

Effect of Surface-Modifying Macromolecules and Membrane Morphology on Fouling of Polyethersulfone Ultrafiltration Membranes

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ABSTRACT: Polyethersulfone (PES) ultrafiltration (UF) membranes with and without surface-modifying macromolecules (SMMs) were prepared and characterized in terms of the mean pore size and pore-size distribution, surface porosity, and pore density. The results demonstrated that both the mean pore size and the molecular weight cutoff (MWCO) of the SMM-modified membranes are lower than those of the corresponding unmodified ones. Membrane fouling tests with humic acid as the foulant indicated that the permeate flux reduction of the SMM-modified mem-

branes was much less than that of the unmodified ones. Therefore, fouling was more severe for the unmodified membranes. Moreover, the dry weight of the humic acid deposited on the membrane surface was considerably higher for the unmodified membranes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3132–3138, 2003

Key words: ESCA/XPS; membranes; poly(ether sulfones); surfaces

INTRODUCTION

Flux reduction is one of the major problems in pressure-driven membrane-separation processes and membrane fouling is one of the causes for this. Membrane fouling may be caused by the deposition of a layer of particles onto the membrane surface. It may either partially or completely block the pores, thereby changing the pore-size distribution and affecting the performance of the membrane.¹

One of the major sources of fouling in membrane filtration of natural waters is dissolved naturally occurring organic matter (NOM) from humic acid substances. Humic acid substances are macromolecules having a low-to-moderate molecular weight. They possess both aromatic and aliphatic components with functional groups. Carboxylic acid groups account for 60–90% of all functional groups. Therefore, humic substances are negatively charged at the pH range of natural water.² Membrane fouling can be prevented or reduced by various methods: (1) by changing the flow regimes across the membrane surface, (2) by regular cleaning, and (3) by changing the surface–foulant affinity (membrane-surface modifications).

The objective of this research was to prepare low-fouling membranes for treatment of natural water. Surface modifying macromolecules (SMMs) having a low surface energy were used to modify the surface of polyethersulfone (PES) ultrafiltration (UF) membranes. The SMMs used had an amphipathic structure consisting of a main polyurethane chain terminated with two low-polarity polymer chains. Since the surface characteristics are largely determined by the low-polarity components, they can be chosen to give a specific property. It is preferable to use a fluorine-based component due to additional features such as surface lubrication, reduced fouling, and increased chemical resistivity associated with carbon–fluorine bonds.³

PES membranes and modified PES UF membranes were prepared using a phase-inversion technique. These membranes were characterized in terms of the pore size, pore-size distribution, pore density, and surface porosity. The performance of the modified and unmodified membranes was evaluated in treating a humic acid feed solution as well as pure water. The membrane performance was characterized in terms of the pure water permeation rate (PWP) and the product rate (PR) with humic acid in the feed solution. The rate of fouling was correlated to the amount of fluorine present in the top surface of the PES UF membranes and the pore size of the modified UF membranes.

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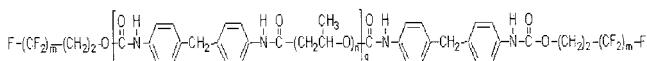


Figure 1 A typical chemical structure of an SMM.

EXPERIMENTAL

Materials

PES, Victrex 4100P, was obtained from ICI Advanced Materials (Billingham, UK). Polyvinylpyrrolidone (PVP), having an average molecular weight of 10,000, 1-methyl-2-pyrrolidinone (NMP), 99.5% purity, and humic acid were purchased from the Aldrich Chemical Co. (Milwaukee, WI). A Teflon filter with a pore size of a 5- μ m-type LS was obtained from the Millipore Corp. The SMMs, synthesized from methylenebis(phenyl diisocyanate), poly(propylene diol), and a fluoroalcohol were provided by the Department of Biomaterials, University of Toronto. The chemical structure of the SMMs are shown in Figure 1, with $m = 4-8$, $n = 7$, and $q = 2$.⁴

Preparation of integrally skinned asymmetric PES membranes with and without SMMs

PES UF membranes were prepared by a phase-inversion technique. The concentration of PES in the casting solutions was varied to give membranes with different pore sizes. The casting solutions having different compositions used to prepare the membranes are shown in Table I. Prior to membrane casting, the solutions were filtered using Millipore filters. PVP was added as an additive to increase the membrane flux and to enable membrane casting with a lower PES concentration.⁵ The concentration of PVP was kept constant at 7% in all the membranes employed in this study. Membranes were prepared by pouring the casting solution onto a glass plate and spreading it with a casting rod at a uniform speed and at room temperature. The wet thickness (gap between the glass plate and casting rod) of all the membranes was maintained at 0.25 mm. Immediately after casting, the membrane together with the glass plate were immersed into a gelation bath containing distilled water and kept at 4°C for 40 min. Membranes were stored in distilled water until use.

For some membranes containing SMMs (MS15, MS17, MS20, and MS22), the membrane together with the glass plate were kept for 3 min in an isothermperature oven at 95°C, before the membrane was immersed in a gelation bath. To indicate the heating period by the membrane code, the period (minutes) is shown in brackets. For example, MS15(0) and MS15(3) mean that membranes with the MS15 composition were heated in the oven for 0 and 3 min, respectively. The purpose of the heating before gelation was to

allow the SMMs to migrate more efficiently to the surface of the membrane.⁴

Membrane testing

UF membranes prepared with and without SMMs were characterized by the solute transport method. The membranes were tested using laboratory test cells, the details of which were described elsewhere.⁶ Four cells were connected in series. All the experiments were conducted at 25–26°C, controlled by a temperature controller, and at 50 psig. Each membrane was compressed at 80 psig for 4–6 h under a pure water flow until the permeation rate became steady. The PWP was then measured. Poly(ethylene glycol) (PEG; molecular weight up to 35,000) and poly(ethylene oxide) (PEO; molecular weight of 100,000 and 200,000) were used as the solutes in the feed solutions for the membrane characterization experiments. The feed concentration was 200 ppm. The feed solutions were circulated through the feed chamber of the permeation cell at a flow rate of 1320 mL/min. PEG/PEO separation experiments were conducted starting from the lower molecular weight solute. The system was thoroughly flushed with distilled water between runs of PEG/PEO solutes of different molecular weight. PEG/PEO contents in the feed and in the permeate were determined from the total organic carbon (TOC) measured by using a TOC analyzer (Dohrmann DC-190, Folio Instruments Inc.).

M15, MS15, M17, and MS17 types of membranes were used for the membrane fouling studies. For these experiments, UF was conducted in the presence of humic acid in the feed. The concentration of humic acid used in the membrane fouling experiments was 10 ppm. The experimental conditions for the fouling tests were similar to those in the membrane characterization experiments. The extent of membrane fouling was determined by comparing the PWP before and after running the humic acid solution through the test cells. The amount of humic acid deposited on the

TABLE I
Composition of the Casting Solutions

Membrane type	PES (%)	PVP (%)	NMP (%)	SMM (%)
M10	10	7	83	
MS10	10	7	81.65	1.35
M15	15	7	78	
MS15	15	7	76.65	1.35
M17	17	7	76	
MS17	17	7	74.65	1.35
M20	20	7	73	
MS20	20	7	71.65	1.35
M22	22	7	71	
MS22	22	7	69.65	1.35

membrane surface at the end of the experiment was also quantified.

Measurement of the mass of humic acid deposited on the membrane

The membranes upon which humic acid was deposited were gently removed from the cells and placed in a 60 mL basic (0.1M NaOH) solution. Deposited humic acid was thus dissolved into the basic solution. After complete removal of humic acid from the membrane surface, the resulting solution and a blank (humic acid-free) solution were placed in an oven and dried at 105°C for 24 h. The deposited humic acid mass was measured by subtracting the dry weight of the blank solution from the dry weight of the solution containing the removed humic acid.²

Membrane characterization based on the solute transport data: mean pore size and pore-size distribution

Solute separation, f , in percent is defined as

$$f = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

where C_p and C_f are the solute concentrations in the permeate and in the bulk of the feed solutions, respectively. It is to be noted that the effect of the concentration polarization on separation is not considered in this equation.

The pore sizes and pore-size distributions of the membranes were determined from UF data of PEG and PEO of varying molecular weights as the solute. Details of the method are described in ref. 5. The feed concentration was 200 ppm and the operating pressure was 50 psig. To determine the exact MWCO value at 90% separation, the mean pore size at 50% separation, and the geometric standard deviation, the results were transferred on a log-normal probability plot of percent separation versus the Einstein–Stokes radius (ESR). The molecular weight of PEG and PEO were converted to ESR from the empirical equation

$$a = 2.122 \times 10^{-8} (M[\eta])^{1/3} \quad (2)$$

where a is the ESR in centimeters; M , the molecular weight in g/mol; and $[\eta]$, the intrinsic viscosity of the solute in dL/g. The $[\eta]$ of PEG was calculated using the equation⁷

$$[\eta] = 4.9 \times 10^{-4} M^{0.672} \quad (3)$$

For PEO,⁸

$$[\eta] = 1.192 \times 10^{-4} M^{0.76} \quad (4)$$

The combination of eq. (2) with eqs. (3) and (4) will yield

$$a = 16.73 \times 10^{-10} M^{0.557} \quad (5)$$

for PEG and

$$a = 10.44 \times 10^{-10} M^{0.587} \quad (6)$$

for PEO, respectively.

The surface porosity, defined as the ratio between the area of pores to the total membrane surface area,⁵ was calculated using the equation

$$\text{Surface porosity} = \frac{N\pi}{4} \left(\sum_{d_{\min}}^{d_{\max}} f_i d_i^2 \right) \times 100 \quad (7)$$

where N is the total number of pores per unit area, and f_i , the fraction of the number of pores with diameter d_i . N was determined using the equation

$$\text{Number of pores} = N = \frac{128\eta\delta J}{\pi\Delta P \sum_{d_{\min}}^{d_{\max}} f_i d_i^4} \quad (8)$$

where δ is the length of the pores; η , the solvent viscosity; ΔP , the pressure difference across the pores; and J , the solvent flux.

X-ray photoelectron spectroscopy (XPS)

The surface of the membranes was analyzed using a Kratos Axis X-ray photoelectron spectrometer (Kratos, Manchester, UK). Samples of 1-mm² size were taken from random positions of the film and analyzed. The analytical method was similar to the angle-resolved XPS technique described by Deslandes et al.⁹ for probing thinner layers of the surface. The sample was tilted to change the angle θ from the normal to the sample and the analyzer. At $\theta = 0^\circ$, the sample was perpendicular to the detector, leading to the maximum sampling depth. The effective sampling depth, z , according to Deslandes et al.,⁹ was equal to

$$Z = 3\lambda \cos\theta \quad (9)$$

where λ is the effective mean path for electrons to escape the surface and was set to a value of 2.1 nm. Therefore, at $\theta = 0^\circ$, $z = 6.3$ nm, and at $\theta = 60^\circ$, $z = 3.15$ nm.

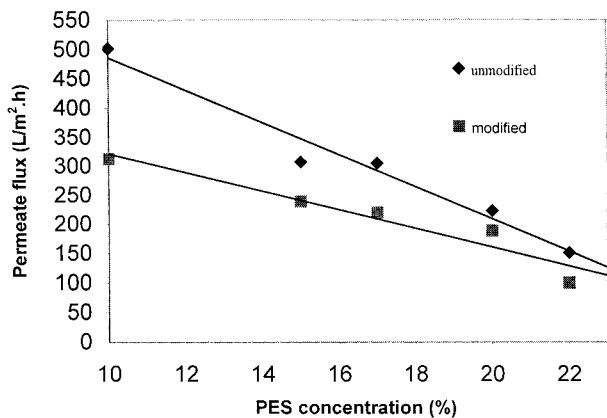


Figure 2 Permeate flux versus PES concentration in the casting solution for the modified and unmodified membranes.

RESULTS AND DISCUSSION

Membrane characterization

The influence of the PES concentration in the membrane casting solution on the PWP is shown in Figure 2. It is observed that PWP decreased with an increase in the PES concentration for both membrane types (modified and unmodified). The permeate flux of the SMM-modified membranes was lower than that of the corresponding unmodified ones, and the slope of the regression line of modified membranes was less than that of the unmodified ones, indicating that the flux reduction due to an increase in PES concentration becomes less in the presence of SMMs in the membranes.

Mean pore size and pore-size distribution

The pore size and pore-size distribution of the UF membranes were obtained from solute transport data with PEG/PEO as the solutes. When plotting the separations of the PEG/PEO solutes in percentage versus their corresponding diameters [$2 \times a$ obtained by eqs. (5) and (6)] on a log-normal probability paper, a straight line was obtained with a good linear relationship (see Fig. 3 for M17 and MS17). The mean pore size was obtained from the corresponding diameter of 50% separation, while the geometric standard deviation, from the ratio of a 84.13% separation rate to that of 50%.⁵ The mean pore size and the pore-size distribution (given as a standard deviation) of each membrane are shown in Table II together with the MWCO data. According to the table, the mean pore size as well as the MWCO of the modified membranes were less than those for corresponding unmodified membranes.

Pore density and surface porosity

The membrane pore density and surface porosity calculated from the solute transport data are shown in

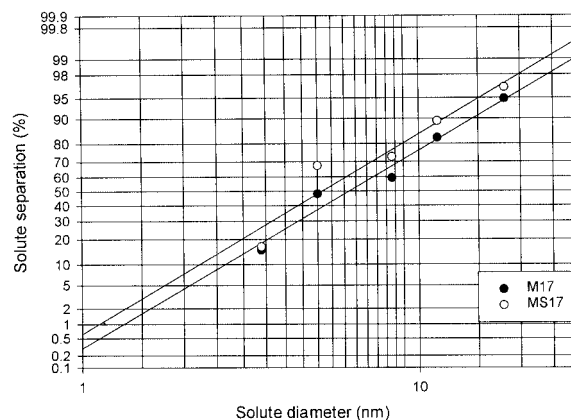


Figure 3 Some examples for the log-normal plot of solute separation versus solute diameter.

Table II. The results showed that the MS22 membrane has the largest pore density and surface porosity, while M10 has the smallest ones.

Membrane fouling

Figure 4 shows the PWP and PR in the presence of 10 ppm humic acid in the feed solution versus the operating time [Fig. 4(a-c)]. Three membranes, namely, M15, MS15(0), and MS15(3), were tested in these experiments. The casting solution compositions for these membranes are given in Table I. As for MS15(0) and MS15(3), these are MS15 membranes prepared with 0 and 3 min of membrane evaporation at 95°C after membrane casting. Figure 4 also presents the permeate flux reduction (Fig. 4d), which is defined as $1-(PR)/(PWP)$. Figure 4 shows that

1. Both PWP and PR data decrease with an increase in the operating time.
2. PWP and PR data at the operating time zero are almost equal. The initial PWP and PR values decrease in the order M15 > MS15(0) > MS15(3).
3. PR decreases with an increase in operating time faster than that of PWP. Therefore, the gap between PWP and PR increases with an increase in the operating time.

TABLE II
Membrane Types for Fouling Test

Membrane	PES (%)	PVP (%)	NMP (%)	SMM (%)	Evaporation (min)
M15	15	7	78	0	0
MS15(0)	15	7	76.65	1.35	0
MS15(3)	15	7	76.65	1.35	3
M17	17	7	76	0	0
MS17(0)	17	7	74.65	1.35	0
MS17(3)	17	7	74.65	1.35	3

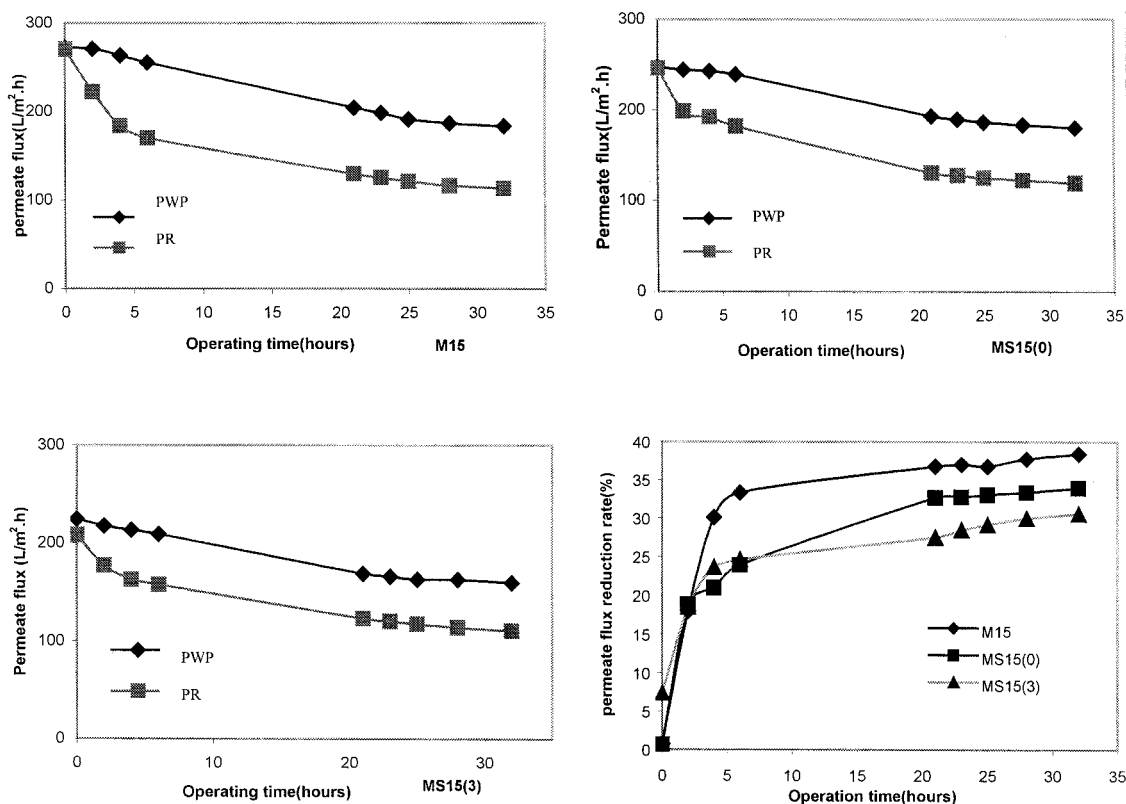


Figure 4 (a–c) Pure water permeation flux and product permeation flux versus operating time and (d) permeate flux reduction versus operating time for M15, MS15(0), and MS15(3) membranes.

4. The gap between PWP and PR decreases in the following order: M15 > MS15(0) > MS15(3).
5. The permeate flux reduction given in Figure 4(d) also decreases in the order > MS15(0) > MS15(3).

It is known that the hydrophobicity of the membrane surface increases when SMMs are blended in the casting solution. It is also known that the hydrophobicity of the membrane surface increases with an increase in the heating period.⁴ Hence, the order in the surface hydrophobicity is M15 < MS15(0) < MS15(3). By combining the information on the membrane fouling and the surface hydrophobicity, the following conclusions may be drawn:

1. As the surface hydrophobicity increases, initial PWP and PR values decrease.
2. As the surface hydrophobicity increases, the permeate flux reduction decreases.

Figure 5(a–d) shows similar experimental data for the membranes M17, MS17(0), and MS17(3). All the tendencies observed in Figure 4 can also be observed in Figure 5. The flux reductions for M17, MS17(0), and MS17(3) are, however, much smaller than those for M15, MS15(0), and MS15(3). Since it is known from

Table III that the mean pore size of M15 is greater than that of M17 and the mean pore size of MS15(0) is greater than that of MS17(0) [pore sizes of MS15(3) and MS17(3) are unknown], we can conclude that the permeate flux reduction depends not only on the surface hydrophobicity but also on the membrane pore size.

It should be noted that the separation of humic acid was practically zero for all the membranes studied. Therefore, only their flux data are presented.

Experiments on humic acid deposition and XPS analysis

Table III shows the mass of humic acid deposited on the surface of each membrane. Clearly, the mass of humic acid is decreasing in the order M15 > MS15(0) > MS15(3) and M17 > MS17(0) > MS17(3). Therefore, the mass of humic acid deposited decreases as the membrane hydrophobicity increases; it also decreases as the mean pore size of the membrane decreases.

Table III also shows the permeate flux reduction for each membrane after 33 h of operation time. In comparing the mass of humic acid deposited and the permeate flux reduction, it is obvious that there is a parallel relationship between them. Moreover, the cor-

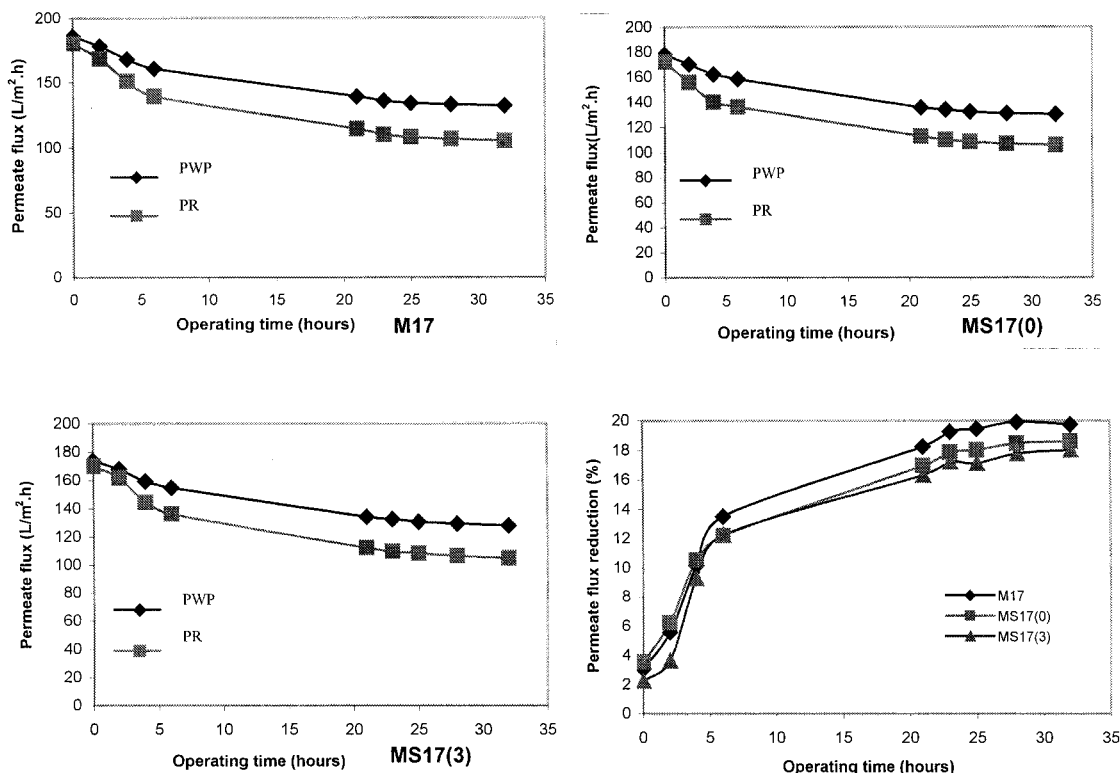


Figure 5 (a–c) Pure water permeation flux and product permeation flux versus operating time and (d) permeate flux reduction versus operating time for M17, MS17(0), and MS17(3) membranes.

relation between the mass of humic acid deposited and the permeate flux reduction seems unique.

The last column of Table III shows the fluorine content at the membrane surface measured by XPS analysis (at $\theta = 60^\circ$). It should be noted that, in our previous work,⁴ fluorine contents were 13.8 and 8.6%, respectively, corresponding to $\theta = 60^\circ$ (depth = 3.15 nm) and $\theta = 0^\circ$ (depth = 6.3 nm). These data confirm that SMMs which contain fluorine migrated to the membrane surface and more SMMs migrated as the

heating time increased. The SMM surface migration was less when the PES concentration in the casting solution was increased from 15 to 17%. This is expected since the viscosity of the casting solution increases, resulting in a decrease in the speed of the SMM migration.

CONCLUSIONS

The experiments on PES UF membranes modified by surface-modifying macromolecules and the testing of their performances led to the following conclusions:

1. The presence of SMMs in PES UF membrane casting solution reduced the mean pore size of the final membrane.
2. More of the SMMs migrated to the membrane surface as the heating time increased.
3. The mass of humic acid deposited on the membrane surface decreased as more SMMs migrated to the membrane surface. It also depends on the mean pore size on the membrane surface.
4. There is a unique correlation between the mass of humic acid deposited and permeate flux reduction.

TABLE III
Fouling Test Data in Terms of Dry Weight of Deposited Humic Acid

Membrane type ^a	Mass of humic acid deposited (g/m ²)	Permeate reduction ^b (%)	Fluorine (%) ^c
M15	6.81	38.4	—
MS15(0)	4.60	33.9	15.5
MS15(3)	2.39	30.6	24.8
M17	1.17	20.4	—
MS17(0)	0.68	18.6	15.1
MS17(3)	0.57	18.1	17.2

^a (0) and (3) correspond to evaporation time of 0 and 3 min, respectively.

^b Permeate reduction after 30 h of operating time.

^c Theoretical pure SMM composition, atomic percent without hydrogen: C(64.0), O(15.0), N(3.8), F(16.4).

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