Preparation and Humic Acid Fouling Resistance of Poly(vinylidene fluoride)–Fabric Composite Membranes for Membrane Distillation

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ABSTRACT: A novel, flat-sheet poly(vinylidene fluoride) (PVDF)–fabric composite membrane used for membrane distillation (MD) was prepared by coating and a wet-phase inversion process. This is a simple and suitable method for preparing large, flat-sheet MD membranes with high strengths and better fouling resistance. The PVDF–fabric composite membrane was a double-layer membrane, containing a PVDF porous membrane layer on the fabric support. The polyester filament woven fabric, which was used as support of the composite membrane, was finished with the water-and-oil repellent agent FK-510 or chitosan before the coating process. The effects of fabric finishing on the preparation and characteristics of the composite membrane were studied. The fouling resistance of the prepared com- posite membrane was investigated by air-gap membrane distillation, with a saturated humic acid solution containing NaCl as the feed. The experimental results indicate that the fabric, finished with 2 g/L FK-510 or 5 g/L chitosan, was suitable for preparing the composite membrane. With the protection of the fabric support, the prepared composite membrane exhibited better humic acid fouling resistance as its fabric support surface was in contact with the feed solu- tion in the MD process, especially when the fabric support was finished with chitosan. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3651–3658, 2010

Key words: coatings; composites; fluoropolymers; membranes; separation techniques

INTRODUCTION

Membrane distillation (MD) is a separation process based on evaporation through the porous hydropho- bic membrane;[1] it has many advantages, such as a lower operating temperature than conventional dis- tillation and a lower operating pressure than con- ventional pressure-driven membrane processes. It can be used for water desalination, the concentration of aqueous solutions, and the removal of organic matter in drinking water production.[2–7]

In the MD process, the volatile component of the feed solution evaporates at the feed/membrane interface and then diffuses through the membrane. The driving force for the mass transport is the vapor pressure difference across the porous membrane. The membrane maintains the liquid–vapor interface at the pore entrances[8] without altering the vapor– liquid equilibrium of the components in the process liquid[9] and prevents the penetration of the aqueous solution into the membrane pores. Therefore, the MD membrane must be porous and hydrophobic, although it also has a high permeability, low thermal conductivity, high liquid entry pressure (LEP) of

water, good thermal stability, and excellent chemical resistance to the feed solution.[10,11]

Most of the commercial membranes used for the MD process so far are initially fabricated for other membrane processes.[11–13] Recently, many studies on the preparation of membranes specifically for the MD process have been carried out.[10–16] The poly- mers, such as polytetrafluoroethylene, polypropyl- ene, and poly(vinylidene fluoride) (PVDF), are popular and available hydrophobic membrane mate- rials because of their low surface energy, excellent chemical resistance, and good physical and thermal stability. Among them, only PVDF membranes can be fabricated by the wet-phase inversion process, a convenient and simple technique, because PVDF is soluble in common organic solvents. However, the mechanical properties of the PVDF porous mem- branes prepared by this method are not satisfactory.

Another problem encountered in the MD process is membrane fouling. Deposits on the membrane cause the clogging of the membrane surface pores, flux decline, and membrane wetting.[17,18] When the MD membrane is wetted, the hydrophobic recovery of the membrane is difficult. Therefore, membrane fouling is one of the major obstacles in MD, although it is less serious in MD than in other mem- brane separations.[9]

Natural organic matter (NOM) in natural water is largely composed of humic substances, which are

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macromolecular mixtures of humic acids, fulvic acids, and humin.[19] Humic substances are amphipathic (hydrophobic and hydrophilic) and negatively charged at the pH range of natural water because of the dissociation of carboxylic acid and hydroxyl functional groups.[20] NOM is mainly responsible for the color in natural water. It is necessary for NOM to be removed during the production of potable water. Soil-based commercial humic acids have been used to study the interactions between NOM and membranes. It was found that humic acid deposited on the membrane surface in the MD process and resulted in membrane fouling,[19,21] especially when the humic acid solution contained salts. The extent of membrane fouling depended on the pH, ionic strength, and humic acid concentration of the feed solution.[2,19]

Membrane fouling limits the efficient application of membrane technology, which results in the deterioration of membrane performance and ultimately shortens membrane life. Solutions for filtration membrane fouling have been studied widely and include feed pretreatment and membrane modification. However, only a few studies on MD membrane fouling were carried out in the past. Recently, researchers have paid more attention to this problem. It has been found that the scaling of salts and the adsorption or deposition of organic foulants on the membrane surface are the major reasons for MD membrane fouling.[21–29] Some researchers have found that MD membrane fouling can be prevented to some extent by feed pretreatment, the selection of the operating conditions, and membrane surface modification.[23–25,30]

In this study, we combined textile finishing technology with the technique of membrane fabrication to prepare an MD membrane with a high strength and better resistance to humic acid fouling. The prepared PVDF–fabric composite membrane was a double-layer, flat-sheet membrane containing a PVDF porous membrane layer on the fabric support layer. The composite membrane was fabricated by coating and the wet-phase inversion process. A polyester filament woven fabric was used as the support of the composite membrane to strengthen the PVDF porous membrane and to protect it from fouling in the MD process. The fabric support was finished with water-and-oil repellent agent and chitosan to obtain different surface properties (hydrophobicity and hydrophlicity, respectively) and penetration resistance to the casting solution. The effects of fabric finishing on the preparation and characteristics of the composite membrane were studied. The influence of contact mode between the composite membrane and the feed solution on the fouling resistance of the membrane was investigated by air-gap membrane distillation (AGMD).

EXPERIMENTAL

Materials

The polyester filament woven fabric had 435 warps/10 cm, 273 wefts/10 cm, and an area weight of 79 g/m². The water-and-oil repellent agent FK-501, a fluorocarbon polymer emulsion, was obtained from CTA-Tex Chemicals Co., Ltd. (Beijing, China). Chitosan is the N-deacetylated derivative of chitin, poly[β-(1,4)-N-acetyl-D-glucosamine]. The deacetylation degree of chitosan used in the experiment was about 70%.

Finishing of the fabric support

To fabricate the double-layer PVDF–fabric membrane, it was essential to impart fabric penetration resistance to the casting solution. The polyester filament woven fabric was finished with the water-and-oil repellent agent FK-501 or chitosan by the pad–dry–cure technique, which is the most common method in continuous chemical processes for textile materials. The water-and-oil repellent finishing formulation contained 1–10 g/L FK-501. The chitosan finishing formulation was composed of 2–10 g/L chitosan, dissolved by acetic acid, and 1 g/L glutaraldehyde as a crosslinker. In the finishing process, the fabric was immersed in the formulation at room temperature and squeezed with squeeze rolls to obtain a wet pickup of 70% or so, then dried for 1.5 min at 100°C, and cured for 3 min at 150°C.

Preparation of the composite membrane

The casting solution, containing 12% PVDF, 3% LiCl, and 85% dimethylformamide, was cast on the top surface of the finished fabric by a coating device (Werner Mathis AG, Zurich, Switzerland). The fabric, having a thin solution film, was immersed into a water bath for some time, rinsed with water to remove the residues of solvent and LiCl from the membrane, and then dried. The double-layer composite membrane, composed of a PVDF porous membrane layer and a fabric support, was thus obtained.

Membrane characterization

The composite membrane was characterized by maximum pore size, mean pore size, overall porosity, water vapor permeability (WVP), tensile strength, and peeling strength. The maximum pore size was estimated by the bubble-point method and calculated according to the Laplace equation. The mean pore size and overall porosity of the composite membrane were determined by a mercury porosimeter. The WVP was determined by a dry cup method at 38°C and 90% relative humidity according to ASTM E 96.

TABLE I
Effect of FK-501 Finishing on the Preparation of the Composite Membrane

FK-501 concentration (g/L)	Contact angle of the water droplet (°)	Leakage of the solution	Integrity of the membrane	Peeling strength (cN/cm)
0	Spreading	Bad	Bad	
1	86.0	Little	Imperfect	26.6
2	118.5	No	Good	27.0
3	123.0	No	Good	16.2
5	131.5	No	Good	11.2
10	142.0			

The adhesive properties between the fabric layer and PVDF membrane layer was estimated by the peeling strength of a 1 cm wide specimen.

The MD performance of the composite membrane was investigated by a batch AGMD process, which was carried out in the daytime and ceased in night. The feed solution was unloaded when the operation was ceased and reloaded before the operation was resumed. The initial feed solution was a saturated humic acid solution prepared at 50°C and pH 8.5, containing 146 mg/L humic acid and 10 g/L NaCl. The effective area of membrane was 300 cm^2, and the air-gap separation distance was 15 mm. The inlet temperatures of the feed solution and the cooling water were maintained at 50 and 20°C, respectively. The initial feed volume was 1.5 L. As the feed volume was less than 1 L, the saturated humic acid solution, containing the same NaCl concentration as the instantaneous feed solution, was added to the feed reservoir. In the AGMD process, the condensed water was collected in the distillate collector, which was replaced once an hour. We measured the flux by weighing the condensate and presented it in terms of normalized flux (J/J_0), which is the ratio of instantaneous flux (J) to initial flux (J_0). The purity of the condensed water was evaluated by its conductivity.

RESULTS AND DISCUSSION

Effect of fabric finishing on the preparation of the composite membrane

Because the fabric had numerous interstices and holes, it exhibited better liquid penetration proper-

ties. The casting solution would have easily penetrated through and leaked from the fabric support in the coating process if the fabric had not been finished beforehand. As a result, it was difficult to obtain a double-layer PVDF–fabric membrane, and the integrity of the PVDF membrane layer was poor, with a lot of large holes, especially when the coat thickness was thin.

Both water-and-oil repellent finishing and chitosan finishing can improve the penetration resistance of a fabric; this was necessary for preparing the double-layer PVDF–fabric membrane. The finishing effect depended on the concentration of chemicals in the formulation. The effects of fabric finishing on the preparation of the composite membrane are listed in Tables I and II.

Water-and-oil repellent finishing is a mature technology in the textile industry. Fluorochemical repellent, with a perfluoroalkyl group in the molecule, is the most effective and durable repellent, which can cover the fiber surface in the finishing process and impart the fiber with an extremely low surface energy. Consequently, the finished fabric exhibited both water repellency and oil repellency.

With increasing FK-501 concentration, the surface tension of the finished fabric decreased, and the contact angle of a water droplet on the finished fabric increased considerably (see Table I). The permeation and leakage of the casting solution on the fabric support decreased with the coating process, and the uniformity of the prepared composite membrane became better. However, the anchor effect between the fabric layer and the PVDF membrane layer

TABLE II
Effect of Chitosan Finishing on the Preparation of the Composite Membrane

Chitosan concentration (g/L)	Spread time (s)	Leakage of the solution	Integrity of the membrane	Peeling strength (cN/cm)
0	<5	Bad	Bad	
2	54	Little	Imperfect	27.0
5	108	No	Good	25.2
7	216	No	Good	19.2
10	>300	No	Good	19.0

deteriorated because less casting solution penetrated the fabric support, which resulted in a lower peeling strength. When FK-501 concentration was above 10 g/L, the surface tension of the finished fabric was so low that the casting solution hardly permeated the fabric support in the coating process. The formed PVDF membrane layer could be separated from the fabric support in the wet-phase inversion process.

Chitosan finishing can decrease the capillary effect of a fabric by narrowing the interstices between fibers. With increasing chitosan concentration, the wetting property of the finished fabric deteriorated, and the spread time of the water droplet on the finished fabric surface increased (see Table II). The penetration and leakage of the casting solution on the fabric support decreased in the coating process, and the uniformity of the composite membrane became better, but the peeling strength between the fabric layer and the PVDF membrane layer decreased.

The experiments showed that the prepared composite membrane exhibited better uniformity and integrity and a higher peeling strength when the fabric support was finished with 2 g/L FK-501 or 5 g/L chitosan. The morphologies and characteristics of the two composite membranes are shown in Figure 1 and Table III.

The scanning electron microscopy (SEM) images showed that the prepared composite membrane was a double-layer membrane, with a PVDF membrane surface and a fabric surface. The permeability of the composite membrane was governed by a PVDF porous membrane layer, and the tensile strength was determined by the fabric support. With the strengthening of the fabric support, the thickness of the PVDF porous membrane layer decreased greatly to improve the membrane permeability.

Humic acid fouling resistance of the composite membrane

The fabric surface and PVDF membrane surface of the composite membrane were different in morphology and properties. The surface properties of the fabric supports finished with FK-510 and chitosan, respectively, were also different. The characteristics of the composite membrane surface exposed to the feed solution had a great influence on MD performance, as shown in Figure 2.

In the AGMD process, the saturated humic acid solution became supersaturated with the evaporation of water in the feed solution. Humic acid in the feed solution aggregated and deposited on the composite membrane surface. Furthermore, the NaCl concentration also increased in the MD process. At a high ionic strength, the humic acid molecules became coiled and spherical because of electrostatic shielding between the negative charges of the carboxyl

functional groups of humic acid molecules by the counter ions,[19] which aggravated the aggregation and deposition of humic acid. As the MD running time increased, the humic acid aggregates in the feed solution became greater in size and amount, more humic acid aggregates deposited, and a fouling layer was formed on the composite membrane surface. The effective surface area of the composite membrane decreased, which resulted in a flux decline. The adhesion of humic acid aggregates on the membrane surface was the main cause for fouling.

The increase in the NaCl concentration was also responsible for the flux decline. As the NaCl concentration increased from 10 g/L to about 30 g/L, the concentration polarization effect increased, and the vapor pressure of the feed solution decreased. Consequently, the vapor pressure difference across the membrane, as a driving force for mass transfer, decreased, and the MD flux decreased.

Therefore, the J/J_0 values of the composite membranes decreased for all cases in this study. The experimental results show that the fluxes nearly recovered when the MD operation was resumed. This revealed that most of the humic acid deposits were removed from the composite membrane surface in the discharging and reloading of the feed solution during the shutdown.

Although the J/J_0 values of the composite membranes fluctuated in a similar way for the three cases, the conductivities of their distillate changed in different ways. This showed that the surface characteristics of the composite membrane were an important factor in membrane fouling. The composite membrane exhibited different fouling resistance when it contacted the feed solution by different surfaces in the MD process.

When the composite membrane contacted the feed solution by its PVDF membrane surface, humic acid aggregates deposited on the surface of the PVDF porous membrane in the MD process. The humic acid deposit layer had two effects on the PVDF porous membrane layer. On the one hand, it caused the clogging of the membrane surface pores, which led to the flux decline. On the other hand, the contaminant deteriorated the hydrophobicity of the PVDF membrane; this resulted in the wetting of some membrane pores and the decrease in the LEP of the PVDF membrane layer. Finally, the feed solution penetrated through the membrane. In the first stage of the MD process, the clogging of the membrane surface pores was the primary effect of membrane fouling; J/J_0 decreased quickly from 1 to 0.83, whereas the increase of distillate conductivity was negligible. The latter effect became greater with increasing MD running time. The feed solution penetrated through the composite membrane and
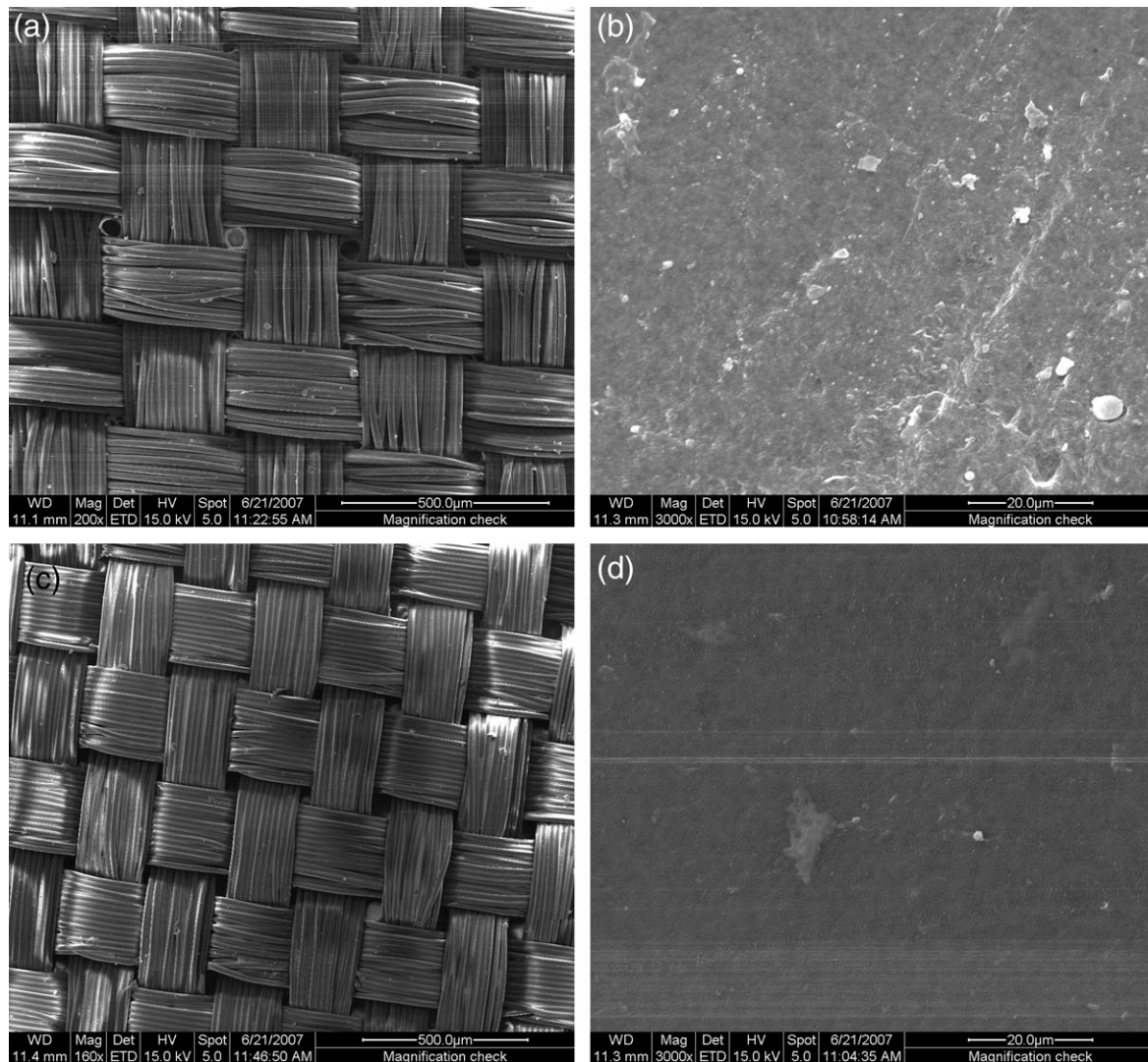
Figure 1 SEM images of the composite membrane surfaces: (a) surface of the fabric support finished with 2 g/L FK-501, (b) surface of the PVDF membrane whose fabric support was finished with 2 g/L FK-501, (c) surface of the fabric support finished with 5 g/L chitosan, and (d) surface of the PVDF membrane whose fabric support was finished with 5 g/L chitosan.

got into the condensed water collector once the LEP of the PVDF membrane was lower than the applied transmembrane hydrostatic pressure. The experimental results show that the distillate conductivity increased at the start of the second stage; meanwhile, the rate of flux decay decreased [see Fig. 2(a)]. This revealed that the wetting of the membrane pores became an important factor in membrane fouling, and the separation factor became lower. With further increasing MD running time, the rate and extent of membrane fouling became greater, the thickness of the humic acid deposit layer on the membrane surface increased, and more membrane pores were wetted. As a result, both the flux decay and the distillate conductivity increased greatly in the fourth MD stage and reached 0.82 for J/J_0 and 0.418 mS/cm for the distillate conductivity after 33 h of MD operation. The composite membrane was susceptible to humic acid fouling if it contacted the feed solution by the PVDF membrane surface.

TABLE III
Characteristics of the Composite Membrane

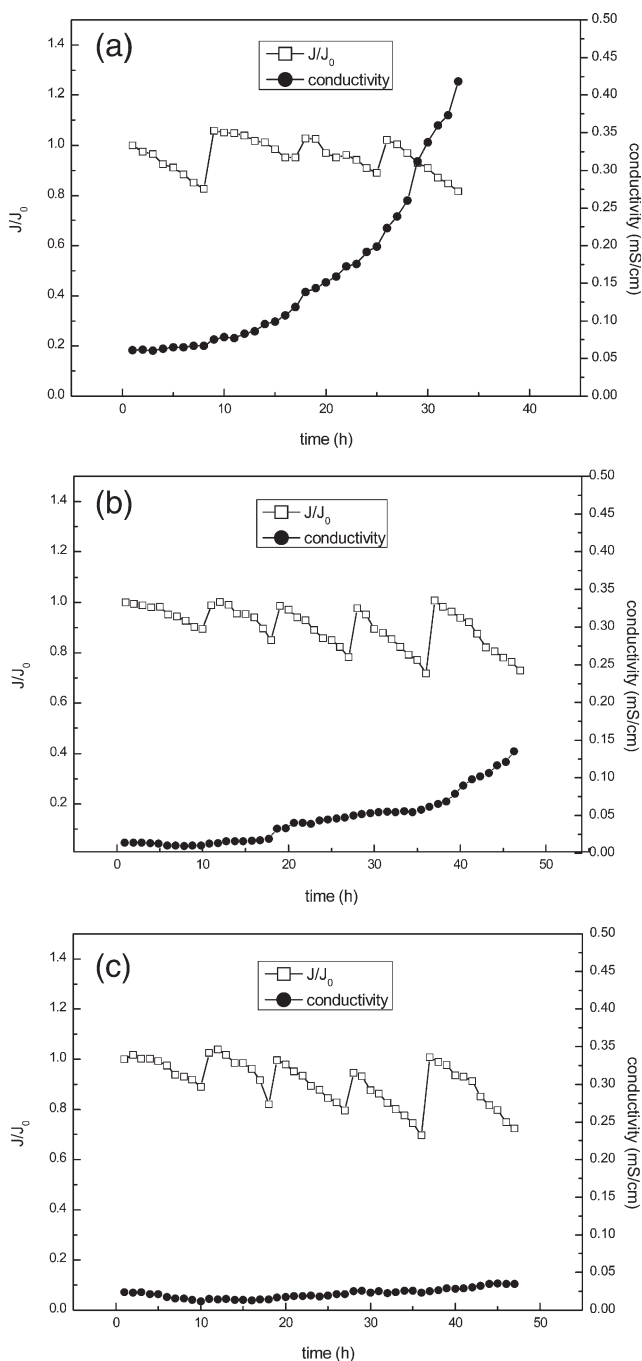| Fabric support	Tensile strength (N/5 cm)	Peeling strength (cN/cm)	WVP (g m^{-2} ·24 h^{-1})	Maximum pore size (μm)	Average pore size (μm)	Overall porosity (%)
Finished with FK-510 (2 g/L)	396.5	27.0	6680	6.4	0.626	57.6
Finished with chitosan (5 g/L)	398.2	25.2	6928	5.0	0.630	55.8

Figure 2 MD performance of the composite membranes with different surfaces in contact with the feed solution: (a) PVDF membrane surface, (b) FK-510 finished fabric support, and (c) chitosan finished fabric support.

When the composite membrane contacted the feed solution by its fabric support surface, humic acid aggregates deposited on the fabric support surface rather than on the PVDF membrane layer. The contaminant had little effect on the permeability and hydrophobicity of the PVDF membrane layer. Moreover, there were numerous and interpenetrative interstices in the fabric support. Although some exterior interstices of the fabric support were clogged by humic acid deposits, the decrease in the mass transfer coefficient of the PVDF porous membrane layer was negligible because the vapor of the feed solution diffused along the interior interstices in the fabric support to the whole interface of the PVDF porous membrane layer. Therefore, the flux decay caused by humic acid aggregates on the fabric support was lower. The feed solution could hardly penetrate through the composite membrane because the PVDF membrane layer remained good hydrophobicity in the MD process. The rate and extent of membrane fouling decreased significantly. In the first MD stage, as the clogging of membrane was dominant in membrane fouling, the flux decay in this contact mode was lower than that in the previous contact mode. (see Fig. 2). In this contact mode, the distillate conductivities for the two composite membranes were lower in the whole MD process, whether the fabric supports were finished with FK-510 or chitosan [see Fig. 2(b,c)]. With the protection of the fabric support, the composite membrane exhibited better resistance to humic acid fouling.

Functional finishing of the fabric support not only influenced the preparation of the PVDF–fabric composite membrane but also had a significant effect on the fouling resistance of the composite membrane. Chitosan is a natural polysaccharide comprising copolymers of glucosamine and N-acetylglucosamine. Chitosan finishing can impart hydrophilicity to a polyester fabric, with the narrowing of interstices in the fabric. On the contrary, the water-and-oil repellent agent FK-510 can impart hydrophobicity to a fabric, without the narrowing of interstices in the fabric. It has been found that organic substances have a higher tendency to deposit on hydrophobic surfaces. The experimental results show that the composite membrane whose fabric support was finished with chitosan had better resistance to humic acid fouling than that whose fabric support was finished with FK-510 when the composite membranes contacted the feed solution by the fabric support surface [see Fig. 2(b,c)]. The increase in the distillate conductivity during the MD process was lower for the former membrane and higher for the latter membrane; it reached 0.035 and 0.135 mS/cm, respectively, after 47 h of the MD operation.

A dark brown thin layer of the humic acid deposits was formed on the surface of the composite membrane in the MD process. The fouling layers formed on different surfaces are shown in Figure 3. The SEM images revealed that the humic acid fouling on the PVDF membrane surface after 33 h of operation was more serious than that on the fabric support surface after 47 h of operation, whether the fabric support was finished with the water-and-oil repellent agent FK-510 or chitosan.
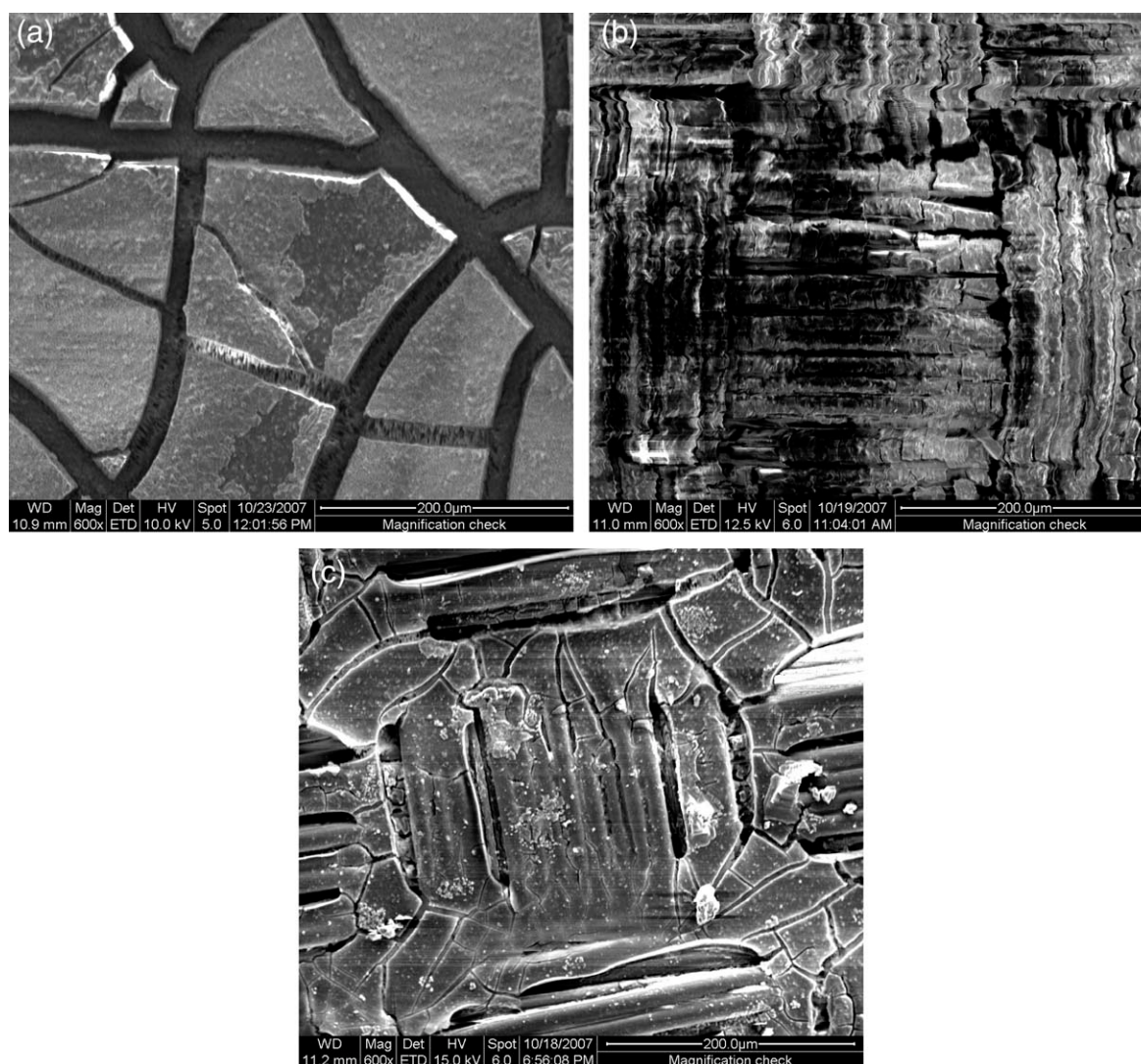
Figure 3 SEM images of the fouling layers of three different surfaces of the composite membranes: (a) PVDF membrane, (b) FK-510 finished fabric support, and (c) chitosan finished fabric support.

This was due to the particular surface of the fabric support, on which there was a coarse surface and a regular array of fine filaments. The boundary layer of the feed solution on the fabric support surface was thinner, and the contact area between the humic acid deposit and fabric support was less. Consequently, humic acid aggregates deposited less on the fabric support surface, and the humic acid deposits were more easily removed from the fabric support surface in the MD process. This further confirmed that the composite membrane had better resistance to humic acid fouling when it contacted the feed solution by the fabric support surface in the MD process.

CONCLUSIONS

A novel flat-sheet PVDF–fabric composite membrane for MD was prepared by coating and a wet-phase inversion process. This was a simple and suitable method for preparing a large, flat-sheet MD membrane with a high strength and better fouling resistance, and it should also be easily realized in industrial production. The prepared composite membrane was a double-layer membrane composed of a PVDF porous membrane layer and a fabric layer. Functional finishing of the fabric support had a significant effect on the preparation and performance of the composite membrane. The fabric support finished with 2 g/L of the water-and-oil repellent agent FK-510 or 5 g/L chitosan was suitable for the composite membrane preparation. With the protection of the fabric support, the prepared composite membrane exhibited better resistance to humic acid fouling when its fabric support surface was in contact with the feed solution in the MD process, especially when the fabric support was finished with chitosan.

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