feed Na_2SO_4 concentration = 1000 ppm, operating pressure = 0.6 MPa.

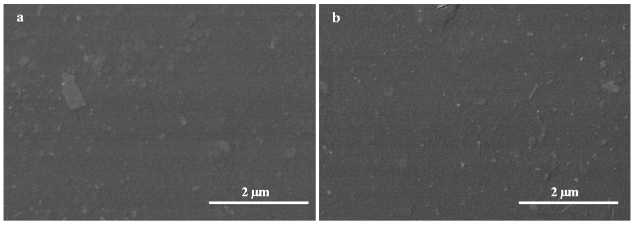

Fig. 10 SEM micrographs of the surface of PVA-APES-1.0 TFC membrane, after exposure to (a) extreme acid condition for about 150 days and (b) 4% (w/v) NaOH aqueous solution for 30 days.

improve the alkali stability of the PVA-APES-1.0 TFC membranes, we should use different materials with much more improved alkali-tolerance as the backing layer, and the results will be reported soon.

Fig. 10 shows the SEM images of the surface of PVA-APES-1.0 membrane after exposure to extreme acid condition for about 150 days (Fig. 10 (a)) and 4% (w/v) NaOH aqueous solution for 30 days (Fig. 10 (b)), respectively. It can be seen clearly from the images, the functional layer is still dense and smooth, and no defect can be observed. These results reveal that no degradation occurs in the cross-linking layer of the membranes during immersing the membranes in extreme pH condition, which is responsible for their high ions rejections.

In order to compare the acid/alkali stability of the PVA-APES-xx membranes with the conventional NF membranes, TFC film based on polypiperazine-amide (PPA) had been fabricated by interfacial polymerization method as reported previously.[40,41] After exposure to 15% (w/v) H_2SO_4 aqueous solution for 30 days, the Na_2SO_4 rejection of the PPA sample decreases from 98.6 ± 1.8% to 31.0 ± 2.7%, with the water flux increasing from 59.3 ± 2.6 $L\ m^{-2}\ h^{-1}$ to 378.8 ± 9.5 $L\ m^{-2}\ h^{-1}$ (Table 2). Furthermore, the PPA sample exhibits no rejection ability and a water flux of 466.7 ± 17.6 $L\ m^{-2}\ h^{-1}$, after soaking the membrane in 4% (w/v) NaOH aqueous solution for 30 days. The reason for the decreasing of the ion-rejection ability can be attributed to the degradation of the amide bond in PPA under extreme pH condition. Additionally, the pH-stability of the commercial NF membrane (HYDRACoRe70) fabricated by Hydranautics/Nitto Denko had also been investigated for comparison under the same condition. HYDRACoRe70 membrane shows excellent acid stability, and no significant change has been observed after exposure to acid aqueous solution. However, its Na_2SO_4 rejection decreases from 97.6 ± 0.7% to 78.0 ± 2.1%, with water flux increasing from 34.7 ± 1.4 $L\ m^{-2}\ h^{-1}$ to 43.3 ± 3.3 $L\ m^{-2}\ h^{-1}$, after exposure to 4% (w/v) NaOH aqueous solution for 30 days. In comparison with conventional PPA TFC membrane and commercial pH-stable NF membrane, PVA-APES-1.0 sample in this study shows no obvious change in the permeation and rejection properties after exposure in the same acid or alkaline media, indicating potential application as NF membranes operating under extreme pH condition.

Conclusions

This study developed a series of novel and low-cost TFC NF membranes which displayed higher Na_2SO_4 rejection and tunable water flux by varying the APES content in coating solution or thermal cross-linking time. The optimized PVA-APES-xx TFC membrane appears to comprise a smooth and defect-free active layer with the thickness of about 200 nm. The best performance of the resulting TFC membranes can be achieved by introducing 1% (w/v) APES in coating solution and thermal cross-linking for 1 h, with a water flux of 13.5 $L\ m^{-2}\ h^{-1}$ and Na_2SO_4 rejection of 98.5% at 2.0 MPa. The rejection to different salts follows by the order of $MgCl_2 < NaCl < MgSO_4 < Na_2SO_4$. Notably, after exposure to 5% (w/v) H_2SO_4, 5% (w/v) HCl, 20% (w/v) H_3PO_4, as well as 15% (w/v) H_2SO_4 aqueous solution successively for total 150 days, the PVA-APES-1.0 membrane still maintains the Na_2SO_4 rejection above 98% with slightly increased water flux, which shows much more improved acid stability than conventional PPA NF membranes. Furthermore, the PVA-APES-1.0 sample also exhibits excellent alkali-tolerance in comparison with PPA and commercial pH-stable NF membrane, indicating potential applications on treating wastewater with extreme pH values.

Acknowledgements

The authors gratefully acknowledge the SINOPEC for their financial support to this work.

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