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Preparation and Characterization of PEI/SPES Composite Nanofiltration Membrane

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A novel composite nanofiltration membrane carrying two kinds of charge was fabricated by coating negatively charged sulfonated polyethersulfone (SPES) microporous membrane with positively charged polyethyleneimine (PEI). Effects of membrane forming and operating conditions on PEI/SPES membrane properties are measured. The separation efficiency was tested by separating salt from dye mixtures. In addition, the morphology was characterized through scanning electron microscopy and atomic force microscopy. The experimental results show that PEI/SPES membranes have high salt permeability whereas retaining PEG1000. Meanwhile, the properties of PEI/SPES membranes were influenced to a great extent by operation pressure and salt concentration. For dye mixture solutions, the separation factors were all more than 8.0, indicating that PEI/SPES membrane can be used for purification of dyes. Since PEI/SPES membrane carries two kinds of charge to facilitate salts transition, this property makes it a promising candidate for the desalination of water-soluble organics mixture system.

Key Words: Nanofiltration, Composite membrane, Charged, Membrane performance.

INTRODUCTION

Nanofiltration is a relatively new membrane separation technique developed in the 1980s based on reverse osmosis (RO). The key difference between nanofiltration and reverse osmosis is that the latter retains monovalent salts, whereas nanofiltration allows them to pass but retains divalent salts. One special application of nanofiltration is water softening[1-3]. Another main application is the removal of organics having a molecular weight range from 200 to 1000[4-6]. At present, most of nanofiltration membranes are charged composite membranes which consist of a charged active thin layer that deposited onto a neutral microporous substrate. Those membranes are mainly negatively or positively charged composite membranes which exhibit high retention to divalent salts and organics due to sieving effect and static electrification. Typically, the rejection is above 95 % for divalent ions that carrying same charge as nanofiltration membrane, whereas the rejection of monovalent ions that carrying same charge can be anywhere between 20 and 80 %[7].

In fact, removal of divalent salts from organics is especially important to chemical industry because of widespread usage of sulfuric acid as a solvent, catalyst and reactant. Such demands can be found in waste water treatment, dye, food, dairy, fermentation, agriculture, pharmaceuticals and mining industries, *etc*. Therefore, it is essential to prepare a novel nanofiltration membrane which could reject organics whereas permeating divalent salt.

This study attempts to investigate the possibility to obtain a membrane separating divalent salt from organics. In this paper, a novel charged composite nanofiltration membrane was fabricated *via* coating and cross-linking methods by using negatively charged sulfonated polyethersulphone (SPES) microporous membrane as support membrane, positively charged polyethyleneimine (PEI) as coating material and glutaraldehyde and sulfuric acid mixed solution as cross-linking agent. As a matter of fact, PEI/SPES nanofiltration membrane owns two kinds of charge which ensures the membrane having high salts permeation. So far, there is no reported literature on the preparation of nanofiltration membrane which carrying two kinds of charge. The properties of PEI/SPES membranes that prepared under different preparation conditions and operating conditions were evaluated as well. Then, the membrane was attempted in the desalination process of dyes solution. In addition, the morphology of PEI/SPES membrane was characterized through scanning electron microscopy (SEM) and atomic force microscopy (AFM).

EXPERIMENTAL

Sulfonated polyethersulphone (SPES) with 20 % sulfonation degree (synthesized by the method[8]); polyethyleneimine (PEI) of analytical grade (from ACROS, US) used as an active coating material; polyethylene glycol (molecular weight 1000 Da, *i.e.* PEG1000), N,N-dimethylacetamide (DMAc), polyvinylpyrrolidone (PVP), butanone, glutaraldehyde, phosphoric acid, NaCl and Na_2SO_4, are purchased from local venders. The dyes, such as reactive blue 21, xylenol orange, methyl green and neutral red (see molecular weights and chemical structures in Fig. 1) used as purchased without further purification.

Preparation of PEI/SPES composite nanofiltration membrane: Sulfonated polyethersulphone (SPES) support membrane was fabricated by phase inversion method. The polymeric solution was prepared by dissolving 20 wt % SPES, 5 wt % PVP, 6 wt % butanone, 4 wt % phosphoric acid in N,N′-dimethylacetamide with continuous stirring. The polymeric solution was cast on a horizontal glass plate with a glass blade at temperature of 25 °C and relative humidity of 40 %. After evaporation in the air for 60s, the membrane was precipitated by immersing it in a water bath for 24 h to remove all N,N′-dimethylacetamide. The membrane with negative charges subsequently served as a support layer for nanofiltration membrane fabrication.

PEI/SPES composite nanofiltration membrane was fabricated by coating and cross-linking methods. The SPES support membrane was immersed into PEI aqueous solution and stood for 25 min. Then, it was taken out of PEI aqueous solution to remove excessive solution. Thereafter, the membrane was crosslinked with agent solution that mixed by 1 wt % glutaraldehyde and 1 wt % sulfuric acid in a container. The crosslinked membrane underwent curing treatment after being taken out of the container. Thus, a novel nanofiltration membrane with two kinds of charge, called PEI/SPES membrane, was obtained.

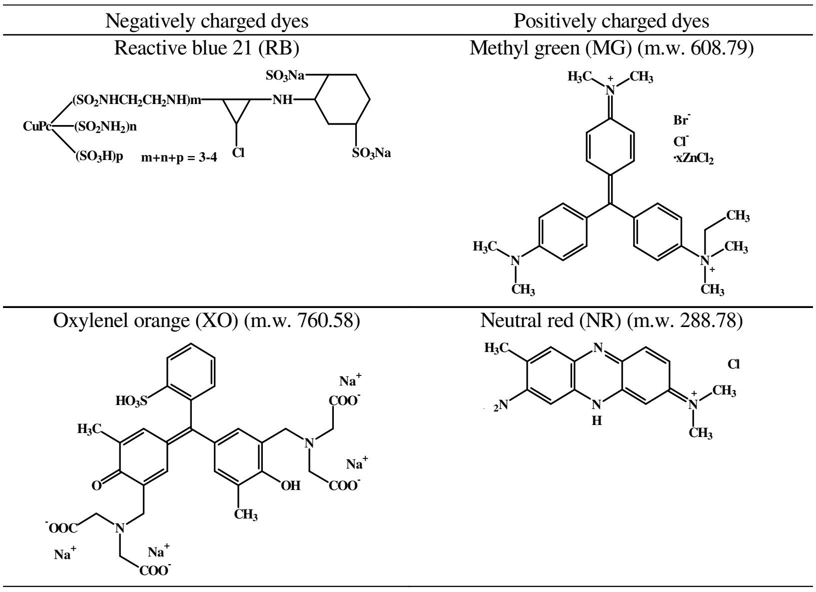
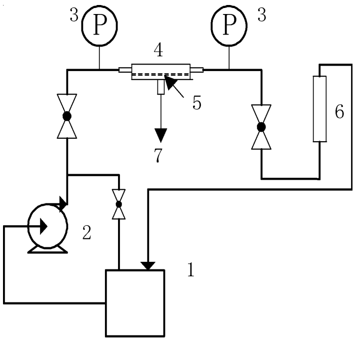


Fig. 1. Chemical structures of various dyes

Permeation experiments: The permeation performance of PEI/SPES membrane was evaluated by permeation experiments with membrane evaluation apparatus which was shown in Fig. 2.



1. feed reservoir; 2. pump; 3. manometer;
4. membrane module; 5. membrane;
6. flowmeter; 7. permeatant

Fig. 2. Scheme of the experimental apparatus

The flux of the membrane was determined by the volume of the permeated fluid through the membrane during a certain period of time and calculated with the following equation:

$$F = V/(A \cdot t) \tag{1}$$

where F is the flux, A is the effective area of the membrane; t is the time for permeation and V is the volume of the permeating fluid passing through the membrane.

Rejection was calculated with the following equation:

$$R = 1 - C_p / C_f \tag{2}$$

where R is the rejection, C_p and C_f are the concentrations of the permeated fluid and the feed concentration, respectively.

Separation experiments: The separation performance of PEI/SPES membrane was characterized by separation experiments of several dye/salt/water mixtures. The salt/organics selectivity of the membrane is defined as follows:

$$\alpha = \frac{y_A / y_B}{x_A / x_B} = \frac{1 - R_A}{1 - R_B} \tag{3}$$

where α is separation factor. y_A and y_B are mole fraction of A, B in permeate fluid, respectively. x_A and x_B are mole fraction of A, B in the feed, respectively. R_A and R_B are A, B rejections of the membrane, respectively. For mixture systems, the higher α is, the more easily the mixtures be separated.

Morphological characterization of PEI/SPES membrane: Scanning electron microscope (*i.e.* SEM, Quanta 200, FEI Co., Ltd., Netherlands) was used to characterize the surface and cross-sectional structures of the PEI/SPES composite nanofiltration membrane and SPES support membrane. To avoid destroying the cross-section structure, the membrane samples were fractured in liquid nitrogen and then sputtered with gold before observation.

As an important complement of the SEM, atomic force microscopy (*i.e.* AFM, Nanoscopy IIIa, Veeco Metrology Group, USA) is a powerful asset as it can scan directly membrane surface in air and without special sample preparation. Atomic force microscopic surface analysis of the PEI/SPES including nanofiltration membrane and SPES supporting membrane was conducted with dry sample in non-contact model.

RESULTS AND DISCUSSION

Preparation of PEI/SPES nanofiltration membrane: Table-1 lists the properties of eight PEI/SPES nanofiltration membranes (M1-M8) which were prepared under different conditions. The performance tests for PEI/SPES membranes were carried out at 25 ºC and 0.40 MPa. The membranes were characterized with pure water flux and rejections of 500 mg/L PEG 1000 and 0.01 mol/L Na_2SO_4. In the permeation experiments, the concentration of PEG1000 was measured by ultraviolet spectrophotometer (UV-2450, Shimadzu, Japan) and that of Na_2SO_4 was got by conduct meter (DDS-12A, Shanghai Dazhong Analysis Instrument, China).

TABLE-1
EFFECT OF PREPARATION CONDITIONS ON
THE PERFORMANCE OF PEI/SPES NANOFILTRATION MEMBRANE[a,b]

No.	Preparation conditions				Membrane performance		
	PEI content (%)	Cross-linking time (min)	Curing temp. (ºC)	Curing time (min)	Water flux (L m^{-2} h^{-1})	PEG 1000 rejection (%)	Na_2SO_4 rejection (%)
M-1	1.0	5	70	20	6.2	82.3	25.5
M-2	1.5	5	70	20	5.8	90.0	29.3
M-3	1.5	15	70	20	5.7	88.7	32.5
M-4	1.5	25	70	20	5.4	86.3	43.2
M-5	1.5	5	80	20	5.4	88.7	38.2
M-6	1.5	5	90	20	2.8	92.3	49.6
M-7	1.5	5	70	40	2.7	89.8	35.4
M-8	1.5	5	70	60	0.8	93.6	43.7

[a]Other preparation conditions: Coated for 25 min, cross-linking agent solution mixed by 1 % glutaraldehyde and 1 % sulfuric acid, cross-linked for 5 min, curing treatment for 20 min.
[b]Testing condition: Operation pressure = 0.4 MPa, concentration of Na_2SO_4 = 0.01 mol L^{-1}, concentration of PEG1000 = 500 mg L^{-1}.

From Table-1, it was found that, when PEI concentration increased from 1.0 wt % to 1.5 wt %, water flux decreased and rejections increased due to that composite layer became thicker. When cross-linking time increased from 5 to 25 min, Na_2SO_4 rejection grew obviously. With curing temperature rising from 70 to 90 ºC, water flux decreased but Na_2SO_4 and PEG1000 rejections increased largely because of denser skin layer therefore leading to smaller pore size. The results also demonstrated the effect of curing time which is similar to the effect of curing temperature.

Compared with those common nanofiltration membranes which have the rejection of more than 95 % to divalent ion[7], PEI/SPES membranes have lower divalent salt (*e.g.* Na_2SO_4) rejection. This phenomenon may be explained as below: during PEI coating process, thanks to charges attraction and porosity permeability, PEI was prone to penetrate into the inner part of support membrane during the PEI coating process. This behaviour could not only reduce pore size so as to increase organics rejection, but also cause support membrane carrying both positive and negative charges which facilitates electrolytes passing through the membrane. Plus, the bond of thin-film composite layer with support membrane became firmer and firmer because of charges attraction and cross-linking action. Since PEI/SPES membrane carries two kinds of charge to facilitate salt transition, it can be used to the desalination process of low-molecular weight organic solutions.

Compared to other seven membranes, M-2 has better performance such as bigger water flux and higher PEG1000 rejection whereas lower Na_2SO_4 rejection. Hence, membrane M-2 was used for further experiments. Here, membrane M-2 was prepared with 1.5 wt % PEI coating solution, coated for 25 min, cross-linked for 5 min with cross-linking agent solution mixed by 1 wt % glutaraldehyde and 1 wt % sulfuric acid and having 20 min curing treatment at 70 ºC.

Permeation characteristics of PEI/SPES nanofiltration membrane: The permeation performance of PEI/SPES membrane was characterized by permeation experiments from which water flux, Na_2SO_4 and PEG1000 rejections were calculated. The testing conditions chosen for present research were as below: testing pressure P = 0.4 MPa, concentration of Na_2SO_4 = 0.1mol/L, concentration of PEG1000 = 500 mg/L.

Effect of operation pressure: The effect of different operation pressure on the membrane performance was investigated. The results are shown in Fig. 3. It is obvious that water flux of the membrane increased linearly with operating pressure which can be explained by Spiegler-Kedem Model[9]:

$$J_v = L_P(\Delta P - \sigma\Delta\pi) \qquad (4)$$

where J_v is the water flux, L_p is the permeability of pure water, ΔP is the operating pressure difference, σ is the reflection factor of the membrane and $\Delta\pi$ is the osmosis pressure. Because pure water is the permeating fluid, $\sigma\Delta\pi$ may be ignored. The permeability of pure water is calculated at 14.6 L/(m^2 h MPa) by the linear fit of experimental data. Fig. 3 also shows that, Na_2SO_4 and PEG1000 rejections went upwards gradually. This can be attributed to rising density of the skin layer as operating pressure increased, which led to corresponding growth of PEG1000 and Na_2SO_4 rejections.

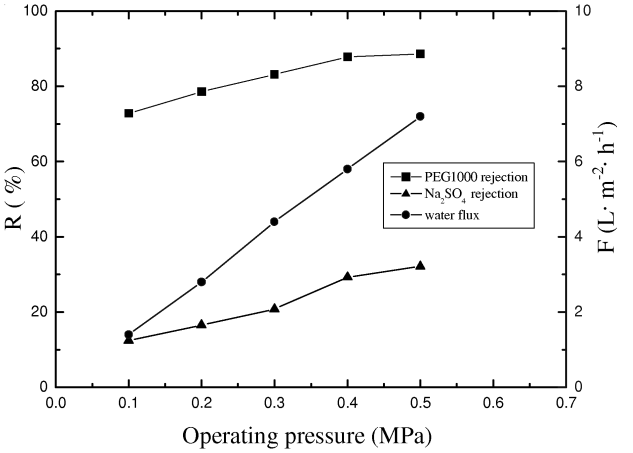


Fig. 3. Influence of operating pressure on the membrane performance

Effect of feed concentration: The effect of PEG1000 concentration on flux and rejection is shown in Fig. 4. It can be seen that PEG1000 rejection decreased as PEG1000 concentration increasing which can be explained as follow: The concentration difference from upstream side to downstream side increased with the increase of PEG1000 concentration which resulted in increasing permeation rate of PEG1000 and therefore decreasing PEG1000 rejections. Meanwhile, the flux of PEG1000 kept steady.

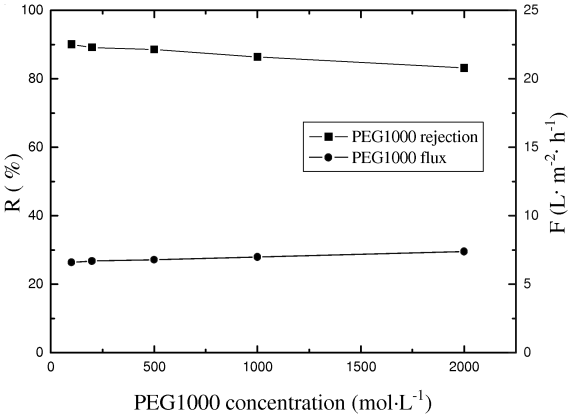


Fig. 4. Influence of PEG1000 concentration on the membrane performance

The effect of Na_2SO_4 concentration on flux and rejection is shown in Fig. 5. It was found that the rejection decreased rapidly while the permeate flux decreased slightly within the whole testing scope. This can be explained by Donnan effect[10]. Since the primary amines on the side chains of PEI can absorb proton of aqueous solution, the active layer of PEI/SPES membrane owns positive charges distribution. When Na_2SO_4 concentration increased, the shield effect of the anions in the solution, for the positively charged groups on the membrane surface, became progressively stronger, *i.e.*, the decrease of the membrane repulsion force on the cation occurred. This effect resulted in decreasing rejection to Na^+. Besides, the concentration of Na^+ on the membrane surface increased with the increase of Na_2SO_4 concentration, which resulted in increasing permeation rate of Na^+. So, the electroneutrality between the two sides of the membrane was broken. In order to maintain the electroneutrality, more SO_4^{2-} permeated from upstream side to downstream side, thereby Na_2SO_4 rejection decreased. Actually, the dependence of rejection on feed concentration is one of the characteristics of charged nanofiltration membranes.

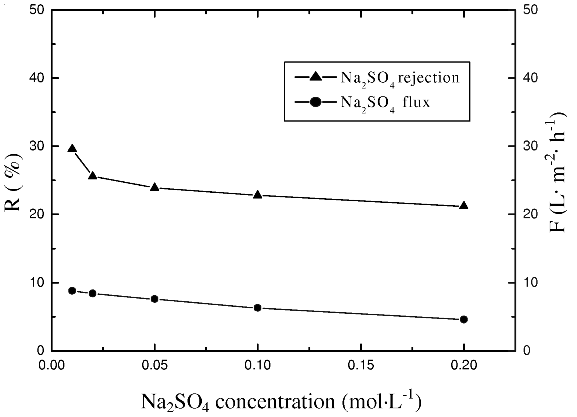


Fig. 5. Influence of Na_2SO_4 solution concentration on the membrane performance

Separation characteristics of PEI/SPES nanofiltration membrane: The separation performance of PEI/SPES membrane was characterized by separation experiments of dye and salt mixture solutions. The dyes include two positively charged dyes (MG & NR) and two negatively charged dyes (RB & XO) and salts include NaCl and Na_2SO_4. In the desalination experiments, the concentration of dye and that of salt in the feed were 500 mg L^{-1} and 0.01 mol L^{-1}, respectively. The operation pressure was 0.4 MPa. For salt and dye mixture solutions, the concentrations of salts were determined by ion selective electrode electric potential method using a numerical pH-meter (pH211, HANNA instruments, Italy). The dyes concentrations were analyzed with UV spectrophotometer (UV-2450, Shimadzu, Japan).

The results were shown in Table-2. It can be observed that PEI/SPES membrane had higher flux for the mixture solutions than that of the pure water (5.8 L m^{-2} h^{-1}). Meanwhile, the flux of NR solution was lower than that of MG solution. Generally speaking, when linear compounds with low molecular weight are used, they can easily get into the pores of the nanofiltration membrane with blocking the pores, reducing the flow of the water and causing flux decreasing[11].

TABLE-2
SEPARATION PERFORMANCE OF PEI/SPES NF MEMBRANE IN DYE-DESALINATION PROCESS

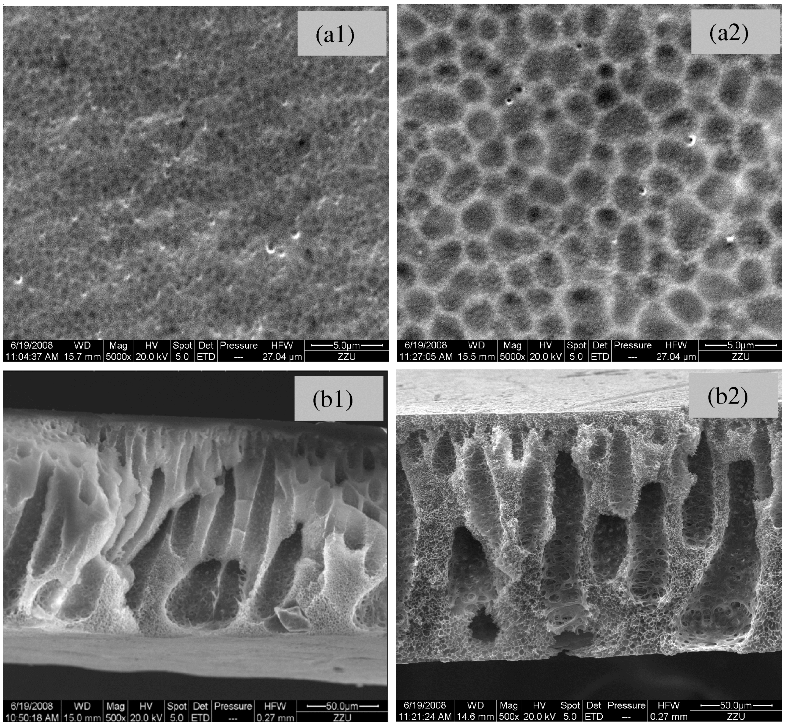
Mixture system	RB/NaCl/ Water	XO/NaCl/ Water	MG/NaCl/ Water	NR/NaCl/ Water	MG/Na_2SO_4/ Water	NR/Na_2SO_4/ Water
Flux (L m^2 h^{-1})	10.3	7.8	11.5	9.1	10.0	7.0
Dye rejection (%)	97.2	90.0	99.0	98.0	93.7	91.3
Salt rejection (%)	2.5	15.9	16.5	20.0	28.9	25.4
Separation factor α	34.8	8.4	83.5	40.0	11.3	8.6

For dyes and salts mixture solutions, the rejections of NaCl and Na_2SO_4 were less than 20 and 30 %, respectively. It seemed that the rejections of dyes were mainly affected by the charge of the dyes. Since PEI/SPES nanofiltration membrane has active layer with positive charges, it has higher retention for positively charged dyes (MG and NR) than that for negatively charged dyes (RB and XO). It was found that the separation factors for the dyes mixture were all more than 8.0, indicating that the dye compounds and salts of the mixture solutions were successfully separated. For positively charged dyes system, such as MG/NaCl/Water and NR/NaCl/ Water, the separation factors of this membrane were up to 83.5 and 40.0, respectively. It indicates that PEI/SPES membrane can completely separate salts from positively charged dyes mixture solution.

As the synthesis process of dyes produces salts and small molecular weight intermediates and residual compounds which reduce the purity of the dyes, the salts and impurities need to be removed before the dyes are dried for sale as powder. Compared with conventional approaches, nanofiltration technology which can produce high-purity product of dye is considered as a competitive method[12]. The research results show that PEI/SPES nanofiltration membrane is a promising technique for purification of dyes, especially for positively charged dyes mixture system.

Morphology characteristics of PEI/SPES composite nanofiltration membrane

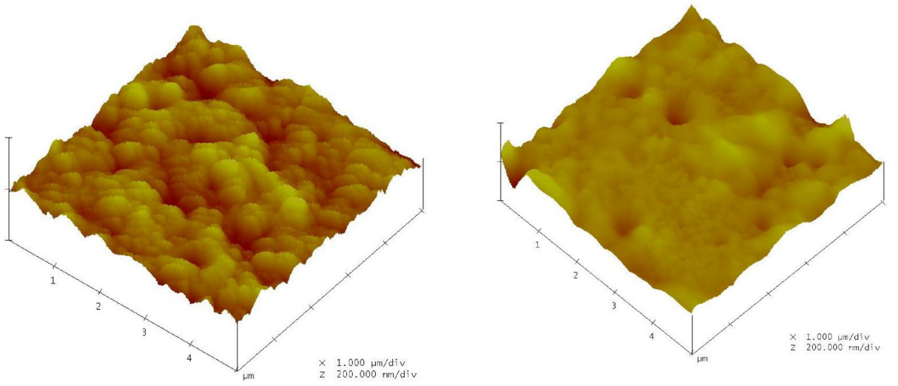
SEM: The skin layer and the cross-section morphology of SPES support membrane and PEI/SPES nanofiltration membrane were observed with SEM as shown in Fig. 6. The skin layer surface images (Fig. 6 a1, a2) show that PEI/SPES nanofiltration membrane has apparently denser surface than SPES support membrane. After coating and cross-linking process, some particles were formed and presented on the membrane surface due to the congregating of some PEI molecules and the cross-linking reaction of PEI with glutaraldehyde. The cross-section images (Fig. 6 b1, b2) show that the SPES membrane is a good microporous support because it has regular finger-like pores enabling good flux and the active skin layer of PEI/SPES nanofiltration membrane was thicker than SPES support membrane which results from deposition of PEI. Besides, it was found that the inner part of support membrane has obviously changed which was likely to be resulted from PEI penetrating into the pores of support membrane. This special composite structure probably determines high permeation of salts.



(a) the surface structures of membrane; (b) the cross section of membrane;
1: SPES support membrane; 2:PEI/SPES composite NF membrane

Fig. 6. Surface and cross section of the membranes by SEM

Atomic force microscopy: Atomic force microscopy images of SPES substrate membrane and the PEI/SPES composite nanofiltration membrane with a projection area of 5 μm × 200 nm are shown in Fig. 7. Atomic force microscopy analysis can provide information on the change of roughness. In fact, roughness is one of the most important surface properties as it has strong influence on fouling and also on local mass transfer. The root-mean square (RMS) roughness for the image is frequently quoted for membranes[13,14]. The RMS roughness of the SPES support membrane and the PEI/SPES nanofiltration membrane are 14.7 and 16.2 nm, respectively. Obviously, the roughness of surface of the PEI/SPES membrane increased slightly than that of the support membrane, which may be attributed to that the coating and cross-linking process where the active layer became thicker. Due to the tendency to valley clogging[15], rough membrane surface would lead to a decline of water flux during the filtration process.



SPES support membrane PEI/SPES composite nanofiltration membrane

Fig. 7. Atomic force microscopy micrograph for the membranes

Conclusion

This study attempts to investigate the possibility to obtain a novel nanofiltration membrane which has both high rejection to organics and high divalent salts permeation. Different from the common charged nanofiltration membranes, the new nanofiltration membrane resorts to charged membrane rather than neutral membrane as support. PEI/SPES composite nanofiltration membrane with two kinds of charge was fabricated by coating positively charged PEI layer on the negatively charged SPES support membrane. The permeation performance of PEI/SPES membrane was characterized by permeation experiment. The performance of PEI/SPES membrane was tested by separation experiments of dye and salt mixture solutions. In addition, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the morphologies.

The research results show that the PEI/SPES membrane can retain PEG1000 while permit divalent salt Na_2SO_4 to pass through. With operation pressure rising, PEG1000 and salt rejection increased but not as faster as water flux did. However, the flux and salt rejection declined when salt concentration grew. PEI/SPES membrane is successfully used for the removal of NaCl or Na_2SO_4 from dye mixture system, especially for positively charged dye mixture solution. SEM and AFM images confirm that a dense composite layer had been coated on the surface of the support membrane. With a high permeability for salts, PEI/SPES nanofiltration membrane can be applied in desalination process from organic mixtures solution.

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