

# Photochemical modification of poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes for control of fouling by natural organic matter

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## Abstract

Poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes were modified by UV irradiation and UV-assisted graft polymerization of N-vinyl-2-pyrrolidinone (NVP) as a strategy for mitigating fouling by naturally-occurring organic compounds (NOM) found in surface waters. Exposure to UV (254 nm) alone increased membrane hydrophilicity, interpreted in terms of either the contact angle,  $\theta$ , or surface wettability ( $\cos \theta$ ). It was possible to increase  $\cos \theta$  above 0.94. FTIR analysis suggests that this was due, in part, to the formation of surface hydroxyl groups. The membrane structure was opened, as evidenced by increased clean water permeability. Fouling by natural organic matter (isolated from a surface water source using reverse osmosis) was reduced significantly, but conditions that minimized fouling also decreased solute (NOM as organic carbon) rejection. In contrast, it is possible to identify UV-assisted graft polymerization reaction conditions which significantly reduced fouling, with clean water permeability and solute rejection similar to as-received membranes. When short reaction times (10 s) were used, clean water permeability decreased and solute rejection increased, presumably as a result of pore blockage by graft polymer chains. The opposite behavior in each respect was observed for long irradiation time (180 s); however, while fouling tendency was reduced relative to as-received membranes, it was not reduced to the same extent as membranes irradiated for 60 s. This observation could be explained by an increase in pore fouling resulting from increased access to enlarged pores by larger molecular weight natural organic matter components.

**Keywords:** Nanofiltration; Membrane fouling; Natural organic matter; Graft polymerization

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## 1. Introduction

New membrane technology has resulted in materials offering improved water flux, salt rejection, and lower operating pressures. However, membrane fouling by colloidal substances can significantly reduce membrane performance, increase operating costs, and shorten membrane life [1]. Understanding fouling mechanisms and developing ways to control them are critical for the economical development of water treatment technologies. Naturally occurring dissolved and colloidal organic matter (NOM) is considered a major contributor to membrane fouling in water treatment applications [1,2,3]. In addition, the removal of natural organic matter prior to disinfectant/oxidant addition during disinfection of potable water represents a primary strategy to control the formation of disinfection by-products, including trihalomethanes and haloacetic acids that form when chlorine reacts with NOM. DBPs in drinking water are suspected to be toxic, carcinogenic and mutagenic to humans, and are regulated by the EPA through the Disinfectants/Disinfection By-products (D/DBP) Rule.

Natural organic matter is present in all surface and ground waters, with total organic carbon concentrations generally ranging from 1 to 8 mg/l and median concentrations of 3.4 mg/l and 0.8 mg/l in surface water and ground water, respectively [4,5]. NOM is a heterogeneous mixture of complex organic materials including humic substances, hydrophilic acids, proteins, lipids, carboxylic acids, amino acids, and hydrocarbons. Humic substances comprise the bulk of organic substances in natural systems; estimates range from 30 to 70% [6,7,8]. The molecular size and weight of humic substances has been estimated to range from 1500 to 5000 g/mol for humic acids and from 600 to 2000 for fulvic acids [6,9,10,11,12,13]. Estimated radii of gyration of humic substances fall in the range of 4.5 to 30 Å [6,14]. In this research, aquatic organic matter was isolated from a surface water source. This is important because it has been shown that

NOM from different environments (e.g. soil, surface water, and groundwater) have significantly different properties [15].

Several approaches to mitigate the negative effects of NOM fouling on nanofiltration membrane performance can be considered. These include (i) selecting a membrane material that minimizes attractive interactions between NOM and the membrane surface [16], (ii) improved pretreatment to selectively remove the most adhesive components in NOM, and (iii) enhanced module design and operation that reduces fouling through more effective hydrodynamics [17]. An important variant of (i) above is to tailor membrane surface chemistry for particular applications. Modifications to polymer substrates can be made through homogeneous reaction in solution [18]; however, an easier, inexpensive and scalable approach involves surface modification of commercial polymers. Two different approaches based on low-temperature plasma [19] and irradiation-grafting [20,21,22] have been applied to the modification of ultrafiltration membranes. In this paper, we describe the efficacy of photochemical radiation (UV) followed by monomer grafting and subsequent polymerization as a way to modify the surface chemistry of commercial poly(ether sulfone) membranes to reduce fouling by NOM. The approach used is based on chemistry described in a US Patent [23] that takes advantage of the intrinsic photosensitivity of poly(aryl sulfones). Membranes made of poly(sulfone) and poly(ether sulfone) offer attractive features for water treatment applications, including wide pH tolerance (2 to 12); good resistance to oxidants, including chlorine; and high temperature limits (on the order of 75°C).

## 2. Experimental

### 2.1. Materials

The nanofiltration membranes used in this research were the NF PES 10 poly(ether sulfone)

(PES) Hoechst AG (Celgard) and the NTR7450 sulfonated poly(sulfone) (PSf) (Nitto-Denko America, Inc.). Deionized, reagent grade water was produced from tap water pretreated by mixed-bed ion-exchange and activated carbon, and processed in a Milli-Q system (Millipore, Bedford MA) that included 0.2 micron micro-filtration.

Natural organic matter was isolated from the Tomhannock reservoir, the drinking water supply for the city of Troy, NY, using a field RO system after Serkiz and Perdue [24]. This source water has a dissolved organic carbon content of about 3 mg/L. Pretreatment reduced source water turbidity from 2.1 NTU to 0.44 NTU (about 80% reduction), and provided greater than 95% removal of cations (mainly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). The pretreated source water was concentrated (by a factor of 10 to 20) using an aromatic polyamide reverse osmosis membrane (Fastek TLC S4040, Osmonics, Inc., Minnetonka, MN) with a feed of 14 L/min, a retentate to permeate flow ratio of 7, and a transmembrane pressure of 550 kPa (80 psi). A low pressure was used to maximize NOM rejection (greater than 99%) and mass recovery (>95%). Filtration solutions were prepared from reverse osmosis isolate of Tomhannock reservoir water diluted to 10 mg/L with reagent-grade water.

## 2.2. Bench scale membrane testing

Solution flux experiments were conducted using the cross-flow bench scale membrane test system depicted schematically in Fig. 1. A membrane sheet and a feed channel spacer are mounted between halves of a stainless steel cell. Recovery was maintained at 85%, and a cross-flow velocity of 0.1 m/s, typical of full-scale systems, was used. The permeate and concentrate flowrate were measured directly, while the feed flowrate was calculated by continuity. Because solution flux can impact the rate and extent of fouling, transmembrane pressure was adjusted

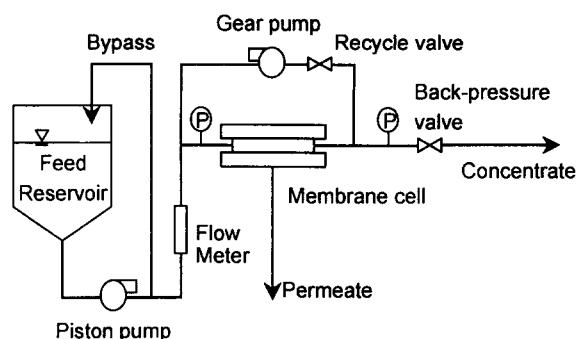


Fig. 1. Schematic diagram of the nanofiltration test system.

to yield the same initial solution flux, 45 L/(m<sup>2</sup>-h) (LMH), for all membrane performance experiments. The transmembrane pressure was then held constant throughout the run, while changes in flux were monitored.

Prior to testing, membrane sheets were soaked in 0.1 M NaOH for 30 min, and rinsed with DI water. The membrane sheet was then transferred to the bench-scale membrane test cell. Clean water flux,  $J_o$ , as a function of transmembrane pressure was measured using Milli-Q water to determine the membrane permeability. Plots of membrane flux vs. pressure were linear over the pressure range studied, and the clean water permeability was taken as the slope of this line. The system was then run for about 5 h, starting at an initial flux of 45 LMH, to allow for membrane compaction.

After a solution filtration run, the membrane was cleaned in two steps; first, a hydrodynamic cleaning was performed, followed by chemical cleaning using NaOH (pH 10) followed by HCl (pH 3).

## 2.3. Membrane modification

Membranes were photochemically modified in photochemical chamber reactor system as described by Pierracci et al. [22]. The photo-

chemical reactor is equipped with sixteen UV lamps with an emission maximum at 254 nm and an intensity of 2.5 mW/cm<sup>2</sup> at the center of the reactor. For irradiation and grafting experiments using the dip technique, the membrane was first dipped in N-vinyl pyrrolidone monomer solution prior to mounting in the quartz vessel. The vessel was then partially filled with distilled deionized water, and purged with nitrogen. For irradiation and grafting experiments using the immersion technique, the quartz vessel was filled with an n-vinyl pyrrolidone monomer solution, and then purged with nitrogen. Following the purge step, the UV lamps were then turned on for a predetermined time. A reaction temperature of 22°C was maintained.

#### 2.4. FTIR

Attenuated total reflection-Fourier transform infrared spectra (FTIR/ATR) of the unmodified and monomer-modified membranes were obtained using a Nicolet Magna-IR 550 Series II spectrometer (Nicolet Instrument Corp., Madison, WI). 256 scans were performed at a resolution of  $\pm 4$  cm<sup>-1</sup> using a germanium crystal at an incident angle of 45°. The IR penetration depth for this incident angle is 0.1 to 1  $\mu$ m (Nicolet 1995).

#### 2.5. Contact angle

Static contact angles of the membrane surface were measured using the captive air bubble technique. Membranes were inverted in deionized water and air bubbles were placed in contact with the surface. The static angle was measured using an SIT camera (SIT66 Dage-MTI, Michigan City, IN) connected to a video screen. The contact angles were averages of measurements on 10 different bubbles; the measurement error was  $\pm 3^\circ$ .

#### 2.6. Filtration parameters

In this research we employ the filtration parameters discussed by Pieracci et al [22]; refer

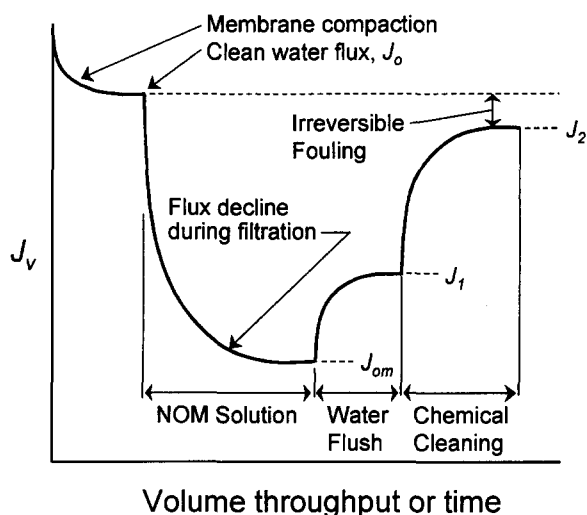


Fig. 2. Schematic depiction of the filtration protocol employed (after Pieracci et al. [22]) and definition of the filtration parameters.

to Fig. 2. The clean water permeability,  $K_w$ , is used to evaluate changes in membrane flow characteristics as a result of membrane modification. Goals of this work are to produce modified membranes that exhibit (i) a low tendency to foul, having a fouling flux ratio,  $J_{om}/J_0$ , larger than that for unmodified membranes (i.e.,  $(J_{om}/J_0)_{modified}/(J_{om}/J_0)_{as-received} > 1$ ) and as close to unity as possible; (ii) solution flux during natural organic matter filtration,  $J_{om}$ , greater than as-received membranes; (iii) solute rejection ( $R = 1 - C_{permeate}/C_{feed}$ ) greater than as-received membranes; and, (iv) flux loss due to fouling ( $J_0 - J_{om}$ ) that is completely recoverable by hydrodynamic cleaning with water only [i.e.,  $(J_0 - J_{om}) \approx (J_1 - J_{om})$ ].

### 3. Results and discussion

#### 3.1. UV irradiation

The effects of UV irradiation on membrane surface energy and hydrophilicity were characterized by measuring contact angles using the

captive air bubble technique. The goal of surface modification is to make contact angles as low as possible, corresponding to a hydrophilic surface that will not promote the adhesion of hydrophobic or amphoteric materials. Previous research has correlated contact angle with a propensity to foul. Cellulosic membranes have low contact angles (generally less than 30°, and in some cases below 20°), are known to be less likely to be fouled by proteinaceous solutions, and are also, in general, easier to clean.

UV irradiation of poly(ether sulfone) membranes has been shown to increase the amount of surface hydroxyl groups present, as detected by increases in the OH-stretch region (between 3200 and 3600 cm<sup>-1</sup>) of FTIR spectra [22]. Similar results were found in this research. UV light at a wavelength of 254 nm has enough energy to break the sulfur-carbon bond of the trunk polymer, forming a radical at that position. The radical terminates with a hydroxyl group, as suggested by FTIR analysis. Surface hydroxyl groups, which can bind water through hydrogen bonds, may be responsible, in part, for the observed increase in hydrophilicity of UV-irradiated membranes.

As is evident from examination of the data tabulated in Table 1, UV irradiation had a significant effect on surface energy, lowering contact angles significantly. The as-received NTR7450 sulfonated poly(sulfone) membrane had a lower contact angle (28.6) than the NFPES10 poly(ether sulfone) membrane (39.6). Contact angles for both membranes were lowered significantly after 1 min irradiation time, and after 10 min, contact angles of the NFPES10 and NTR7450 were lowered 51% and 42% respectively. It should be noted that the contact angles of both membrane types could be made lower (suggesting a more hydrophilic surface) than commercially-available polyamide membranes. Indeed, for both the PSf and PES materials, achieving contact angles less than 20°C was shown to be possible, making the UV

Table 1  
Summary of contact angle measurements

Membrane	Contact angle	95% C.I.	Cos ( $\theta \pm 95\%$ CI)
As-received			
NTR7450	28.58	2.62	0.855, 0.899
NF-PES-10	39.60	2.25	0.745, 0.795
UV irradiated			
NTR7450-1min*	17.83	1.11	0.946, 0.958
NTR7450-10 min*	16.63	0.97	0.953, 0.963
NF-PES-10-1 min*	27.00	1.79	0.876, 0.905
NF-PES-10-10 min*	19.32	1.31	0.936, 0.951
Graft polymerized (Dip method)			
NF-PES-10-10 s*	29.00	1.03	0.866, 0.883
NF-PES-10-30 s	24.35	0.90	0.904, 0.917
NF-PES-10-60 s	ND	ND	
NF-PES-10-180 s	20.95	0.62	0.930, 0.938
Graft polymerized (Immersion method)			
NF-PES-10-3 min*	24.68	0.71	0.903, 0.914
NF-PES-10-5 min*	22.35	0.72	0.920, 0.930
NF-PES-10-10 min*	22.00	0.72	0.922, 0.932

irradiated surfaces as hydrophilic as the most hydrophilic membranes manufactured. The kinetics of the surface hydroxyl formation were faster than those observed in previous research [22], in which it was found that significant changes in contact angle occurred only after 7 min or irradiation time.

UV irradiation had a marked effect on clean water permeability. Clean water permeability values for all membranes are tabulated in Table 2. The increase effect was significant for an irradiation time of 1 min (76% for the PSf membrane and 26% for the PES membrane) and dramatic for the 10 min irradiation time (a factor of 6.7 for the PSf membrane and 2.4 for the PES membrane). Pieracci et al. [22] found similar

Table 2  
Summary of membrane performance experiments

Membrane	NOM solution (10 mg DOC/L, 10 mM NaCl, pH 7)					$J_s$ (DOC), mg/m <sup>2</sup> /h	$R$ (DOC)
	$K_w$ , LMH/kPa	$J_0$ , LMH	TMP, $\Delta P$ kPa	$J_{om}$ , LMH	$J_{om}/J_0$		
As-received							
NTR7450	0.097	45.8	457	35.7	0.78	55.9	83.3
NF-PES-10	0.123	45.4	374	37.9	0.83	139	57.9
UV irradiated							
NTR7450-1min*	0.171	45.0	274	34.6	0.77	88.1	71.5
NTR7450-10 min*	0.646	45.6	76	35.4	0.78	223	33.0
NF-PES-10-1 min*	0.155	45.1	322	39.5	0.88	154	57.7
NF-PES-10-10 min*	0.295	45.8	159	42.0	0.92	289	28.7
Graft polymerized (Dip method)							
NF-PES-10-10 s*	0.052	44.6	896	35.8	0.80	96.0	72.9
NF-PES-10-60 s	0.074	45.1	643	42.2	0.94	207.3	49.8
NF-PES-10-180 s	0.383	45.3	124	39.5	0.87	263	29.3

Note: Flux in LMH is L/(m<sup>2</sup>-h).  $J_v$  is the volumetric solution flux;  $J_0$  is the initial solution flux, and  $J_{om}$  is the solution flux after 10 h of filtration.  $J_s$  is the solute flux, as dissolved organic carbon;  $J_s = J_v C_{feed} (1-R)$ .  $R$  is solute rejection,  $1 - C_{permeate}/C_{feed}$ .

results, and attributed their findings to facile bond cleavage along the backbone of the polymer chain, and subsequent increase in pore size. In contrast to the findings of Pieracci et al. [22], the increase in clean water flux was accompanied by a decrease in rejection, and an increase in solute flux. This suggests that for this system, the effects of pore enlargement dominate over any effects of increased membrane surface charge, which can act to decrease solute flux by electrostatic repulsion. This is consistent with the high molecular weight BSA and fully retentive 10 kDa UF membranes studied by Pieracci et al. [22], in contrast to the much lower molecular weight humic substances and partially retentive NF membranes studied here.

As shown in Fig. 3, the tendency for the NF PES 10 membrane to foul was reduced by UV irradiation, for both irradiation times. This effect

is related, in part, to an increased solute flux (reduced rejection) which resulted from irradiation for 10 min; however, for the membrane irradiated for 1 min, solute flux and rejection were similar to the as-received membrane. In contrast, there was no apparent effect of UV irradiation on the tendency for the PSf (NTR7450) membrane to foul, even though solute flux was increased for both irradiation times. Pieracci et al. [22] observed an *increase* in the tendency to foul after UV irradiation; possible explanations cited were an increase in available surface area and surface roughness.

Examination of the data in Table 2 reveals that little of the flux lost by the as-received NTR7450 membrane was recoverable by hydrodynamic cleaning, and only about 34% was recovered by the caustic cleaning. UV irradiation for 1 min improved the flux recovered by

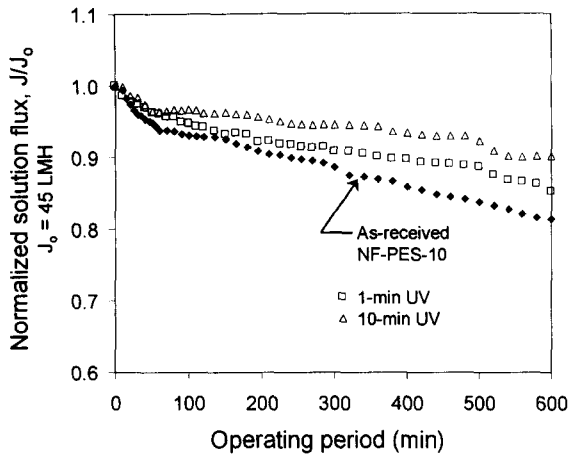


Fig. 3. Effect of UV irradiation on the performance of the NF-PES10 membrane in terms of constant pressure flux (normalized to  $J_0 = 45$  LMH) of a natural organic matter solution. UV irradiation times as indicated. Solution conditions: Tomhannock reservoir organic matter, 10 mg/L as organic carbon, pH = 7, 10 mM NaCl;  $T = 20^\circ\text{C}$ .

caustic cleaning to 60%, but did not increase the flux recovered by hydrodynamic cleaning. In contrast, after UV irradiation for 10 min, about 56% of the flux loss was recovered by hydrodynamic cleaning only. The PES membrane exhibited higher overall flux recovery, and flux recovery by hydrodynamic cleaning. While the overall recovery of flux was relatively high for the as-received membrane (87%), cleaning by caustic was required to recover 21% of this. The overall recovery was not improved by UV irradiation; however, the same overall recovery could be achieved without caustic when the PES membrane was irradiated for 10 min. The continuous decrease in the fraction of fouling recovered by caustic cleaning,  $(J_2 - J_1)/(J_0 - J_{om})$ , with increasing UV irradiation time was consistent with previous findings [22].

### 3.2. Polymer grafting

The NF PES 10 membrane was chosen for further studies to evaluate the effects of surface modification using UV assisted graft polymeriza-

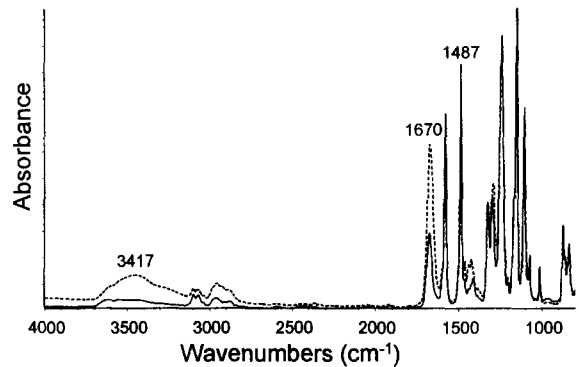


Fig. 4. FTIR spectra of as-received (solid line) and graft polymerized (dashed line) NF-PES10 membrane. Reaction conditions: dip method, reaction time 30 s. The OH stretch absorbance peak at  $3417\text{ cm}^{-1}$  and the amide I carbonyl stretch at  $1670\text{ cm}^{-1}$  are significantly increased as a result of modification; the benzene carbon-carbon double bond at  $1487\text{ cm}^{-1}$  remains constant. The degree of grafting (absorbance @  $1670$ /absorbance @  $1487$ ) for the modified membrane in the figure is 0.74. The as-received membrane exhibits some modification, with a degree of grafting of 0.31.

tion. System variables include monomer type, monomer solution concentration, and irradiation time. N-vinylpyrrolidinone (NVP) was chosen as the monomer type because previous studies have identified it as superior to other hydrophilic monomers, and NVP-modified PES membranes were shown to outperform commercial regenerated cellulose membranes in terms of low fouling and high flux [22]. A 3% (w/w) aqueous solution concentration was chosen to minimize the chance of exhausting the monomer available for grafting at the surface, with subsequent trunk polymer scission and possible loss of previously grafted polymer. FTIR was employed to verify graft polymerization of NVP to the NF-PES10 membrane surface. As demonstrated by the spectra shown in Fig. 4, the OH stretch absorbance peak at  $3417\text{ cm}^{-1}$  and the amide I carbonyl stretch at  $1670\text{ cm}^{-1}$  are significantly increased as a result of modification. The presence of the amide I carbonyl peak is taken as evidence that grafting has occurred. The degree

of grafting is quantified by normalizing the peak height of the carbonyl stretch at  $1670\text{ cm}^{-1}$  by the benzene carbon–carbon double bond absorbance peak at  $1487\text{ cm}^{-1}$ , which remains constant after modification. Note that the as-received NF PES 10 membrane displays a degree of grafting of 0.31; this suggests that the manufacturer has incorporated a hydrophilic moiety into the membrane polymer, onto the membrane surface, or both. This could provide an explanation for the lower contact angle of this membrane as compared to the PES UF membrane studied previously [22].

Both the dip and immersion techniques were effective in producing membranes that have hydrophilic surfaces, interpreted in terms of either the contact angle,  $\theta$ , or surface wettability ( $\cos \theta$ ). Using the dip method, the contact angle was lowered to below  $25^\circ$  ( $\cos \theta > 0.90$ ) using a reaction time of only 30 s; increasing the reaction time to 3 min lowered the contact angle to  $21^\circ$ . Using the immersion method, about 3 min were required to lower the contact angle below  $25^\circ$  ( $\cos \theta > 0.90$ ), and 10 min were required to lower the contact angle to  $22^\circ$ . The surface wettability increases most significantly as the degree of grafting is increased from 0.31 (as-received membrane) to about 0.7 to 0.8, above which  $\cos \theta$  reaches a near constant value of about 0.93. The relationship between  $\cos \theta$  and degree of grafting does not appear to be influenced by the modification technique (dip vs. immersion); differences in the two techniques appear to be confined to kinetic effects only.

For irradiation times 10 or 60 s, graft modification reduced clean water permeability 58 and 40%, respectively. However, for the longest irradiation time, 180 s, the clean water permeability was increased by a factor of about 3. A reduction in clean water permeability is consistent with the findings of Pieracci et al. [25], who modified a 50 kDa UF membrane using the dip technique with a 5% NVP solution. It was assumed that grafted poly(vinyl pyrolidone)

(PVP) chains blocked pores, and thus decreased permeability. Pieracci et al. [25] also observed increases in membrane permeability when lower (1%) NVP solutions were employed, citing the possibility that during the longer irradiation time, NVP was exhausted from the surface, and either previously grafted polymer was lost, trunk polymer scission occurred, or both. It should be noted that in this study, a decline in the degree of grafting (Fig. 5) with increasing irradiation time was not observed; therefore, there is no direct evidence that exhaustion of polymer on the membrane surface occurred.

As shown in Table 2, significant changes in membrane rejection for natural organic matter were observed as a function of irradiation time. Pieracci et al. [25] observed only decreases in rejection; however, we observed both increases and decreases depending on irradiation time. For the shortest irradiation time, 10 s, we observed an increase from 57.9% (as-received membrane) to 72.9%. For the longest irradiation time, 180 s, we observed a significant decrease in rejection to 29.3%. For their system, Pieracci et al. [25] conclude that irradiation times greater than 10 s should be avoided; for the NF membrane studied here, longer irradiation times, on the order of 40 s, appear feasible without causing significant decreases in rejection. The magnitude of the change in rejection that results from graft modification of the membrane should depend, in part, on the pore size (or size distribution) relative to the solute molecular size (or, in the case of natural organic matter, size distribution). It is likely that the different results obtained in this study relate, in part, to the smaller size of the NF membrane pores relative to the NOM solutes, as compared to the 50 kDa UF membrane employed by Pieracci et al. [25] to filter BSA.

The flux decline observed for the polymer grafted membranes are compared to the as-received membrane in Fig. 5; filtration parameters are tabulated in Table 2. As depicted in this figure, the graft polymerization approach



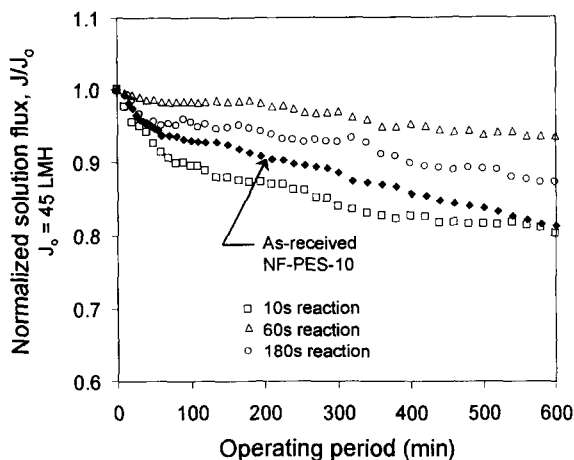


Fig. 5. Effect of graft polymerization on the performance of the of the NF-PES10 membrane in terms of constant pressure flux (normalized to  $J_0 = 45$  LMH) of a natural organic matter solution. Reaction conditions: 3% NVP solution, dip method, reaction time as indicated. Solution conditions: Tomhannock reservoir organic matter, 10 mg/L as organic carbon, pH = 7, 10 mM NaCl;  $T = 20$  °C.

using irradiation times 60 s or greater produced membranes with a significantly lower propensity to foul (higher  $J_{om}/J_0$ ). In contrast, the membrane irradiated for only 10 s shows a slightly greater fouling tendency. In part, the results are correlated to changes in solute rejection. The  $J_{om}/J_0$  for the membrane irradiated for 10 s decreased modestly from 0.813 to 0.803 while rejection increased 26% and solute flux decreased more than 30%. The increase in  $J_{om}/J_0$  for membranes irradiated for 60 and 180 s was not in proportion to irradiation time; the best performance was observed for the membrane irradiated for 60 s. It is possible that the enlargement of the membrane pore structure caused by long irradiation times allowed additional pore fouling by larger molecular weight natural organic matter components that were previously rejected. Under this hypothesis, the decrease in rejection of the membrane irradiated for 180 s could result in a lower fouling tendency as compared to the as-received membrane, but a higher fouling ten-

dency as compared to the membrane irradiated for 60 s, as a result of a change in the fouling mechanism. While the rejection by the 60 s-irradiated membrane was somewhat lower than the as-received membrane, it appears possible, using somewhat shorter irradiation times, to produce membranes that have both higher  $J_{om}/J_0$  and somewhat higher rejection than the as-received membranes.

Examination of the flux parameters in Table 2 shows that in addition to a lower fouling tendency, the graft modified membrane irradiated for 60 s was also easier to clean. Hydrodynamic cleaning alone recovered the same fraction of the initial flux ( $J_1/J_0 = 0.976$ ) as achieved by cleaning the as-received membrane with caustic.

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