

Effects of Preparation Conditions on the Surface Modification and Performance of Polyethersulfone Ultrafiltration Membranes

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ABSTRACT: The impact that some membrane preparation steps had on ultrafiltration (UF) membrane characteristics and performance was studied. Polyethersulfone (PES) was employed as base polymer, while *N*-methyl pyrrolidone (NMP) was used as a solvent, and polyvinylpyrrolidone (PVP) was used as a nonsolvent pore-forming additive. The manufacturing variables studied were solvent evaporation time and membrane surface modification, using a fluorine-based copolymer referred to as surface-modifying macromolecule (SMM). The flat sheet membranes, prepared via phase inversion, were characterized using solute transport data, X-ray photoelectron spectroscopy (XPS), and contact angle measurements. Membrane performance was evaluated via filtration test protocol that included a 6-day filtration of concentrated river water. The flux reduction with

time was modeled using single and dual mechanisms of fouling. The pore blockage/cake filtration model described better the behavior of the permeation rate along the experiments. Increasing the solvent evaporation time decreased the size of the pores and the permeation rate. However, it did not significantly affect the removal of the organic compounds naturally present in the river water used as feed. XPS and contact angle measurements proved that the short evaporation periods did not allow enough SMM migration to the surface to provoke a significant effect on the membrane performance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2978–2988, 2006

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INTRODUCTION

In the last few years the use of membrane technology in drinking water treatment has increased exponentially. Nevertheless, one of the limitations of these processes is the susceptibility of the membranes to become fouled. Membrane fouling is the decay in permeate flux with time and is caused by specific physical and/or chemical interactions between the membrane and the components of the feed stream.¹ Therefore, the strength of these interactions will determine the rate and extent of fouling. Membrane foulants not only decrease the water productivity but also alter the membrane selectivity.

Mechanisms leading to membrane fouling have been described by different physicochemical phenomena. In his study, Hermia² described four different fouling mechanisms, according to their physical causes: complete blocking of the pores (pore plug-

ging); intermediate blocking or long-term adsorption; cake filtration or boundary layer resistance; and standard blocking or direct adsorption (internal adsorption). In a filtration experiment, it is reasonable to expect a complex succession of these fouling mechanisms.³ The first three fouling mechanisms may occur when the membrane retains the solute, whereas the last one can appear when the solute molecules are smaller than the membrane pores.⁴ Complete blocking occurs when each particle arriving to the membrane causes blocking of some pore or pores with no superposition of particles. Intermediate blocking takes place when each particle settles on a previously arrived particle that already blocks some pores or directly blocks some membrane area. In contrast, during cake filtration, each particle locates on (or attaches to) other already arrived particles that already block some pores and there is no room for the newly arrived particle to directly obstruct some membrane area. When each particle arriving to the membrane is deposited into the internal pore walls, leading to a decrease in the pore volume, the mechanism is called standard blocking.³

Some of the existing approaches used to control membrane fouling include the selection of a membrane material, pretreatment of the feed solution, ef-

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fective cleaning regimes, module design, and process conditions.⁵⁻⁷ Since membrane-solute interactions determine the nature and extent of membrane fouling, the surface of the membrane material can be modified in order to minimize the attractive interactions between the solutes present in the water being treated and the membrane. The use of fluorinated-based surface-modifying macromolecules (SMMs) compatible with polyethersulfone (PES) allows the surface modification of PES membranes, using a single-step preparation procedure. Although it is widely accepted that hydrophobic surfaces foul more easily than hydrophilic surfaces, it is also believed that characteristics associated with the fluorinated-based compounds used in the SMM synthesis (i.e., surface lubrication and low surface free energy) will cause the PES/SMM membranes to exhibit low adhesive energy and consequently have more fouling resistant characteristics.^{8,9}

During membrane manufacturing, several preparation variables can be adjusted to control the membranes characteristics, and ultimately the performance of the membrane. The effect that several conditions had on the performance of a PES ultrafiltration membrane during the treatment of a surface water is presented in Mosqueda-Jimenez et al.^{8,10} Membranes prepared containing 18 wt % PES and the SMM prepared with methylene bis-*p*-phenyl diisocyanate (MDI), polypropylene diol (PPO) as polyol, and the fluoroalcohol BA-L, maximized the total organic carbon (TOC) removal and final flux. Besides having a higher permeation rate, membranes with PVP/PES ratio of 1:3 had the additional advantage of better casting properties (i.e., more viscous solution) and were mechanically stronger. Nevertheless, when PVP was present in the casting solution, the addition of the SMM showed no significant effect on their performance. Previous kinetic studies of the SMM migration to the surface showed that the solvent evaporation time was an important factor in the preparation of surface modified membranes. After a lag time of at least 10 min, depending on different variables, a complete SMM migration was observed.¹¹ Therefore, the aim of this project was to study the effect that the manufacturing conditions (i.e., solvent evaporation time and surface modification) had on the characteristics, performance, and fouling of ultrafiltration PES membranes.

EXPERIMENTAL METHODS AND ANALYSIS

Materials

The base polymer used in the membrane preparation was polyethersulfone (PES, 4100P), supplied by ICI Advanced Materials (Billingham, Cleveland, England). *N*-Methyl pyrrolidone (NMP), used as a sol-

vent, and polyvinylpyrrolidone (PVP powder with an average molecular weight of 10,000 Da), used as a nonsolvent pore-forming additive, were both obtained from Aldrich Chemical Company (Milwaukee, WI). The SMM was synthesized according to the methodology outlined by Ho et al.¹² It has an amphiphatic structure that consists of a polyurethane chain end-capped with two fluorine-based (low-polarity) polymer chains.¹¹ Reagent-grade water was prepared with a Milli-Q Water System by Millipore (Bedford, MA), using mixed bed ion exchange resins, synthetic activated carbon, organic scavengers, and membranes. This ultrapure water was referred to as Milli-Q water.

The test water used was concentrated Ottawa River water (CORW). Raw water was collected at the intake of the Britannia Water Treatment Plant (Ottawa, Canada) and concentrated fivefold via a portable Reverse Osmosis System by RealSoft (Norcross, GA), which included a prefilter and a FT30 composite membrane (Filmtec Membranes, Midland, MI).

Membrane preparation

Membranes were prepared using the phase inversion technique as described by Matsuura.¹³ Casting solutions were prepared using four different ingredients: PES, PVP, SMM, and NMP in concentrations of 18, 6, 1.5, and 74.5 wt %, respectively. Control membranes were prepared without SMM; therefore, for these membranes the NMP concentration was 76%. Filtered homogeneous solutions were degassed and cast onto a glass plate at room temperature (wet thickness = 0.25 mm). For those membranes prepared using a solvent evaporation period, the glass plate was placed inside an oven at 95°C during this period. After the solvent evaporation period (or immediately after the membrane film was cast in the case of the membranes without solvent evaporation), the glass plate was immersed into ice-water at 4°C, where membranes harden and eventually peeled off from the plate. Details on membrane preparation are presented elsewhere.¹⁴ Membranes were cut from flat sheets into 20-cm² coupons and stored at 5°C in Milli-Q water until they were tested.

Analysis

TOC concentrations were measured using a total carbon analyzer (Model DC-180, Dohrman, Santa Clara, CA), as described in the standard method 5310 C.¹⁵ UV absorbance was measured at 254 nm, using a spectrophotometer (DU-40; Beckman Instruments, Irvine, CA) with a 1-cm quartz cell. In this analysis, Milli-Q water was used as a blank.

The surface of the membrane coupons was analyzed using a Kratos Axis X-ray photoelectron spectrometer (Kratos, Manchester, UK). Each randomly-taken sam-

ple was analyzed at take-off angles of 0° and 60°, which corresponded to X-ray penetration depths of 6.3 and 3.15 nm, respectively.¹¹ The XPS analyses were conducted at the Institute for Chemical Process and Environmental Technology (National Research Council of Canada).

Contact angle was determined using the sessile drop technique with a 20- μ L droplet of distilled water and a standard goniometer apparatus (Ramé-Hart, model 100, Mountain Lakes, NJ). Advancing and receding angles were measured at least 10 times, and the contact angle hysteresis was calculated as the difference between the two of them.

Testing protocol

The performance of fresh membranes was evaluated using CORW in a six-cell in-series system, where membranes were randomly located.¹⁶ The existence of a possible cell effect or cell order effect within the cells in-series was discarded using an analysis of variance (ANOVA) test of a Greco–Latin square type of design.¹⁷

Prior to each run, the membranes were subjected to a precompaction protocol. This precompaction protocol consisted of installing the new membrane coupons in the test cells and filtering Milli-Q through each new coupon at 620 kPa (90 psi g) for 52 h. Then the pure water permeation rate (PWP) was monitored during a period of 50 h at 345 kPa gauge (50 psi g). Later, the UF membranes were characterized on the basis of solute transport data of probe solutes (polyethylene glycols (PEG) and polyethylene oxides (PEO) with different molecular weights).¹⁸ Finally, the permeation rate of the CORW at a feed flow rate of 1.1 L/min and an operating pressure of 345 kPa gauge (50 psig) was measured at different intervals during 6 days of continuous operation. Feed and permeate samples were collected during this testing phase to assess the TOC removal. The amount of natural organic matter (NOM) accumulated on top of the individual membranes at the end of the 6-day test (referred to as NOM deposition) was measured using the technique described by Hong and Elimelech.¹⁹

Modeling

To study the mechanisms leading to membrane fouling when analyzing experimental data, the common practice consists of assuming that only one of the fouling mechanisms takes place, frequently it is standard blocking or cake filtration.³ Hermia² developed a power-law equation for dead-end filtration under constant pressure with the general form that relates the change of the permeate flux with the time of operation:

$$\frac{dJ}{dt} = kJ(J)^{2-n} \quad (1)$$

where k is a fouling coefficient and n is a dimensionless filtration constant, which depends on the type of filtration and has values of 0, 1, 1.5, and 2, for cake filtration, intermediate blocking, standard blocking, and complete blocking, respectively.

To consider the cross-flow filtration, Field et al.²⁰ used the following equation:

$$\frac{dJ}{dt} = k(J - J^*)(J)^{2-n} \quad (2)$$

where J^* is a critical flux and n can take the same values as explained above. Field et al.²⁰ physically defined the critical flux as that flux below which fouling is not observed.

Kilduff et al.⁷ modified a model originally developed for dead-end filtration by Ho and Zydney²¹ that combines both mechanisms pore blockage and cake filtration. Kilduff et al.⁷ incorporated a back transport term to consider cross-flow applications.

$$A_{\text{open}} = A_T \exp \left[-\alpha C_b t \left(\frac{\Delta P}{\mu R_m} - J^* \right) \right] \quad (3)$$

where A_T ($= A_{\text{open}} + A_{\text{blocked}}$) is the nominal membrane area (m^2); A_{open} , the area of unblocked or clean membrane (m^2); A_{blocked} , the area of membrane blocked by foulant (m^2); α , the pore blockage parameter (m^2/kg); C_b , the bulk concentration of solute (kg/m^3); ΔP , the applied pressure (Pa); μ , the solution viscosity [$\text{kg}/(\text{m s})$]; R_m is the membrane resistance (m^{-1}).

The following equation for the resistance of the cake is integrated analytically from $R_{c,0}$ to R_c :

$$\frac{dR_c}{dt} = \alpha_c (A_T - A_{\text{open}}) C_b \left(\frac{\Delta P}{\mu (R_m + R_c)} - J^* \right) \quad (4)$$

where α_c is the specific resistance of the cake ($\text{m}^{-1} \text{kg}^{-1}$) and $R_{c,0}$ is the resistance of the initial deposit (m^{-1}).

Finally the modeled flux is calculated with the equation:

$$J_T = \frac{\Delta P A_{\text{open}}}{\mu R_m} + \frac{\Delta P (A_T - A_{\text{open}})}{\mu (R_m + R_c)} \quad (5)$$

In this paper, Field's²⁰ and Kilduff's⁷ models were used to model the behavior of the flux reduction with time for a single or combined mechanism, respectively. Calculations of the parameters (k , n , J^* , α , α_c , $R_{c,0}$) were performed using E-Z Solve (IntelliPro, Piscataway, NJ distributed by John Wiley and Sons) and

TABLE I
Membrane Characteristics

Evap. time (min)	μ_p (nm)	σ_p	MWCO (kD)
No SMM			
0	4.2	2.1	36
3	3	2	22
4	2.6	2.3	21
5	1.6	2.2	8
SMM			
0	3.5	2.2	34
3	2.3	2.4	21
4	1.5	2.5	7
5	1.9	2.5	16

μ_p , geometric mean pore size; σ_p , geometric standard deviation about the mean pore size; MWCO, molecular weight cut-off.

the Optimization Toolbox 2.0 with MATLAB 6.5 (MathWorks, Natick, MA).

RESULTS AND DISCUSSION

Results from a previous study⁸ showed that the effect of the surface modification in the membrane performance was overshadowed by the effect of the pore-former PVP in the casting solution. Therefore, a lack of sufficient time for the SMM to migrate to the membrane surface was suspected. According to Suk et al.¹¹ a longer solvent evaporation time would favor the SMM migration. Characteristics and performance of membranes prepared with solvent evaporation times of 3, 4, and 5 min were compared with control membranes prepared without solvent evaporation time. Membranes prepared using evaporation times longer than 5 min were transparent and were very sensitive to dehydration, shrank very easily as soon as they started to dry, and were impermeable to water at low transmembrane pressures. Results presented in this paper correspond to an average of two to four repeats, tested randomly during three different runs.

Membrane characterization

Results from the solute transport tests using PEG solutions as probes were as follows. A consistent reduction in MWCO and mean pore size (μ_p) was observed when increasing the solvent evaporation time, for both membranes prepared with and without SMM (Table I), with exception of the membrane prepared with SMM and 4-min evaporation time. This trend is similar to those observed in previous studies^{14,22} that have shown a decrease on the mean pore size with a longer solvent evaporation period because of the densification of the surface layer. The effect of the surface modification on the pore size distribution is not significant. The same observation was made when mem-

branes prepared with 18 wt % PES were prepared with and without PVP in previous studies.^{8,14} Only in the case of more porous membranes prepared with 12 wt % PES, the effect of the surface modification on the pore size was important. However, these membranes were brittle and hard to handle.¹⁰

Membrane performance parameters

Pure water permeation rate

As the membrane pore size decreased, the pure water permeation decreased upon the increase of solvent evaporation time. In the case of surface modified membranes this change was very drastic when evaporation time was increased from 3 to 4 min (Fig. 1). This effect of evaporation time on the water permeation has been observed in numerous studies, including Pei et al.,²³ who tested polysulfone membranes, Bindal et al.,²⁴ for polyetheramide hydrazide polymer with a novel solvent exchange technique, and Jian et al.,²⁵ with a poly(phtalazine ether sulfone ketone) membrane. Although the base polymer and the membrane preparation techniques were different, all of them observed a decrease on the water permeation rate with an increase of the solvent evaporation period.

TOC removal

After the determination of the PWP, Milli-Q water was substituted by CORW to determine the performance of the membrane when using a natural surface water with high humic material content [TOC = 28 mg/L, SUVA = 3.9 m⁻¹ mg⁻¹ L (SUVA = UV absorbance at 254 nm (1-cm cell)/DOC) and color = 180 cu]. Alka-

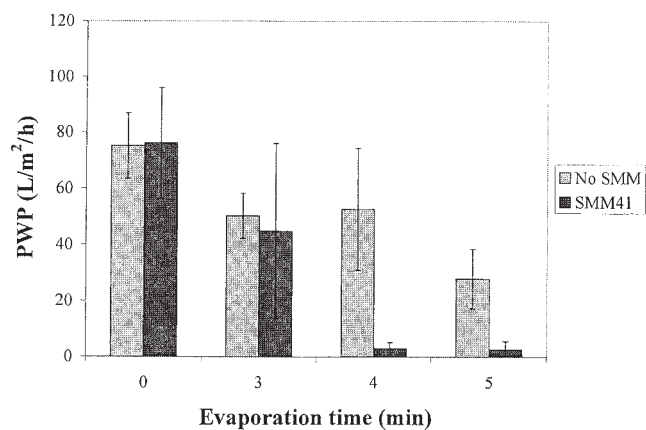


Figure 1 Pure water permeation rate (PWP) of surface-modified and unmodified membranes prepared with different evaporation times. Casting solution: PES = 18 wt %, PVP = 6 wt %, SMM41 = 1.5 wt % (In the case of the surface-modified membranes).

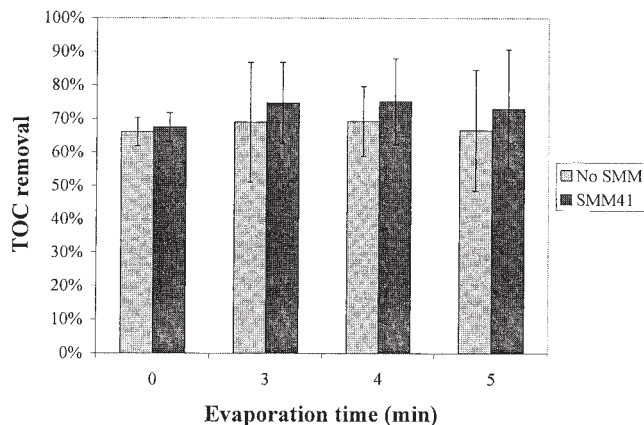


Figure 2 TOC removal for surface modified and unmodified membranes prepared with different evaporation times. Casting solution: PES = 18 wt %, PVP = 6 wt %, SMM41 = 1.5 wt % (In the case of the surface-modified membranes).

linity and hardness of this water were 120 and 153 mg/L as CaCO_3 , respectively.

TOC removal, using the different feed solutions, was calculated by the following equation:

$$\text{TOC removal}(t) = 100 \left(1 - \frac{C_{p(t)}}{C_f} \right) \quad (6)$$

where $C_{p(t)}$ is the permeate concentration at time t and C_f is the feed concentration (mass/volume).

The average TOC removals (at the plateau) were statistically the same for all membranes tested (Fig. 2), independent of the conditions used in the membrane preparation (surface modification and evaporation time). Even for membranes prepared using solvent

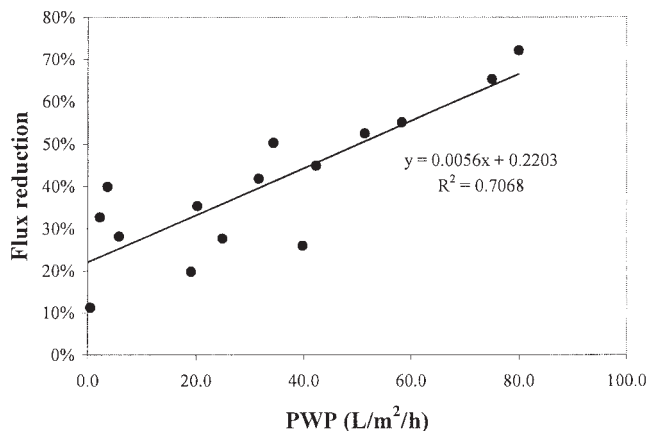


Figure 4 Flux reduction as a function of PWP.

evaporation, which in most cases were slightly tighter, the increase in TOC removal was not statistically significant. This may be an indication of a similar mechanism of TOC removal, which is independent of the membrane surface-modification (i.e., cake layer formation).

Permeation rate

Figure 3 shows the variation of the permeation rate (or permeate flux) during a 6-day test period, using CORW as the feed solution. A continuous decrease of permeation rate was observed. Moreover, it is observed that for membranes prepared with the same evaporation time the control membrane (unmodified) always had a higher permeation rate than the surface-modified membrane.

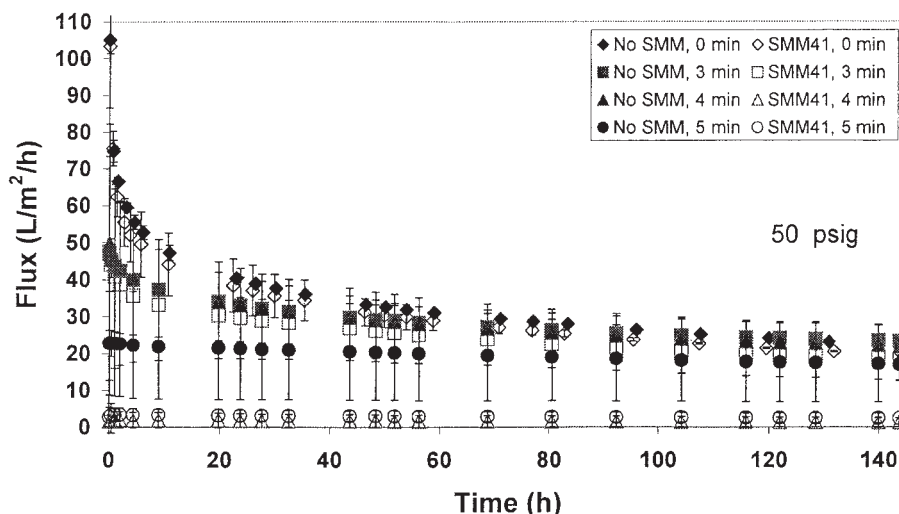


Figure 3 Flux reduction with continuous tests of surface-modified and unmodified membranes prepared with different evaporation times. Casting solution: PES = 18 wt %, PVP = 6 wt %, SMM41 = 1.5 wt % (In the case of the surface-modified membranes). Test water: Concentrated Ottawa River water (CORW).

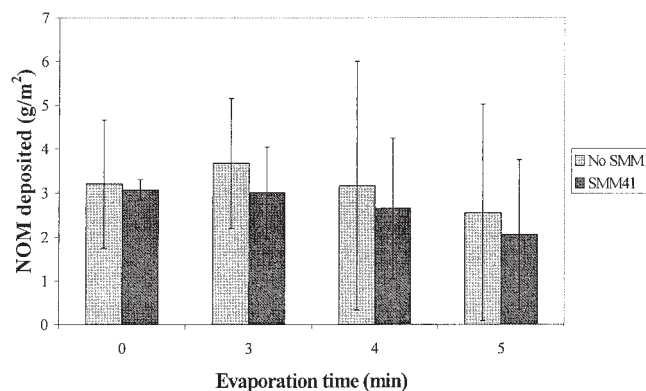


Figure 5 Amount of NOM deposited on the surface-modified and unmodified membranes prepared with different evaporation times. Casting solution: PES = 18 wt %, PVP = 6 wt %, SMM41 = 1.5 wt % (In the case of the surface-modified membranes).

In Figure 4, it is observed that the percent of flux reduction in treating river water is somewhat linearly related to the initial PWP conducted with Milli-Q water. Statistically, 70% of the change of flux reduction for the different membranes tested is related to the PWP. In other words, when the PWP is small at the beginning of the test, the flux reduction is small and *vice versa*.

NOM deposited

The amount of NOM deposited on the membrane surface was measured at the end of the 6-day experiments. Results presented in Figure 5 show a very high variation due to complexity in the measurement of NOM deposited. As mentioned in the methodology, these results correspond to an average of two to four repeats, tested randomly during three different runs. However, a general trend is observed where the surface modified membranes have an average NOM deposition that is lower than that deposited on the surface of the control membranes. Moreover, the average NOM deposition seems to decrease with the solvent evaporation time. It is very possible that the amount of NOM deposited is related to the membrane permeation rate. Hence, membranes with higher permeation rate are subjected to more NOM deposition because more water goes through their pores.^{10,26} Nevertheless, as in the case of the TOC removal, none of the trends are statistically significant.

Fouling mechanisms

Trying to understand the mechanisms responsible for the membrane flux reduction observed in this study, the previously developed power-law equation (Eq. (2)) for single mechanisms was tested for the average

flux reduction curves presented in Figure 3. Table II presents the regressed model coefficient values as well as the mean square error (MSR). Having in mind that the dimensionless filtration constant, *n*, is 0 in the case of cake filtration, 1 for intermediate blocking, 1.5 for standard blocking, and 2 for complete blocking, and based on the magnitude of the MSR, it is observed that for every single case, the mechanism that best fitted (i.e., had the lowest MSR) the fouling behavior was that for cake filtration. A couple of typical exam-

TABLE II
Fitting Parameters for Power-Law Equation for Single Fouling Mechanisms

<i>n</i>	<i>k</i>	<i>J</i> *	MSR
0 min			
No SMM			
0	3.46E-05	25.64	0.239
1	2.70E-03	27.88	0.51
1.5	3.50E-02	29.01	0.678
2	2.95E-01	29.16	0.75
SMM			
0	3.16E-05	21.48	0.376
1	5.38E-03	26.25	0.816
1.5	4.84E-02	26.55	1.093
2	4.35E-01	29.88	1.315
3 min			
No SMM			
0	2.36E-05	22.33	0.019
1	9.32E-04	23.48	0.03
1.5	5.80E-03	23.86	0.038
2	3.59E-02	24.16	0.047
SMM			
0	2.85E-05	17.13	0.117
1	1.10E-03	18.87	0.165
1.5	6.30E-03	19.41	0.199
2	3.80E-02	19.82	0.238
4 min			
No SMM			
0	2.29E-05	20.77	0.03957
1	9.35E-04	22.34	0.061
1.5	5.90E-03	22.83	0.076
2	3.70E-02	23.21	0.094
SMM			
0	2.69E-03	0.84	0.004
1	6.48E-03	1.08	0.005
1.5	9.63E-03	1.15	0.006
2	1.40E-02	1.2	0.006
5 min			
No SMM			
0	6.57E-06	3.83	0.00066
1	2.44E-04	11.21	0.00068
1.5	1.32E-03	12.7	0.0007
2	6.95E-03	13.74	0.00072
SMM			
0	1.37E-03	2.16	0.012
1	4.50E-03	2.23	0.013
1.5	8.60E-03	2.28	0.014
2	1.62E-02	2.33	0.015

n, dimensionless filtration constant; *k*, fouling coefficient (dimensions depend on the fouling mechanism); *J**, critical flux (L/m² h); MSR, mean square error.

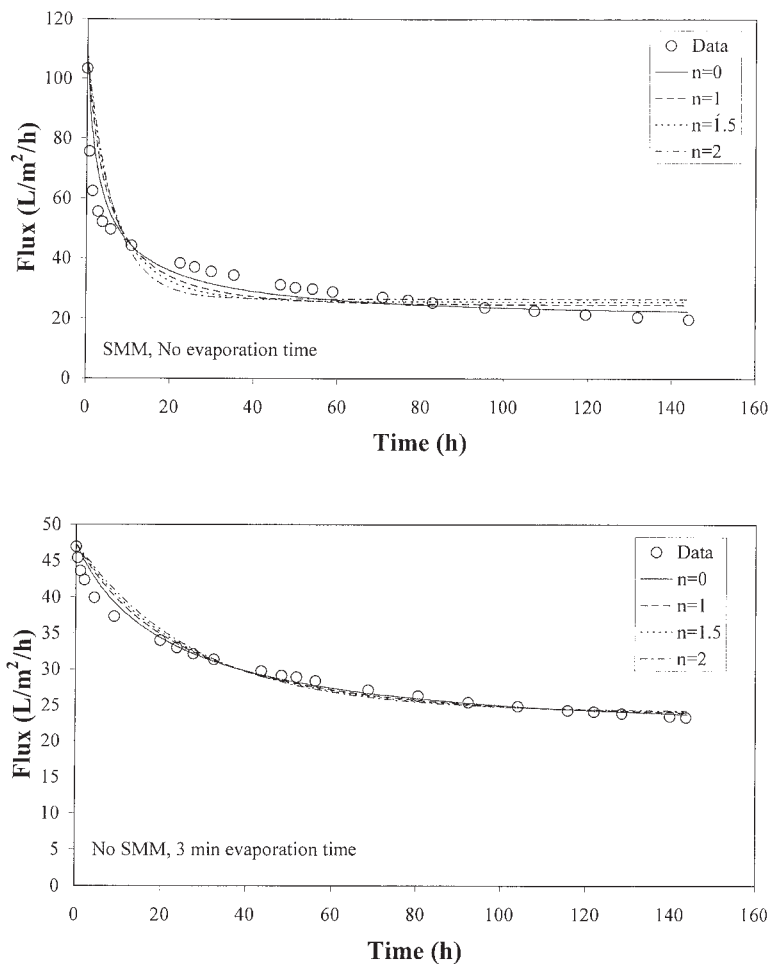


Figure 6 Flux reduction with time for different single-mechanism model. (a) Surface modified membrane with no evaporation time, (b) control membrane with 3-min evaporation time.

ples are shown in Figure 6, where circles represent the experimental data while lines represent the fitted curves for different fouling mechanisms. It is worth noting that the user-defined function required by the MATLAB function used for data-fitting this problem, "lsqnonlin," was entered as a weighted sum of squares. This was absolutely necessary especially in those cases where the flux reduction was very drastic, since a regular sum of squares minimization gives more importance to the fitting of the data with larger absolute values.

Since the cake filtration mechanism prove to best-fit all the data, the following comments focus on the parameters obtained for this mechanism. Smaller values of k represent less dramatic flux decline²⁷; therefore, when increasing the solvent evaporation time k decreased. The values of k for the surface modified membranes prepared with 4 and 5 min evaporation time can not be compared, since the initial flux is much smaller than all the other membranes. The values of J^* are proportional to the final fluxes achieved after 6 days of testing. Terminal fluxes could be used

as fixed values for J^* in the model, to reduce one parameter to fit; however, we observed a considerable improvement when the value of J^* was regressed, and hence the use of an extra parameter is justifiable.

Although a single-mechanism model fit the data reasonably well, it was believed that this could be improved by using a double-mechanism model. Table III shows the results of the data-fitting analysis using Kilduff's double mechanism model.⁷ This model has four fitting parameters instead of three (two if the n for the fouling mechanism is fixed to a particular case) that the single-mechanism model possesses. The values of J^* and the final fluxes were very close (within a 5% difference) for just the membranes with short or no solvent evaporation time and whose final fluxes were relatively high (more than 18 L/(m² h)). Parameters related to the cake layer mechanism (i.e., the specific cake resistance parameter, α_c , and the resistance of the initial fouling layer $R_{c,0}$), do not seem to be affected in a particular way by the solvent evaporation time. This is in agreement with the aforementioned results from the measurement of the NOM deposited on the mem-

TABLE III
Fitting Parameters for Double-Fouling-Mechanism Model

Evap. time (min)	α	α_c	$R_{c,0}$	J^*	MSR	MSR (single) ⁺
No SMM						
0	0.2861	2.49E+23	1.51E+16	23.3	0.053	0.239
3	0.3147	7.87E+23	1.02E+16	23.4	0.003	0.019
4	0.3411	5.73E+23	1.13E+16	22	0.005	0.04
5	0.0325	9.25E+23	1.41E+16	4.6	0.001	0.0007
SMM						
0	0.3319	3.00E+23	1.70E+16	19.9	0.041	0.376
3	0.5118	3.52E+23	1.42E+16	17.5	0.008	0.117
4	261,490	1.66E+23	9.85E+15	0.6	0.004	0.004
5	986,260	6.59E+22	1.31E+16	1.7	0.006	0.012

α , pore blockage parameter (m^2/kg); α_c , specific resistance of the cake ($\text{m}^{-1} \text{kg}^{-1}$); $R_{c,0}$, resistance of the initial deposit (m^{-1}); MSR, mean square error; ⁺MSR for single mechanism model from Table II included for comparison purposes.

brane surface at the end of the experiment, which did not show any statistical effect with the solvent evaporation time. On the other hand, the pore blockage parameter, α , is within the same order of magnitude in the case of the membranes with high final fluxes mentioned above. This parameter is seven orders of magnitude higher in the case of the surface-modified membranes with smaller pores and very low permeation rate (Table I, and Fig. 1). This might be an indication that the small molecular weight fraction of NOM causes pore fouling in the surface modified membranes that have smaller average pores.

Figure 7 shows the experimental data for the permeation flux reduction with time together with the fitted curves for membranes prepared without and with surface modification [Figs. 7(a) and 7(b), respectively]. It is observed that, as expected from the comparison of MSR for single and double mechanisms (Table III), the flux data for all membranes were better simulated when a double-fouling mechanism was assumed.

Surface characterization

These results are discussed at this point and not in the membrane characteristics section because chronologically they were obtained after the filtration tests, due to equipment constraints (availability).

XPS analysis

The elemental analysis performed in the surface of the membranes with the objective of tracking down the migration of the SMM yielded the results presented in Table IV with respect to fluorine content.

Fluorine concentration at the membrane surface is better indicated by the data obtained closer to the surface (3.15-nm depth, 60° take-off angle). Therefore,

this information was used to calculate the relative fluorine concentration at the surface with respect to the concentration if the fluorine was uniformly distributed throughout the membrane (Fig. 8). It shows there is a slight increase of this ratio with solvent evaporation time. It is worth noting that previous studies^{11,12,28,29} have shown very high fluorine content (up to 35–48 at %, versus 2.8 at % in this study), using evaporation times longer than 24 h. On the other hand, Pham et al.³⁰ observed fluorine concentrations at the surface that were less than 2.5 at % (very similar to those obtained in this study) when using 10 min evaporation time at 110°C (PES concentration = 25%) and 24 h at room temperature. It is therefore observed that even when there is some evidence of SMM migration for the short evaporation times used in this study, migration was very limited.

Contact angle determination

The measurement of the contact angle of a water drop deposited on the membrane surface indicates its relative hydrophobicity. Therefore, contact angles were measured to determine whether the evaporation time used in these experiments allowed enough SMM migration to the membrane surface to increase the surface hydrophobicity. In Figure 9, it is observed that advancing contact angles are statistically the same in all cases for membranes with and without SMM. This is due to the relatively large variation in the contact angle measurements. The variation of the measurements is probably due to the heterogeneity of the surface. These results are in agreement with those obtained by the XPS analysis in that they showed very limited migration upon these short evaporation times. This also agrees with results presented by Suk et al.,¹¹ who found that some time is required to achieve complete migration of the hydrophobic SMM to the sur-

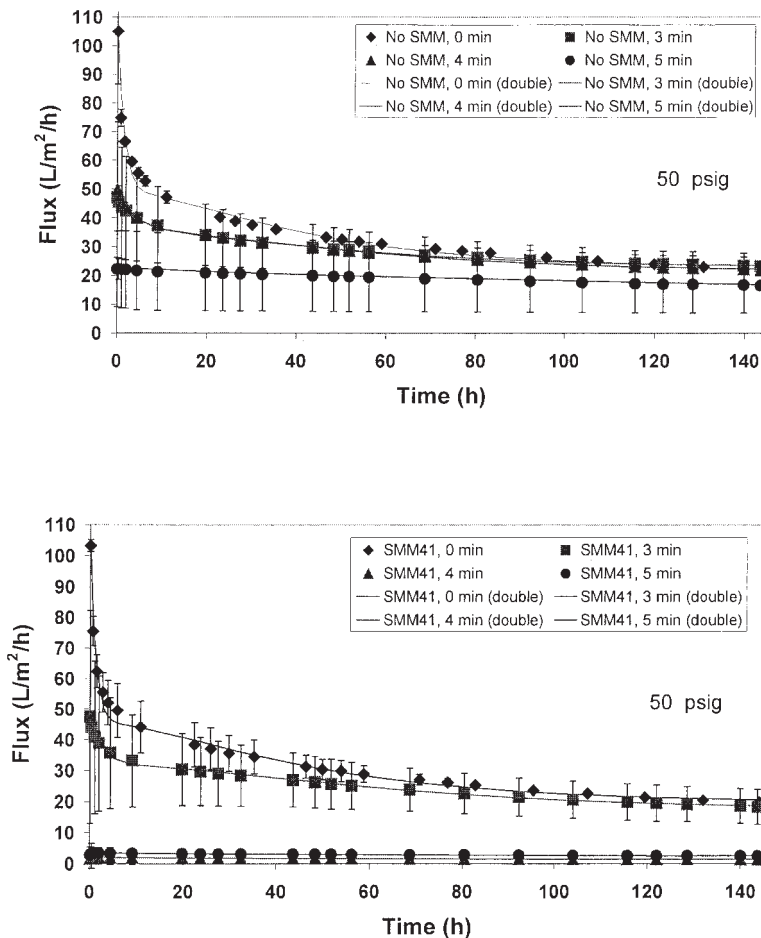


Figure 7 Flux reduction with time for different double-mechanism model. (a) Control membranes, (b) surface-modified membranes.

face. In that report they showed that the required time was around 7 min; however, in their next report,²⁸ when using a different batch of SMM, this time considerably increased up to 30 min or more, showing a large dependence of the results on the batch of SMM synthesized.

Therefore, the addition of SMM did not result in significant surface modification (measured in terms of contact angles and surface fluorine concentration) when evaporation times of 5 min or less are used. On

the other hand, evaporation times beyond 4 min yielded membranes with such low fluxes that they would be impractical for ultrafiltration.

CONCLUSIONS

1. An increase of the solvent evaporation time employed during the preparation of PES membranes caused a reduction on their MWCO and membrane pore size and consequently on the PWP.
2. The removal of humic materials from a natural surface water was not affected by the increase of solvent evaporation time.
3. The reduction of the river water permeation rate with respect to the time of operation is believed to be caused by a double mechanism of membrane fouling, i.e., cake filtration and pore blockage.
4. Results from elemental analysis (XPS) agreed with the contact angle measurements showing that the short evaporation time did not allow

TABLE IV
Fluorine Content (at %) at Two Different Depths

Solvent evaporation time (min)	Take off angles (depth)	
	0° (6.3 nm)	60° (3.15 nm)
0	1.6 (0.1)	1.5 (0.0)
3	2.8 (0.7)	2.8 (0.4)
4	2.3 (0.3)	2.3 (0.3)
5	2.1 (0.5)	2.3 (0.1)

Numbers in parenthesis correspond to the standard deviation of the measurements.

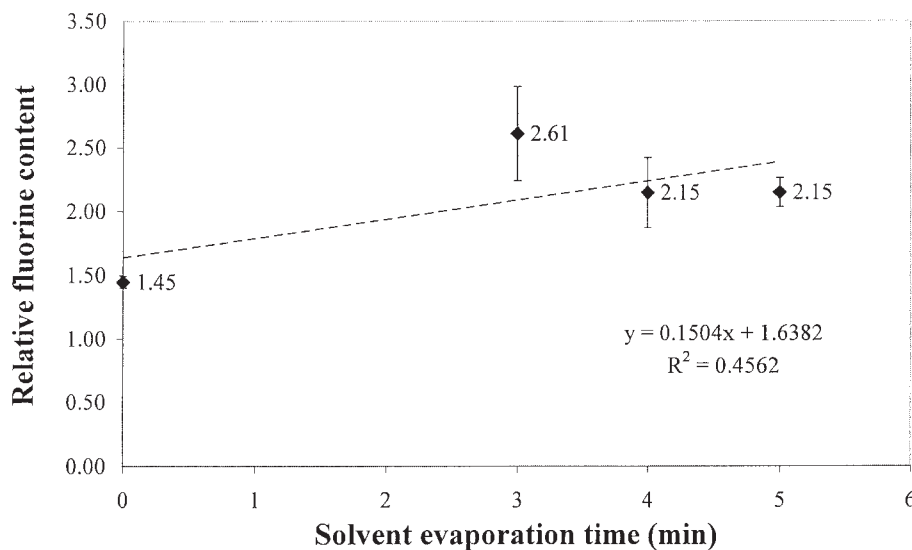


Figure 8 Variation of fluorine content at the membrane surface with respect to the theoretical fluorine content if it was uniformly distributed throughout the membrane as a function of the solvent evaporation time.

enough fluorine migration to cause an increase of the membrane hydrophobicity. Hence, no significant effect of the surface modification was observed on the membrane characteristics and performance.

NOMENCLATURE

A_{blocked} = area of membrane blocked by foulant (m^2)
 A_{open} = area of unblocked or clean membrane (m^2)
 A_T = nominal membrane area (m^2)
 C_b = bulk concentration of solute (kg/m^3)
 C_f = feed concentration (kg/m^3)
 $C_{p(t)}$ = permeate concentration at time t (kg/m^3)

J^* = critical flux [$\text{L}/(\text{m}^2 \text{ h})$]
 k = fouling coefficient (dimensions depend on the fouling mechanism)
MSR = mean square error
 n = dimensionless filtration constant
PWP = pure water permeation rate [$\text{L}/(\text{m}^2 \text{ h})$]
 $R_{c,0}$ = resistance of the initial deposit (m^{-1})
 R_m = membrane resistance (m^{-1})
 α = pore blockage parameter (m^2/kg)
 α_c = specific resistance of the cake ($\text{m}^{-1} \text{ kg}^{-1}$)
 ΔP = applied pressure (Pa)
 μ = solution viscosity [$\text{kg}/(\text{m s})$]

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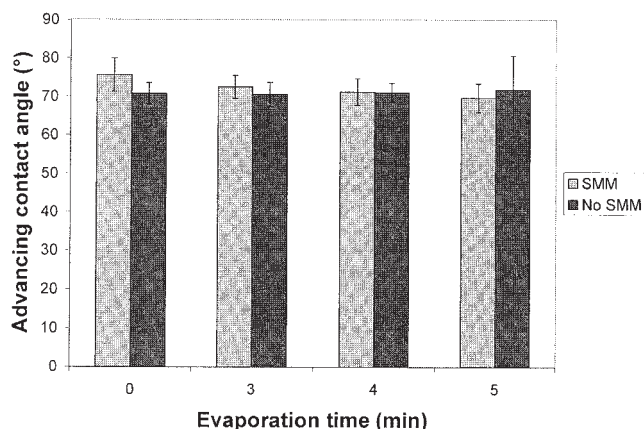


Figure 9 Advancing contact angles of surface-modified and unmodified membranes prepared with different evaporation times. Casting solution: PES = 18 wt %, PVP = 6 wt %, SMM41 = 1.5 wt % (In the case of the surface-modified membranes).

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