Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1157041

57 (2016) 24807–24819
November

Taylor & Francis
Taylor & Francis Group

New method of synthesis of sulfonated polyethersulfone (SPES) and effect of pH on synthetic gray water filtration performance by negatively charged SPES/PS UF membranes

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Received 24 February 2015; Accepted 25 January 2016

ABSTRACT

All polymeric membrane-based water purification systems suffer serious membrane fouling problem due to protein adsorption and bacteria attachment. Increasing the negative surface charge density of the membrane will increase its hydrophilicity; this would hinder the colloidal and bacteria attachments. This can be achieved through inclusion of sulfonated group ($-SO_3^-$) as part of the moiety of the polymer that made up of the membrane. In this work, a new method of synthesis of sulfonated polyethersulfone (SPES) is reported. In this method, concentrated sulfuric acid was used as the solvent for polyethersulfone (PES) and also as the source of SO_3(g) when the PES/H_2SO_4 solution was heated to 90˚C. The degree of sulfonation of the polyethersulfone polymer was assessed by ATR-FTIR spectra and ion-exchange capacity determination. Nine polysulfone membranes, containing various amounts of SPES, were fabricated via phase inversion process with a continuous membrane casting machine. The membranes were also characterized using techniques such as SEM, AFM, water permeability, water content, molecular-weight-cut-off, and the negative surface charge. Effects of pH of the synthetic gray water feed (with common domestic wastewater composition, excepting microbiological components) on membrane fouling were evaluated for all nine SPES/PS membranes.

Keywords: Sulfonated polyethersulfone; Ultrafiltration membranes; Membrane fouling; Wastewater

1. Introduction

Rapid worldwide industrialization and global economic growth for past few decades have created great demands for membrane separation technology for industrial, environmental, and domestic applications [1–3]. Since Loeb and Sourirajan first introduced the phase inversion method for preparation of asymmetric membranes in the early 1960's, research and development works on membrane technology in the areas of water desalination [4], municipal [5] and industrial wastewater reuse [6], pharmaceutical production processes [7], and recovery of toxic volatile organic matter from liquid media [8] has received much attention in

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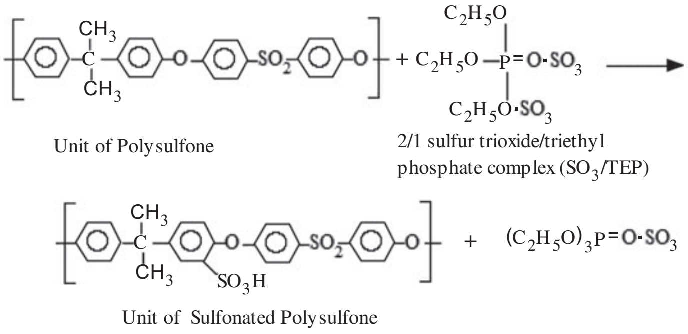
recent years. In spite of the success of membrane technology, all membrane separation systems suffer serious membrane fouling problems [9]. Membrane fouling is caused mainly by; (a) plugging the pore openings at the surface of microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes, and (b) the attachment of bacteria and subsequently colonization on the membrane surface [10]. For porous and non-polyamide membranes, biofouling can be minimized by periodical cleaning with sodium hypochlorite solution which deactivates the biofilm, making it easy to wash it away. Thus, the membrane system regains most of its permeate flow. The membrane fouling due to plugging by solid particles or by large solutes present in the feed stream is an irreversible process and simple chemical cleaning method do not recover the loss of permeate flow. However, periodical backwashing with permeate or gas would slow down such fouling process.

Organic matter like proteins is generally adsorbed more strongly to hydrophobic polymeric surfaces than hydrophilic polymers [11,12]. Initial biofilm formation is achieved by bacteria attachment through exopolymer synthesis at the membrane surface. This process can be avoided if the membrane surface was hydrophilic in nature. Most of the hydrophilic porous membranes have fixed negative surface charges due to the presence of sulfonated group ($-SO_3^-$) as part of the polymer that make up the membrane [13]. This fixed negative surface charge makes the negatively charged colloidal particles difficult to settle down on the membrane surface due to the columbic repulsive force. Columbic repulsive forces prevent negatively charged particles to attach on the negatively charged surfaces, and this slows down the membrane fouling process [12]. Furthermore, the negative charge of the sulfonate group ($-SO_3^-$) attracts the positive end of the dipole water molecule. As a result, this absorption of water onto membrane surfaces by sulfonated groups makes the membrane more hydrophilic, which in turn, hinders the bacteria from attaching onto the membrane surface.

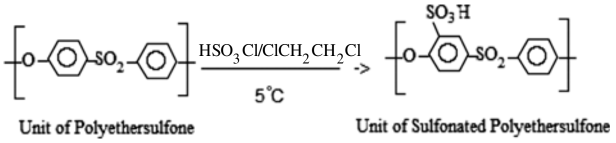
In order to obtain a well-characterized hydrophilic microfiltration or ultrafiltration membrane, sulfonated polymer is needed as one of the polymer components that are made up of the membrane casting solution. Polysulfone and polyethersulfone are two of the most common polymers used by membrane manufacturers to produce MF and UF membranes. Methods of synthesis of sulfonated polysulfone (PSF-SO_3H) had been reported previously; the synthesis of PSF-SO_3H involved using polysulfone as the starting polymer dissolved in 1,2-dichloroethane ($ClCH_2CH_2Cl$) (DCE), Noshay and his co-worker [14] carried out their synthesis by adding sulfur trioxide/triethyl phosphate complex (SO_3/TEP) as the sulfonating agent, this synthesis is shown in Reaction (1) below:



(1)

Conventional method of synthesis of sulfonated polysufone polymer.

This process of synthesis of PSF-SO_3H depends on the ratio of SO_3/TEP as a degree of sulfonation which is hard to be controlled. Moreover, 1,2-dichloroethane solvent used in this synthesis is harmful to health. The synthesis process for preparing sulfonated polyethersulfone (PES-SO_3H) via Reaction (2) shown below was reported in US Patent [15].



(2)

US Patent method of synthesis of sulfonated polyethersufone polymer.

It stated that PES was hard to be sulfonated, this synthesis process also involved using solvent

1,2-dichloroethane which is not desirable for nowadays synthesis work.

In this work, we report a simple and efficient method of synthesizing sulfonated polyethersulfone polymer with various degrees of sulfonation. The yield on sulfonation reaction of polyethersulfone polymer was close to 100% due to the replacement of H-atom in PES by the heavier $–SO_3H$ group. A series of nine UF membranes, containing various amounts of SPES and PS, was fabricated via phase inversion method, characterizations of these hydrophilic and negative charged UF membranes were performed. Effect of the synthetic gray water pH on fouling of these membranes was evaluated.

2. Experimental

2.1. Materials

Polyethersulfone (GASFONE 3000P) was obtained from Solvay, USA.

Polysulfone (P3500) was purchased from AMICO, USA.

The above polymers were dried at 110˚C for 3 h and then stored in an air-tight container.

Crane fabric 414 (0.01 cm in thickness) was used as the support for all of the membrane fabrications.

Reagent grades of concentrated sulfuric acid (98%), sodium hydroxide, hydrochloric acid, and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich Chemicals, USA. and were used without further treatment.

Synthetic gray water (prepared in our laboratory).

2.2. Equipment

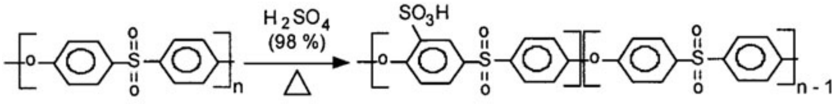
SEM: TESCAN Model VEGA 3.

AFM: Agilent Technology (Molecular Imaging) SPM 5100.

FTIR: Perkin Elmer 400 FT-IR Spectrometer with ATR.

2.3. Sulfonation of polyethersulfone

In this work, a simple method of synthesizing sulfonated polyethersulfone with high yield was developed; in this new method, SPES with different degrees of sulfonation were prepared according to the following reaction:



Synthesis of Sufonated Polyethersulfone

The sulfonation of polyethersulfone was carried out by adding 253.3 g of dried polyethersulfone into a large Erlenmeyer flask containing 3,040 g of concentrated sulfuric acid (98%). The mixture was stirred gently at room temperature for 48 h to produce a homogeneous PES/sulfuric acid solution; at this time, a small weighed amount of sample of PES/sulfuric acid solution was removed for analysis of sulfonation of PES at room temperature and the rest of the PES/sulfuric acid homogeneous solution was heated rapidly to 95˚C. At elevated temperature, the concentrated sulfuric acid decomposes to produce SO_3(g), the SO_3(g) reacts with the dissolved PES to form SPES-H^+. Quantized amount of samples of the reacting solutions was removed from the reaction flask for sulfonation analysis at time of 0.5, 1.0, 2.0, and 3.0 h of heating at 95˚C. After the collected samples were cooled to room temperature, the sulfonated polyethersulfone was recovered by pouring the collected sample solution into cold deionized water; the precipitate of the sulfonated polyethersulfone was washed with plenty of deionized water to remove the free sulfuric acid and dried to a constant weight at 100˚C. The degrees of sulfonation of SPES-H^+ were determined by dissolving a quantized amount of SPES-H^+ in a measured amount of mixed solvent containing 90% 1-methyl-2-pyrrolidinone and 10% of water, three drops of 0.1% phenolphthalein indicator solution were added into this solution before titrating it with a dilute standardized NaOH aqueous solution. The ATR-FTIR spectra of the polyethersulfone and the synthesized sulfonated polyethersulfone are shown in Fig. 1. The degrees of sulfonation of these sulfonated polyethersulfone samples are tabulated in Table 1.

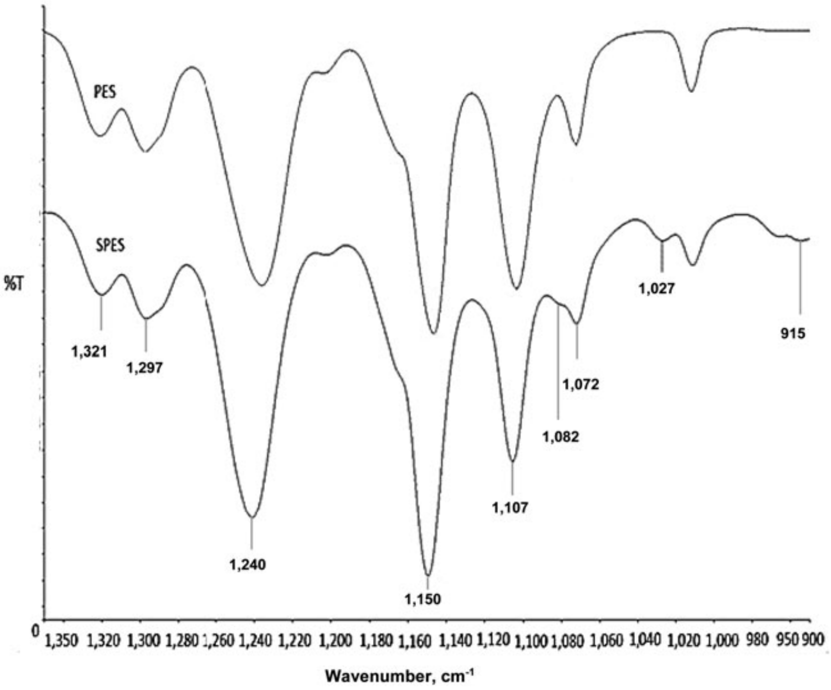


Fig. 1. FTIR spectra of polyethersulfone and synthesized sulfonated polyethersulfone.

Table 1
Dependence of % sulfonated product and degree of sulfonation of polyethersulfone on reaction time

Reaction time (h)	Reaction temperature (℃)	Yield in weight (%)[a]	Degree of sulfonation (SPES:PES)
48	25	99.6	1:19.7
0.5	95	106.0	1:14.3
1.0	95	97.9	1:7.1
2.0	95	97.8	1:4.9
3.0	95	103.2	1:3.4

[a] The products were washed with plenty of distilled water before blending with a blender. The polymer–water slurry was then filtered with a fine filter paper and washed with distilled water until the filtrate reached pH ~6. The filtered products were then dried at 100℃ for 6 h to constant weights.

2.4. Fabrication of hydrophilic and negatively charged ultrafiltration membranes using sulfonated polyethersulfone/polysulfone polymers

In hydrophilic UF membrane fabrication, it is accustom to blend a few percentage of hydrophilic polymer with a major component hydrophobic polymer to produce a mechanically strong and yet hydrophilic membrane. Five sample solutions were collected from PES/H_2SO_4 reactor for degree of sulfonation analysis: one at 48 h at 25℃ and four at 95℃ at reaction times of 0.5, 1.0, 2.0, and 3.0 h. In this work, the degree of sulfonation of $1/x$ means that for every one unit of PES is sulfonated, there are x units of PEI not sulfonated. The degrees of sulfonation of these five reaction samples were calculated from the base–acid titration method; they are listed in Table 1. The quantity of SPES-H with degree of sulfonation of 1/4.9 was the largest sulfonated polymer sample collected during the synthesis process; therefore, this SPES-H was chosen to blend with PS to fabricate 9 FL-Series membranes.

2.4.1. Preparation of membrane casting solutions

Nine membranes were fabricated via phase inversion method using a continuous membrane casting

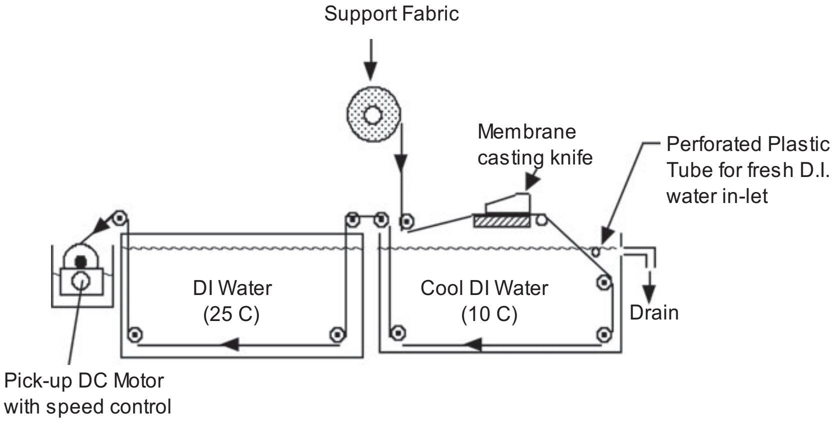


Fig. 2. Drawing of continuous membrane casting machine via phase inversion method.

Table 2
The compositions of nine FL-Series membranes casting solutions

Increasing the solid content in membrane casting solution

Increasing hydrophilic polymer in membrane casting solution

FL-1 PSf = 18 % SPES = 0 % NMP = 82 %	**FL-2** PSf = 20 % SPES = 0 % NMP = 80 %	**FL-3** PSf = 22 % SPES = 0 % NMP = 78 %
FL-4 PSf = 15 % SPES = 3 % NMP = 82 %	**FL-5** PSf = 17 % SPES =3 % NMP = 80 %	**FL-6** PSf = 19 % SPES = 3 % NMP = 78 %
FL-7 PSf = 12 % SPES = 6 % NMP = 82 %	**FL-8** PSf = 14 % SPES = 6 % NMP = 80 %	**FL-9** PSf = 16 % SPES = 6 % NMP = 78 %

Notes: PSf: Polysulfone; SPES: sulfonated polyethersulfone; NMP: N-methyl-2-pyrrolidone.

machine shown in Fig. 2. The casting solutions were prepared by mixing the appropriated amount of polysulfone, synthesized sulfonated polyethersulfone (S-5) and 1-methyl-2-pyrrolidinone (NMP) in glass bottles. The compositions of these membranes casting solutions are tabulated in Table 2. After obtaining homogeneous polymer solutions by tumbling the above mixture solutions in glass bottles overnight, the polymer solutions were then degassed by pulling vacuum at −85 kPa pressure until no gas bubble was formed in the solution, the purpose of the removal of air trapped inside the membrane casting solution is to avoid the pin-hole formation at the porous membrane surface during the phase inversion process in quenching bath.

2.4.2. Fabrication of 9 FL-Series membranes

A laboratory continuous membrane casting machine (Fig. 2) was used to cast all 9 FL-Series Membranes via phase inversion method. 25°C DI water was used as the coagulating media for all membrane casting works. The membrane casting solution was doctored with a casting knife, set at 0.18 mm gap, onto

Table 3
Characterization of nine FL-Series membranes

Increasing the solid content in membrane casting solution

Increasing hydrophilic polymer in membrane casting solution

FL-1 PSf = 18 % SPES = 0 % NMP = 82 % **A-value** = 758 x10^{-5} **Water uptake** = 71.3 % **Surface charge density** = 0 70 kDa< **MWCO**<162 kDa	**FL-2** PSf = 20 % SPES = 0 % NMP = 80 % **A -value** = 359 x10^{-5} **Water uptake** = 80.7 % **Surface charge density** = 0 40 kDa< **MWCO**<70 kDa	**FL-3** PSf = 22 % SPES = 0 % NMP = 78 % **A-Value** = 64x10^{-5} **Water uptake** = 72.8 % **Surface charge density** = 0 40 kDa< **MWCO**<70 kDa
FL-4 PSf = 15 % SPES = 3 % NMP = 82 % **A-value** = 2,668 x10^{-5} **Water uptake** = 78.0 % **Surface charge density** = 1.51 162 kDa< **MWCO**<298 kDa	**FL-5** PSf = 17 % SPES =3 % NMP = 80 % **A-value** = 2,554 x10^{-5} **Water uptake** = 80.9 % **Surface charge density** = 1.58 70 kDa< **MWCO**<162 kDa	**FL-6** PSf = 19 % SPES = 3 % NMP = 78 % **A-value** = 876 x10^{-5} **Water uptake** = 78.7 % **Surface charge density** = 1.36 70 kDa< **MWCO**<162 kDa
FL-7 PSf = 12 % SPES = 6 % NMP = 82 % **A-value** = 3,835 x10^{-5} **Water uptake** = 85.1 % **Surface charge density** = 2.49 162 kDa< **MWCO**<298 kDa	**FL-8** PSf = 14 % SPES = 6 % NMP = 80 % **A-value** = 2,827 x10^{-5} **Water uptake** = 83.9 % **Surface charge density** = 1.88 162 kDa< **MWCO**<298 kDa	**FL-9** PSf = 16 % SPES = 6 % NMP = 78 % **A-value** = 2,007 x10^{-5} **Water uptake** = 82.7 % **Surface charge density** = 2.19 70 kDa< **MWCO**<162 kDa

Notes: *A*-value = g/(cm^2 atm. s); surface charge density = meg/cm^2.

a porous Crane fabric laid flat on a granite plate. The membrane casting speed was set at 0.76 m/min. During the process of membrane casting, fresh deionized water was continuously flushed onto the area of surface where coagulation took place; this was to avoid the accumulation of solvent leached out in that area. After finishing membrane casting, the membrane was immediately removed from the membrane casting machine and rinsed with plenty of deionized water several times in 3 h, the membrane was then placed in nine individual plastic bags filled with deionized water and stored in the refrigerator to retard the bacteria growth.

Characterization of hydrophilic and negatively charged ultrafiltration membranes fabricated from sulfonated polyethersulfone/polysulfone polymers.

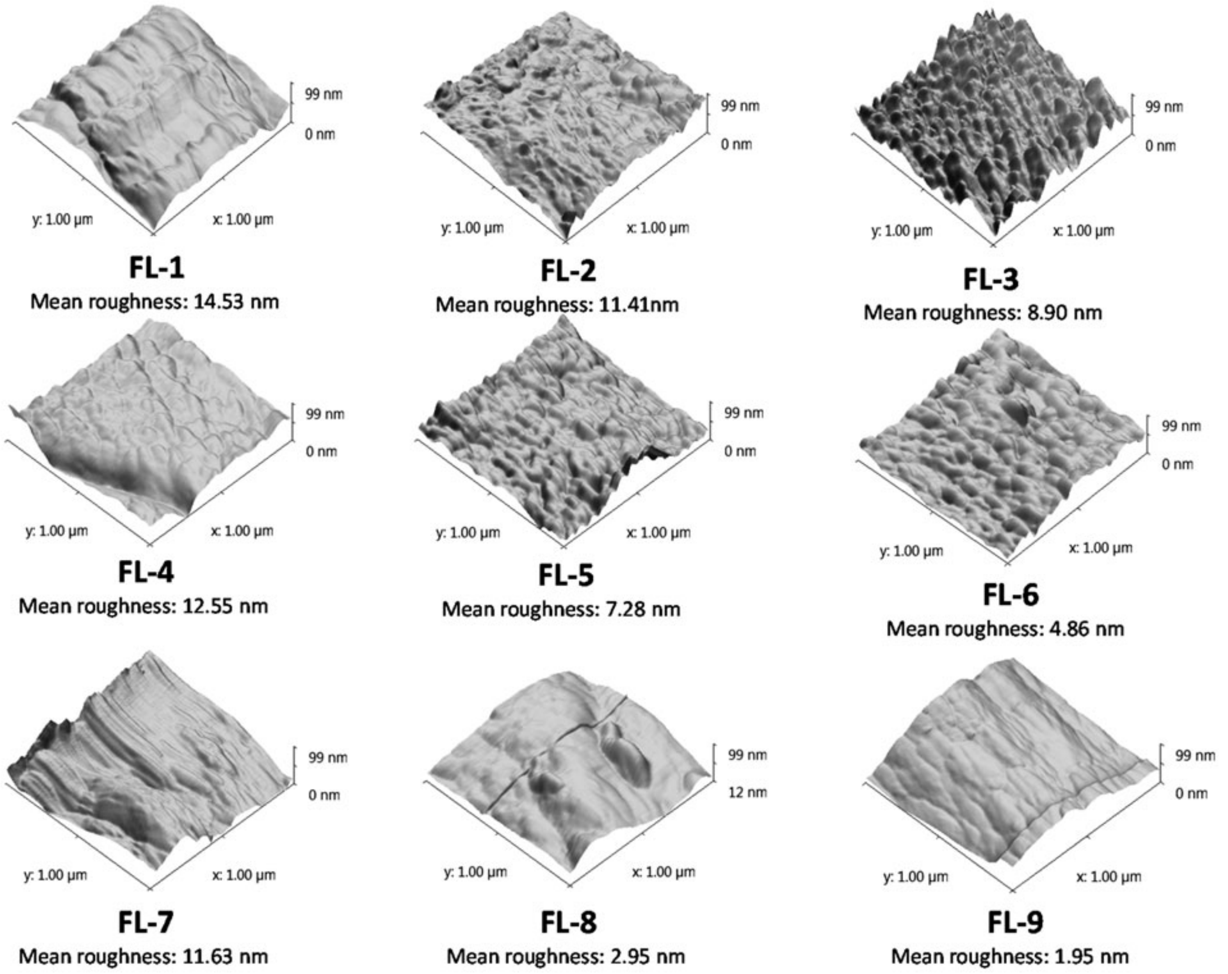
After nine FL membranes were fabricated, they were characterized as follows.

2.5. Pure water permeability determination

The pure water permeability of nine FL-Series membranes was determined with a cross-flow filtration membrane system using distilled water as feed, a membrane coupon of 3.8 × 8.9 cm^2 was cut from 9 FL-Series Membranes; the membrane coupon area within the test cell gasket was determined to be 22.12 cm^2. All pure water permeabilities of nine membranes were done under applied cross-flow pressure of 275.6 kPa. In this work, water permeate fluxes were collected at 15 s after starting the cross-flow filtration operation, the membrane pure water permeability is expressed by "*A*-value" in unit of g/(cm^2 atm. s). The experimental results of *A*-value determination [16] are tabulated in Table 3.

2.6. Water content determination

The nine FL-Series membranes prepared in our laboratory are porous membranes, the water occupies the pore voids, the dam membranes were weighed, then the membrane samples were dried in oven at 100℃ to constant weight, the weight loss due to removal of water from the voids of the membranes were obtained, the percentage of water content of the nine membranes is shown in Table 3.



FL-1
Mean roughness: 14.53 nm

FL-2
Mean roughness: 11.41nm

FL-3
Mean roughness: 8.90 nm

FL-4
Mean roughness: 12.55 nm

FL-5
Mean roughness: 7.28 nm

FL-6
Mean roughness: 4.86 nm

FL-7
Mean roughness: 11.63 nm

FL-8
Mean roughness: 2.95 nm

FL-9
Mean roughness: 1.95 nm

Fig. 3. Atomic force micrographs of nine FL-Series membranes (scanning area = 1.0 µm × 1.0 µm, z = 0–99 nm).

2.7. *Membrane surface charge density determination*

As stated in the synthesis of sulfonated polyethersulfone polymer, the sulfonation reactions of polyethersulfone were carried out in the media of 95°C concentrated sulfuric acid; therefore, the sulfonated polyethersulfone polymer used in membranes of FL-3 to F-9 listed in Table 3 was in –SO_3H. To ensure that all of the sulfonated groups in the polymers used were in –SO_3H form; the test membrane coupons were treated with aqueous HCl (1.0 M) to replace any sodium ions that might be present. The membrane coupons were then rinsed with deionized water until the rinsing water reaches pH 7.0. This membrane was mounted onto a special circular Teflon Ring having an opening area of 0.022 m^2. The water droplets on the membrane surface were removed by paper towel, a 50 mL of standardized NaOH (0.010 N) solution was then poured onto the membrane surface and the contact time was set at 1 min. After this time, the sodium hydroxide solution was poured into a beaker, a measured amount of this solution was immediately titrated with standardized HCl (0.100 N) solution. The negative surface charge density (meq/m^2) of the membrane was determined from the amount of NaOH used to neutralize the counter ion-H^+ at the membrane surface area of 0.022 m^2. The experimental results are shown in Table 3.

2.8. *Molecular-weight-cut-off (MWCO) determination*

A cross-flow membrane filtration test system was used in the determination of the MWCO of 9 FL-Series Membranes, the average molecular weights of dextran 70, 162, 298, and 500 kDa were used. The 1% dextran solution was prepared by dissolving individual dextran in a 0.10 M NaCl solution buffered with potassium phosphate at pH 7; the water used for the make-up of dextran solutions was derived from the

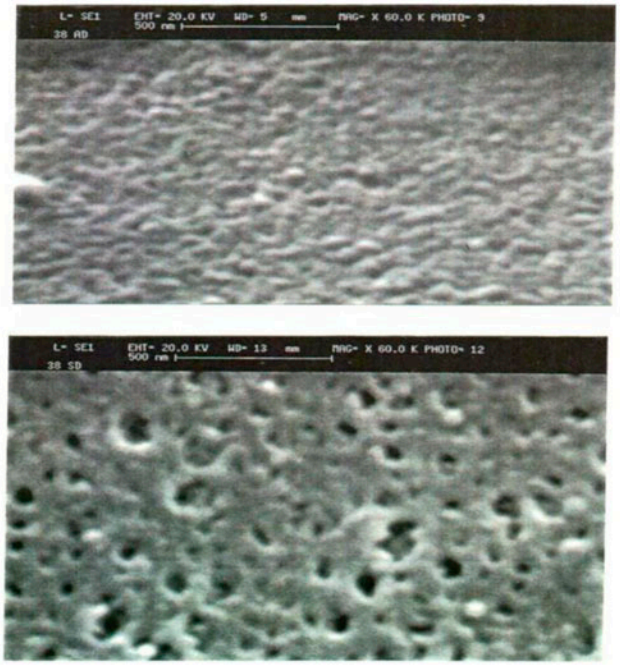


Fig. 4. Scanning electron micrographs of porous polysulfone membranes: upper SEM; membrane dried from wet membrane sample. Lower SEM; solvent exchange-dried membrane sample.

distillation of the deionization water. The MWCO of each membrane was determined by the separation efficiency which is defined as:

$$R = (1 - C_{\mathrm{p}}/C_{\mathrm{f}}) \times 100\% \qquad (1)$$

where C_{p} is the concentration of the dextran present in permeate and C_{f} is the concentration of the dextran in the feed. Test runs were carried out at an applied cross-flow filtration pressure of 275.6 kPa and at 25℃. 1 mL of permeate was collected at 6, 12, and 16 min after the test run was started. The refractive index of permeate was determined at 30 min after the permeate sample was collected. The contents of the dextran in the feed and in the permeate were determined by measuring the refractive index of the standard solutions containing 0 and 1.0% dextran with an Abbey-type Refractometer (0–10%) at 25℃. The average MWCO of the test membrane is defined as the membrane sample having a 90% or better rejection of a given average size dextran in the feed. The results of the average MWCO of the 9 FL-Series Membranes are shown in Table 3.

2.9. Atomic force microscopy (AFM)

In order to preserve the original physical dimensions of the wet membrane surface, the membrane surface morphologies of the wet membranes were characterized by contact mode with a Burleigh AFM; this equipment is equipped with a non-contact/contact head and a 100 μm scanner that was operated at a constant force mode (reference force 5 nN). The wet membrane coupons were attached to a platinum sample holder that was mounted onto the piezo scanner of the AFM. AFM images were acquired at a scan rate of 1.0–2.0 kHz and at an information density of 256 × 256 pixels (area = 1 μm^2). The mean height is given by the average of the individual height determinations within the selected height profile. The AFM of this series membranes is shown in Fig. 3.

2.10. Scanning electron microscopy (SEM)

Method of drying membrane samples for SEM works is prime important. Fig. 4 shows the scanning electron micrographs of the polysulfone membrane

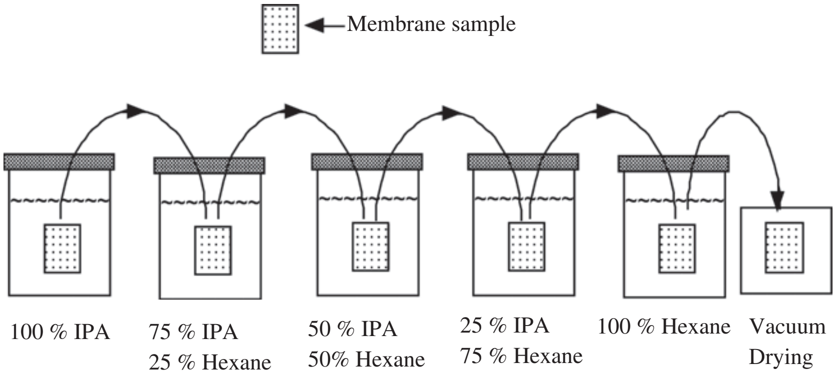


Fig. 5. Schematic process of solvent exchange drying of wet porous polysulfone membrane.

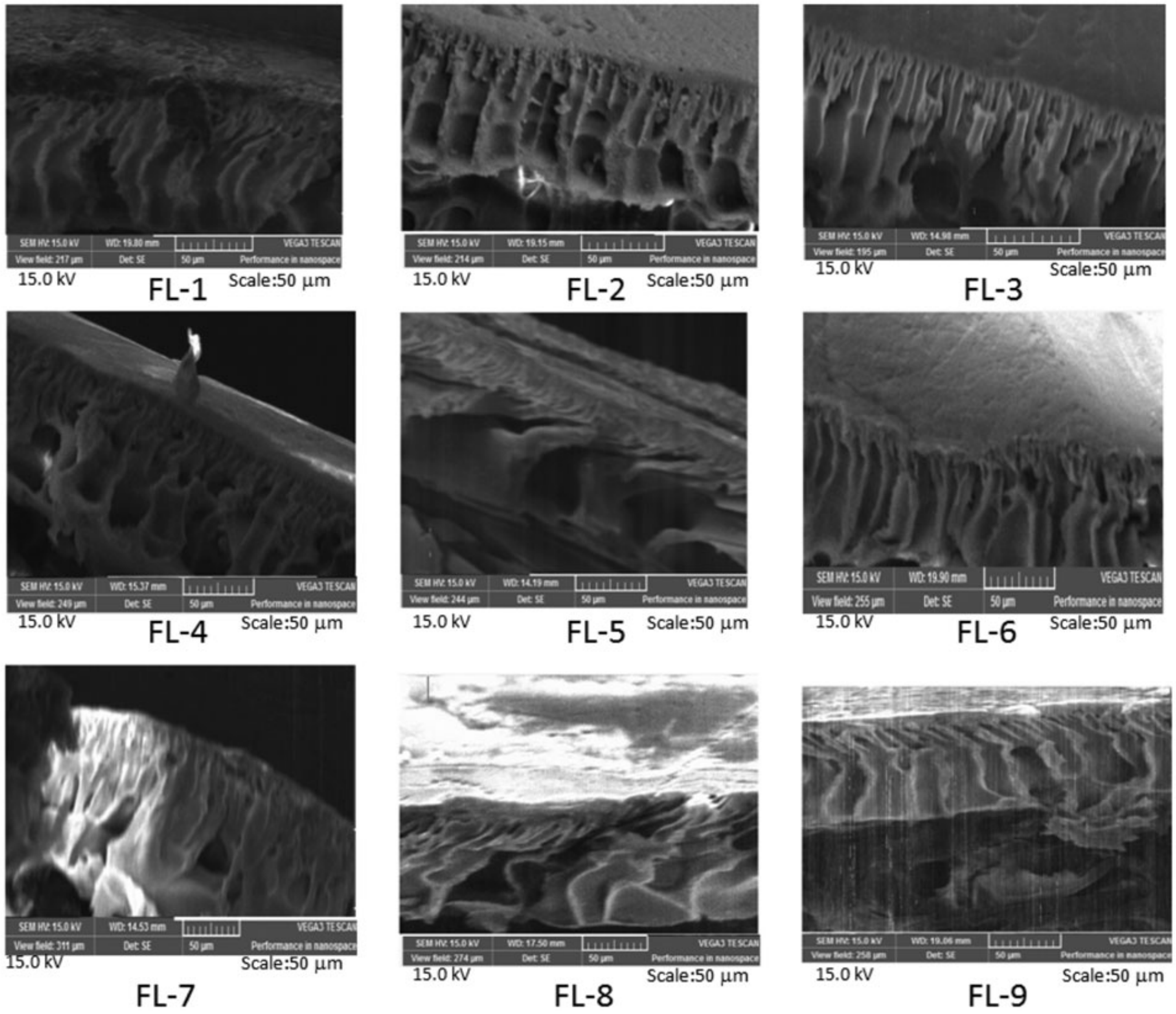


Fig. 6. Scanning electron micrographs of solvent-exchange dried nine FL-Series membranes.

Table 4
Composition of synthetic wastewater used for nine FL-Series membranes fouling tests

Ingredient	Quantity/5 l
Powder detergent (Ariel)	435 g
Canned dog food	10 g
Starch	2 g
Gelatin	750 mg
5%-Ammonium chloride solution	50 mL
Sodium chloride 1.0 M	15 mL
Trisodium phosphate 1.0 M	2.5 mL
Sodium bicarbonate 1.0 M	10 mL

obtained from membrane samples that had gone through air-drying and solvent-exchange-drying. In order to minimize the change of the original physical dimensions of the porous structure of the wet membrane, the water inside the wet membrane sample must be removed by solvent-exchange-drying as illustrated in Fig. 5. In this process, the wet membrane coupon was first soaked in pure isopropyl alcohol for 15 min, after that, this membrane coupon was subsequently soaked in isopropyl alcohol/hexane mixed solutions of 75/25%, 50/50% and 25/75% for 15 min each, finally the membrane sample was soaked in 100% Hexane for 15 min. The hexane inside the membrane sample was then removed by vacuuming in a vacuum chamber for 5 min.

In order to reveal the cross-section structure of the membranes, a solvent-exchange-dried membrane sample was fractured while it was immersed in liquid nitrogen. The fractured membrane samples were sputter-coated with gold (Technic's Hummer 5 Sputter)

Table 5
Parameters of synthetic wastewater

Parameter	Stock wastewater	Diluted sample
Total solids concentration	60,000 mg/L	3,000 mg/L
Conductivity	35.6 mS/cm	5.3 mS/cm
Turbidity	350 FAU	11 FAU
pH	12	10
Total suspend solids	317 mg/L	7 mg/L
COD	>1,650 mg/L	162 mg/L

and then the cross-sectional feature of each membrane was analyzed with a Scanning Electron Microscope (TESCAN Model VEGA 3, at 20 kV). The Scanning Electron Micrographs of 9 FL-Series Membranes are shown in Fig. 6.

Membrane fouling tests using synthetic wastewater feed.

2.11. Preparation of synthetic wastewater for the membrane fouling tests

Synthetic wastewater was prepared simulating domestic wastewater composition, excluding microbiological components. This synthetic sample was prepared by boiling a mixture of ingredients (see Table 4) for 1 h. After the synthetic wastewater was cooled to room temperature, the remaining solid was then filtered off with a filter paper. The quantity of the total dissolved matter in the filtrate was determined by slow drying a 50 g portion of this solution in the oven at 80℃. The dried solid was further dried at ~100℃ to a constant weight and then cooled in the desiccator to room temperature. Finally, the weight of dissolved matter in 50 g solution was determined from the weight of the dried solid, it was determined that the filtered synthetic grey water contained 60,000 ppm of water soluble matter.

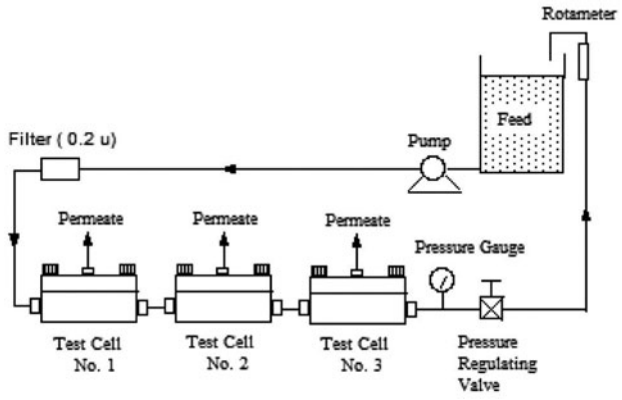


Fig. 7. Cross-flow membrane filtration system used for membrane fouling tests.

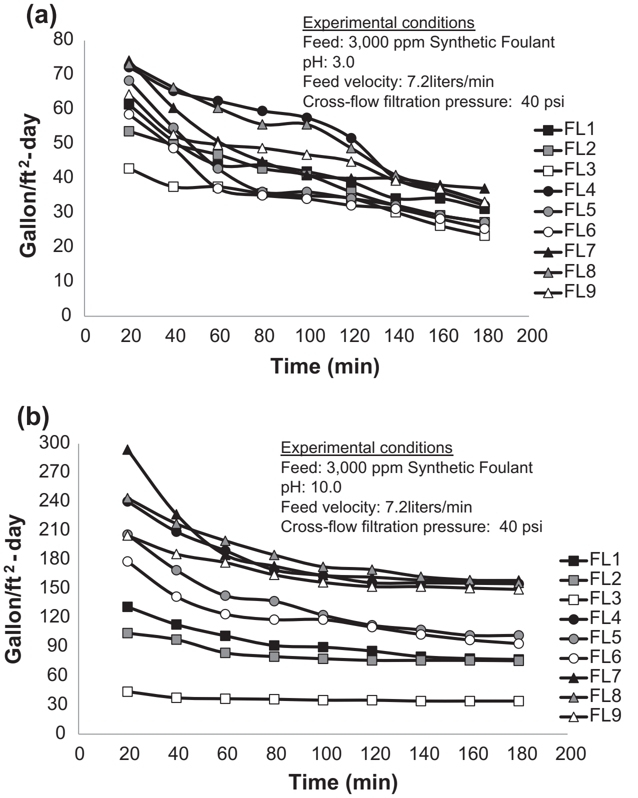


Fig. 8. Dependence of 9 FL-Series membranes fouling on pH of the synthetic wastewater feed: pH 3.0 (a) and pH 10.0 (b).

The wastewater feeds for all of the membrane fouling tests were obtained by diluting this filtered stock synthetic wastewater. Some parameters of this synthetic wastewater are shown in Table 5.

2.12. Membrane fouling tests of 9 FL-Series membranes at pH 3 and pH 10 using feed containing 3,000 ppm of synthetic foulent

The membrane fouling tests of nine FL-Series membranes were carried out with a cross-flow membrane filtration system as shown in Fig. 7. The synthetic wastewater feed containing 3,000 ppm of solids was obtained from diluting the synthetic stock wastewater (Table 5).

Separated test runs were performed at pH 3.0 and pH 10.0, the cross-flow filtration pressure was maintained at 275.6 kPa and the temperature of the feed was kept constant at 25℃ throughout all test runs. Membrane permeate flows were recorded at 20 min interval after each test run was started. The plots of membrane permeate flows against time of the test run is shown in Fig. 8.

3. Results and discussion

3.1. ATR-FTIR spectroscopy characterization

Comparing the ATR-FTIR (Perkin Elmer 400 FT-IR Spectrometer equipped with ATR) spectra of PES and SPES in Fig. 1, the SPES absorption peak appeared as the shoulder at ~1,027 cm^{-1} is the characteristic of the aromatic SO_3H symmetric stretching vibrations as reported by Guan et al. [17]. This absorption peak is absent in the PES spectrum and this confirms that the $–SO_3H$ groups has been introduced into the PES polymer chains during the synthesis process. The rest of signals are commonly present and are described as following: signals at 1,321 and 1,297 cm^{-1} correspond to doublet resulting from asymmetric O=S=O stretching of sulfone group; signal at 1,240 cm^{-1} is for asymmetric C–O–C stretching of aryl ether group, at 1,150 cm^{-1} the signal of symmetric stretching of sulfone groups appears, the peaks at 1,107 and 1,072 cm^{-1} are related to aromatic ring vibrations, signal at 1,082 cm^{-1} is for vibrations of aromatic ring bonded to sulfonate groups, the band at 915 cm^{-1} reflects the substitution of H atom in the aromatic ring by a sulfonic group [18–20].

3.2. Degree of sulfonation

As shown in Table 1, our simple and straight forward method of synthesis of sulfonated polyethersulfone by heating a homogeneous solution of PES/sulfuric acid (98%) at elevated temperature performed well. By this method, a yield of 99.6% with degree of sulfonation of 1:19.7 at 25˚C was reached at 48 h of reaction time; this insignificant degree of sulfonation was improved by raising the temperature of the homogeneous solution of PES/H_2SO_4 (98%) to 95˚C. The experimental results revealed that the degree of sulfonation of PES depends on the period of heating at 95˚C (Table 1). In this report, we define the degree of sulfonation of PES by the ratio of one SPES polymer unit to the number of non-sulfonated PES polymer units; for example, the degree of sulfonation of 1:5 means that for every one polymer unit of PES is sulfonated, there are 5 non-sulfonated PES polymer units. As indicated in Table 1, the sulfonation of PES polymer at 25˚C went very slow, this may be due to the fact that concentrated sulfuric acid is stable at room temperature, there is very little decomposition of the acid to give SO_3(g) which is needed for the process of sulfonation of PES; therefore, the degree of sulfonation of PES was about 1:20 for 48 h at 25˚C. Four sulfonated PES sample solutions were collected at 0.5, 1.0, 2.0, and 3.0 h period of heating at 95˚C, the degrees of sulfonation of these samples were determined to be 1:14.3, 1:7.1, 1:4.9, and 1:3.4, respectively.

3.3. UF membrane preparation

For hydrophilic UF membrane fabrication, it is desirable to blend the sulfonated polymer with regular polysulfone. In this investigation, SPES with the degree of sulfonation of 1:4.9 was chosen to blend with polysulfone polymer to make UF membranes FL-4 to FL-9; the reason for such choice was based on the observation of forming milky suspension in membrane aqueous coagulation bath when membrane casting solution contained SPES with degree of sulfonation of 1:3.4. This indicated that this sulfonated PES is water soluble. SPES of 1:4.9 was not water soluble; also, this SPES contains more $–SO_3H$ per unit weight of PES in comparison of other three water insoluble SPES list in Table 1. In this work, nine FL-Series UF membranes were fabricated to study the effect of inclusion of various amounts of SPES (1:4.9) in these membranes. The compositions of the polymer solutions used to fabricate this series of membranes are listed in Table 2. In this series of membranes, the weight percent of the total polymer solid in the membrane casting solution was varied from 18 to 22 weight percentage, while the weight percent of SPES (1:4.9) was increased from 0 to 6 weight percentage. Our experimental results indicate that the basic membrane characteristics, such as permeation capacity, morphological properties, surface charge density, porosity, and roughness depend on the composition of SPES/PS membrane casting solutions. The trends of these changes are summarized in Table 3; for a given horizontal row of membranes, as the weight percent of the total polymer content in the membrane casting solution increases, the pure water permeability and the average molecular-weight-cut-off of the membranes decrease, this is due to the fact that during the phase inversion process of formation of porous membrane in water, at the moment when polymer solution is in contact with water, polymer precipitates immediately to form a freshly condensed thin film, solvent in the polymer solution is squeezed out rapidly through this freshly condensed membrane thin film; this action produces pore openings at the membrane surface. Higher polymer content in the polymer solution would give stronger freshly condensed polymer thin film; this in turn would yield smaller pore openings at the surface of the membrane. However, for a given column of the membranes, the pure water permeability and the surface charge density of the membranes increase due to the increase in SPES in the resultant membranes. The pore volume in the final coagulated membrane is controlled mainly by the concentration of polymer in the membrane casting solution. Increasing the polymer content leads to higher polymer concentration at the interface, this implies that the volume fraction of polymer increases and, consequently, a lower porosity is expected. Thus, the pore size of the very top layer of the coagulated membrane can be controlled by changing the polymer content in the membrane casting solution.

3.4. Morphological properties of membranes

The AFM of nine FL-Series Membranes shown in Fig. 3 revealed that the membrane surface roughness greatly depend on the composition of the membrane casting solution, for membranes containing PS only as for FL-1, FL-2, and FL-3 membranes; the higher the PS content in the membrane casting solution yielded rougher membrane surface. However, increasing the amount of SPES in the membrane casting solution gave a smoother surface as shown in AFM photos of FL-3, FL-6, and FL-9, the later phenomena may due to the fact that SPES is a hydrophilic polymer while PS is hydrophobic, during the phase inversion coagulation process, SPES condensed together with some water molecules, the resultant membrane swells due to the presence of water molecule adsorbed by SPES, thus inclusion of SPES in the membrane casting solution gave smoother membrane surface.

In the work of recording SEM photos of nine FL-series membranes, care was taken on how to prepare dried membrane samples. The importance of solvent-exchange drying of wet porous polysulfone membrane is demonstrated by the SEMs of air-drying and solvent-exchange drying shown in Fig. 4, the SEM photo of air-dried PS sample does not show clearly the membrane surface pore openings as the solvent-exchanged PS sample does; therefore, in order to retain the physical dimension of wet membrane pore openings, it is necessary to dry the wet membrane via solvent-exchange process as illustrated in Fig. 5. As shown in Fig. 6, the cross-sectional SEM of FL-1, FL-2, and FL-3 reveal that without addition of SPES, the increase PS polymer content in membrane casting solution yielded finger-like substrate under the membrane surface after the polymer solution coagulated in deionized water, this may due to the fact that NMP solvent might be forced quickly out of the freshly gelled PS polymer layer during the phase inversion process. However, at constant total polymer weight percentage such as FL-3, FL-6, and FL-9 in the membrane casting solution, the increase in the sulfonated polyethersulfone content increase the void size of the finger structure under the membrane surface.

3.5. Fouling resistance of membranes

In this work, extensive membrane fouling test runs at 275.6 kPa cross-flow filtration pressure and at 25˚C were performed to investigate the dependence of nine FL-Series Membranes fouling on pH of the feed containing 3,000 ppm of synthetic foulant (Table 4). The plots of membrane permeate flow vs. test run time are shown in Fig. 8 (a) pH 3.0 and (b) pH 10.0, these plots clearly reveal two valuable information about these 9 FL-Series Membranes towards the pH of the feed: (1) at pH 3.0, the membrane permeate flows continue to decrease due to the fouling by the added foulant in the feed, yet at pH 10.0, the membrane permeate flows became constant after ~160 min of cross-flow filtration operation and (2) at pH 10.0, membranes made from higher percentage of SPES tend to have higher permeate flows for the entire fouling test run. At higher percentage SPES, the membrane surface is more hydrophilic, the foulant cannot settle well at the highly hydrophilic surface during the cross-flow filtration operation. This same series of membranes suffer faster fouling when tests were done at pH 3.0 feed, this may due to the fact that at pH 3.0, most of the sulfonated groups in SPES/PS membrane would stay as $-SO_3H$, the membrane surface may bear very little negative surface charge, thus the membrane surfaces are hydrophobic in nature, foulants, like protein and emulsified oil, would likely be adsorbed at hydrophobic membrane surface. However, at pH 10.0, the sulfonated groups in SPES/PS membrane mainly stay as $-SO_3^-$, the counter ions were Na^+ (aq) and they are mobile, since water molecule is a dipole molecule, $-SO_3^-$ adsorbs H_2O molecules, thus the membrane surface becomes hydrophilic, foulant has much less tendency to settle at hydrophilic membrane surface during the cross-flow filtration operation, this would slow down the membrane fouling. In a close look at the cross-flow filtration fouling test runs for membranes FL1 and FL7 at pH 3 and pH 10 (Fig. 8), it revealed that membrane (FL1), contains no SPES polymer, tended to continue to foul with time, but fouling of membrane containing SPES (FL7) was leveled off and became more constant even after three hours of fouling test run.

4. Conclusions

In this work, a simple and relatively economical method of synthesis of sulfonated polyethersulfone polymer was developed and evaluated in our laboratory. Simplicity of our method to produce SPES is related to the use of less reagents and not so critical reaction conditions. This entire research works were done only using common laboratory glassware with no complex purification steps needed. The yields of SPES were determined to be close to 100% due to the replacement H-atom in PES by $-SO_3^-$ group during the sulfonation reaction. The degree of sulfonation of polyethersulfone polymer was found to depend on the time of heating at 95˚C. For example, the degree of sulfonation of 1:4.9 SPES was achieved with 97.8% yield by simply heating the PES/H_2SO_4 (98%) homogeneous polymer solution at 90˚C for 2 h. In order to demonstrate the usefulness of our synthesized SPES to wastewater treatment process, nine FL-Series Membranes were fabricated using various amount of SPES blended with PS; these membranes were then subjected to fouling tests at 275.6 kPa cross-flow filtration pressure and using synthetic gray water feed containing mostly protein and emulsified oil. Experimental results of membrane fouling tests clearly demonstrated that SPES/PS membranes suffer less fouling when fouling tests were done at pH 10.0 feed; therefore, our method of synthesis SPES polymer may find use in the domestic and the industrial wastewater treatment membrane manufacturing industries.

Acknowledgments

The authors would like to take this opportunity to thank CONACYT for the fellowship support for M.C. Fernando Javier Lopez doctoral study and the Direccion General de Educacion Superior Tecnologica for funding this investigation under the project number 4373.11-P (Convocatoria Cientifica y Tecnologica 2011).

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