

Characterization of Membrane Properties & Adsorptive Fouling of UF membranes

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A set of ultrafiltration (UF) membranes were cast from polysulfone (PS) blended with a block copolymer, sulfonated polyethersulfone/polyethersulfone (SPEES/PES), using the phase inversion process. The hydrophilicity, charge density, pore size, and porosity of the membranes were varied and controlled by changing the blending ratio of SPEES/PES to PS and the total solids content. Physicochemical properties of the membranes were characterized by contact angle, streaming potential, polyethylene glycol (PEG) retention, and Atomic Force Microscopy (AFM). Fouling characteristics of the membranes were also investigated with adsorption (without permeation) and crossflow filtration experiments using Suwannee River humic acid (SRHA) as a model foulant.

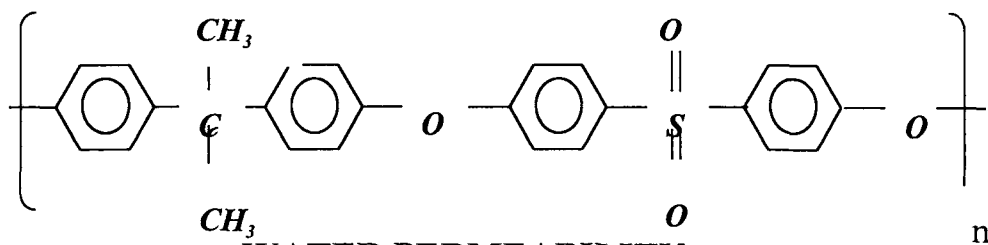
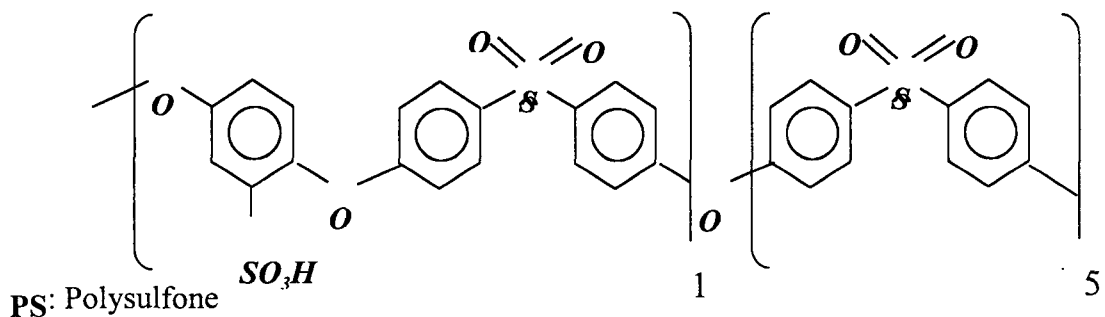
There was an absolute tendency of the water permeability to increase with the SPEES/PES content, but decrease with the total solids content. The introduction of SPEES/PES to the PS membrane enhances the hydrogen bonding capacity of the membrane matrix due to the ionized sulfonyl groups in the SPEES/PES, so the hydrophilicity increases with the SPEES/PES content. At the same time, the ionizable groups in the SPEES/PES provide electric repulsion, and increase the effective pore size. As a result, the water permeability increases with the SPEES/PES content. Considering the results of water permeability, PEG retention, and AFM analysis, it was found that the porosity of the membranes tends to decrease with the total solids content, although the pore size remains approximately the same. The results of a series of the adsorption experiments showed that the higher SPEES/PES content of the membranes (i.e., the higher the hydrophilicity), the lower the adsorption of SRHA. The crossflow filtration results showed a good correlation with the adsorption testing results, i.e., the greater the adsorption of SRHA, the greater the fouling. A higher total solids content (i.e., lower porosity) was also found to cause less fouling by SRHAs.

SPEES/PES-PS ULTRAFILTRATION MEMBRANES

CASTING PARAMETERS

% solid content			
SPEES/PES to PS ratio	MC20 SPEES/PES : 0 % PS : 17.9 % NMP+PA : 82.1 %	MC23 SPEES/PES : 0 % PS : 19.93 % NMP+PA : 80.07 %	MC26 SPEES/PES : 0 % PS : 21.93 % NMP+PA : 79.07 %
	MC21 SPEES/PES : 1.65 % PS : 16.28 % NMP+PA : 82.1 %	MC24 SPEES/PES : 1.65 % PS : 18.28 % NMP+PA : 80.07 %	MC27 SPEES/PES : 1.65 % PS : 20.28 % NMP+PA : 79.07 %
	MC22 SPEES/PES : 3.33 % PS : 14.6 % NMP+PA : 82.1 %	MC25 SPEES/PES : 3.33 % PS : 16.6 % NMP+PA : 80.07 %	MC28 SPEES/PES : 3.33 % PS : 18.6 % NMP+PA : 79.07 %

SPEES/PES: Sulfonated-polyethersulfone/Polyether sulfone



WATER PERMEABILITY

Filtration tests were performed using a 28.7cm² diameter UF cell with magnetic stirrer (Amicon, Minnetonka, MI). The pressure was applied via a compressed nitrogen tank, and was varied between 68.9 kPa and 206.7 kPa (10psi and 30psi).

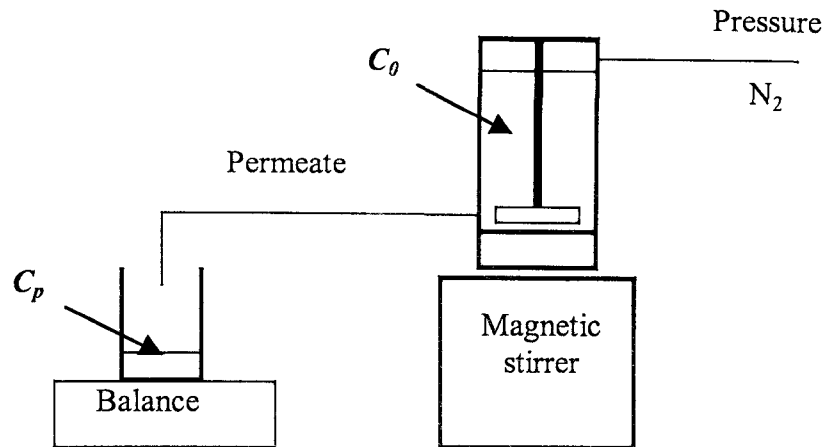


Figure 1 Amicon cell dead-end setup

The variation of water flux was plotted versus applied pressure and the slope represents the membrane water permeability symbolized by L_p .

Table 1 Water permeability and thickness of membranes

MC20 L_p (10^3 LMH/Pa) = 4.57 Total Thickness (μm) = 177.8 Skin Thickness (μm) = 76.2	MC23 L_p (10^3 LMH/Pa) = 1.53 Total Thickness (μm) = 210.8 Skin Thickness (μm) = 109.2	MC26 L_p (10^3 LMH/Pa) = 0.95 Total Thickness (μm) = 193.0 Skin Thickness (μm) = 91.4
MC21 L_p (10^3 LMH/Pa) = 11.27 Total Thickness (μm) = 231.1 Skin Thickness (μm) = 129.5	MC24 L_p (10^3 LMH/Pa) = 4.00 Total Thickness (μm) = 274.3 Skin Thickness (μm) = 172.7	MC27 L_p (10^3 LMH/Pa) = 4.00 Total Thickness (μm) = 246.4 Skin Thickness (μm) = 144.8
MC22 L_p (10^3 LMH/Pa) = 15.73 Total Thickness (μm) = 241.3 Skin Thickness (μm) = 139.7	MC25 L_p (10^3 LMH/Pa) = 6.8 Total Thickness (μm) = 304.8 Skin Thickness (μm) = 203.2	MC28 L_p (10^3 LMH/Pa) = 5.15 Total Thickness (μm) = 269.2 Skin Thickness (μm) = 167.6

XPS ANALYSIS: SURFACE ELEMENTARY COMPOSITION

This technique is used to determine the elementary composition of a surface sample. It is known under several names: X-ray photoelectron spectroscopy (XPS), electron spectroscopy for chemical analysis (ESCA), high-energy photoelectron spectroscopy (HEPS), induced emission spectroscopy (IEES0, photoelectron spectroscopy of the inner shell (PESIS) and energy dispersion system (EDS). The principle is simple: the sample surface is bombed by X-rays and the kinetic energies of photoelectrons ejected are measured. Because the binding energy of those electrons, also called core electrons, is a characteristic of an individual element, each chemical element is identifiable (Oldani and Schock, 1989; Clark and Feast, 1975). For each element, the binding energy depends on the energy level of the core electron, which can be 1s, 2s, 2p_{1/2}, and/or 2p_{3/2}. In general, the ESCA spectrum of a given core level consists of well resolved peaks corresponding to electrons escaping without undergoing energy losses, superimposed in a background tailing to lower kinetic energy arising from inelastically scattered electrons.

This technique provides information related to surface, subsurface, or essentially bulk properties, depending on differences in escape depths for photoemitted (or Auger) electrons corresponding to different kinetic energies. By varying the incident energy, it is possible to use ESCA to depth profile samples to investigate their homogeneity. Hence, if an element gives two or more signals from levels with very different escape depths, it ought to be possible to use the relative intensities of the signals to calculate the thickness of the layer containing that element (Clark and Feast, 1975).

The principle advantages of this technique are:

- the sample may be solid, liquid or gas, and the technique is essentially non-destructive
- the sensitivity of this technique is such that a fraction of a monolayer coverage may be detected
- high sensitivity is independent of the spin properties of any nucleus and is applicable in principle to any element of the periodic table. Hydrogen and helium are exceptions, being the only elements for which the core levels are also the valence levels
- information can be obtained on both the core and the valence energy levels of molecules
- only the top 50-100 Å of the samples are analyzed (Clark and Feast, 1975; Stengaardh, 1988)

In our experiments the data were collected by a Perkin-Elmer/Physical Electronics Division model n° 5400 X-ray photoelectron spectrometer with Mg K α X-radiation, 1253.6 eV

(15kV, 400W). For the determination of the atomic composition of each element, data were collected for multiplex spectra at 0.05 eV/step for 100 mses/step with a 35.75 pass energy. The atomic composition was determined using peak area sensitivity factors described by Wagner et al. (1979). The accuracy of the instrument is 0.1 eV, and the minimum detection limit in the relative chemical composition determination is about 0.2%. Prior to analysis pieces of membranes (about 1 cm²) were put in petri dishes and let at room temperature for one day. Before starting the analysis the samples were placed in a vacuum for about 15 min, under a base pressure of 1 to 1.4.10⁻¹¹ psi. The analysis pressure was in the range 0.2 to 1.0.10⁻¹¹ psi. In our experiments ESCA measurements were carried out to determine the atomic composition (C, O, S, N) of the clean membranes.

Table 2 Elementary composition obtained by XPS of some SPEES/PES membranes

Membrane	MC 20	MC 21	MC 22	MC 24	MC 27
C (%)	76.28	74.82	75.53	72.97	70.99
O (%)	19.15	19.97	19.75	22.17	22.68
N (%)	1.87	1.94	0	3.16	1.88
S (%)	2.7	3.28	4.76	1.7	4.45

PEG RETENTION: DETERMINATION OF MWCO

In order to characterize the membrane pore size, molecular weight cut-off (MWCO) was determined using model solutes. Synthetic polymers, such as polyethylene glycol (PEG), dextran, polyvinylpyrrolidone are usually chosen because they do not interact strongly with the membrane material. In this study we used a group of four PEG, with molecular weights of 300, 600, 3350 and 10000 Da purchased from Sigma (St Louis, MO). Lentsch et al. (1993) used an empirical equation to calculate the Stokes radius of PEG. Experimental PEG diffusion coefficient measurements were combined with the Stokes-Einstein law to give the following relation:

$$r_s = 0.045 M^{0.44} \quad (1)$$

where r_s : PEG Stokes radius (nm)

M: molecular weight (Da)

The Stokes radii calculated for the PEG used in this study are presented in Table 3.

Table 3 Solute radius of PEG calculated by empirical Lentsch's equation (1)

MW (Da)	300	600	3350	10000
r_s (nm)	0.5	0.75	1.6	2.6

Filtration tests were performed using a 28.7cm² diameter UF cell with magnetic stirrer (Amicon, Minnetonka, MI). The pressure was applied via a compressed nitrogen tank, and was varied between 68.9 kPa and 206.7 kPa (10psi and 30psi). Membrane water permeability was measured before and after each filtration experiment in order to check for membrane fouling by PEG. For each applied pressure, PEG concentrations in the retentate and permeate were measured by a TOC analyzer (Phoenix 8000, Dohrmann) and PEG retentions were calculated using the following equation:

$$R = 1 - \frac{C_p}{C_0} \quad (2)$$

Because of concentration polarization occurring in the retentate side, an intrinsic retention must be defined by:

$$R^* = 1 - \frac{C_p}{C_m} \quad (3)$$

where C_m represents the concentration at the membrane surface [14]. The film model is used to relate R and R^* :

$$\ln\left(\frac{1-R}{R}\right) = \ln\left(\frac{1-R^*}{R^*}\right) + \frac{J}{k} \quad (4)$$

R^* is obtained by the intercept of the slope of $\ln\left(\frac{1-R}{R}\right)$ versus flux J . The plot of intrinsic retention versus flux is used to determine the membrane MWCO.

In order to get the average corresponding pore radius, we used a model of steric exclusion as presented by Ferry (Deen, 1987). When size exclusion is the only selectivity phenomena the intrinsic retention extrapolated to no flux is equal to

$$R_{J=0}^* = (1 - (1 - \lambda)^2)^2 \quad (5)$$

with $\lambda = \frac{r_s}{r_p}$ r_s , solute radius, r_p pore radius

The first approximation is to consider that the membrane pores are all the same size. In this case an average pore radius can be calculated from the values of R^* determined by the retention experiments and PEG radius. This method allows the calculation of the pore radius of the homogeneous membrane equivalent to the membrane tested. This is a good method in our case where we want to compare different membranes.

Table 4 MWCO and pore radius determined by PEG retention experiments

MC20 MWCO (Da) = 3350 r_p (nm) = 1.9	MC23 MWCO (Da) = 1000 r_p (nm) = 1.14	MC26 MWCO (Da) = n.a. r_p (nm) = n.a.
MC21 MWCO (Da) = 2700 r_p (nm) = 1.76	MC24 MWCO (Da) = 2850 r_p (nm) = 1.8	MC27 MWCO (Da) = 2850 r_p (nm) = 1.8
MC22 MWCO (Da) = 9450 r_p (nm) = 3.06	MC25 MWCO (Da) = r_p (nm) =	MC28 MWCO (Da) = n.a. r_p (nm) = n.a.

CONTACT ANGLE: HYDROPHOBICITY

The captive air bubble method was used in this research. It is based on measuring the contact angle between an air bubble and the membrane covered with water.

Prior to measurement, membranes were stored in petri dishes at 4°C. They were soaked in milli-Q water for three hours, with three water changes, and then soaked in 5% NaCl solution for one hour. All membranes were then flushed in the stirred cell in order to remove any trace organic compounds used by the manufacturer to prevent drying and preserve the membrane.

The membranes were cut into pieces and stored in water. Membrane strips were tapped inside a glass cell. After this cell was completely filled with water, an air bubble was injected using a microliter syringe. This bubble moved vertically and rised the membrane surface. A light source was placed behind the sample and the light was focussed through a slit. The contact angle was measured with the goniometer.

Table 5 Contact angles obtained by captive air bubble. Comparison with data measured by Orange County District

MC20 CA = 76.6 ± 3.6 CA (Orange Dist.) = 64.9	MC23 CA = 78.4 ± 2.8 CA (Orange Dist.) = 65.4	MC26 CA = 79.55 ± 2.7 CA (Orange Dist.) = 67.1
MC21 CA = 77.6 ± 4.6 CA (Orange Dist.) = 61.5	MC24 CA = 77.8 ± 3.3 CA (Orange Dist.) = 61.6	MC27 CA = 76.17 ± 4.8 CA (Orange Dist.) = 61.8
MC22 CA = 79.6 ± 4.4 CA (Orange Dist.) = 61.2	MC25 CA = 78.4 ± 2.6 CA (Orange Dist.) = 61.6	MC28 CA = 78.8 ± 3.6 CA (Orange Dist.) = 61.6

AFM: MEAN DIAMETER

Atomic Force Microscopy (AFM) is used for direct analysis of membrane surface properties, such as pore size distribution, pore shape, and surface roughness. This technique does not require any special preparation of the sample, and the sample can be imaged in either air or liquid. The wet membranes are studied in contact mode. In this case the probe tip scans across the sample surface and is in direct physical contact with the sample. It can then respond to very short-range repulsive interactions with the sample.

The AFM observations were performed on a Digital Nanoscope II instrument. Cantilevers, made from silicon nitride, are 200 μ m long and have a triangular shape. The spring constant of the narrow cantilever is $k=0.032\text{N/m}$. The tip is also made of silicon nitride and has a pyramidal shape. Square pieces (5mm*5mm) of the membrane were cut and attached to the magnetic holder using doubled-sided tape. The wet membrane surface was studied by contacting the surface with a drop of ultrapure water after sample mounting.

Pore sizes are estimated from AFM images and calculated by AFM surface analysis software. Line profiles are selected to traverse the AFM image and pass through the pores. To determine pore size, the operator must choose points on each height profile where the pore is considered to start and end. The pore radius is then the horizontal distance between these points. The porosity of the membrane was estimated using the measured average pore diameter and the “lakes analysis” included with the software.

Table 6 Pore diameter (dp in nm) and average roughness (Rms in Å) measured after AFM images. Comparison with values obtained at Orange County District

MC20		MC23		MC26	
UI dp = 56 Rms = 40.6	OC dp = 86 Rms = 43.6	UI dp = 86.7 Rms = 70.8	OC dp = 108 Rms = 74.2	UI dp = 69.4 Rms = 65.9	OC dp = 90 Rms = 48.8
MC21		MC24		MC27	
UI dp = n.a. Rms = n.a.	OC dp = 92 Rms = 14.8	UI dp = n.a. Rms = n.a.	OC dp = 45 Rms = 78.9	UI dp = n.a. Rms = n.a.	OC dp = 58 Rms = 24.4
MC22		MC25		MC28	
UI dp = 415 Rms = 308	OC dp = 153 Rms = 275	UI dp = n.a. Rms = n.a.	OC dp = 115 Rms = 120	UI dp = n.a. Rms = n.a.	OC dp = 120 Rms = 165.6

STREAMING POTENTIAL: PORE CHARGE

Zeta potential of membrane surface were obtained from streaming potential measurements on an instrument build according to Nyström's research (Nyström et al., 1989; Nyström and Zhu, 1997). The measuring cell consists of two cylindrical half-cells made in plexiglass. To prepare the electrodes 18 X 18 per linear inch copper mesh is cut into two disks of 17mm and 29mm diameter. These disks are soldered to a 0.5mm copper wire. Both disks and wire are silver plated by electrolysis and chloridized by electrolysis in 0.1N HCl at a total current of about 2mA during half an hour. After silver plating they are washed for a few hours to eliminate any excess chloride ions until the voltage is constant when no differential pressure is applied.

A peristaltic pump with a variable speed drive 6-600rpm is used to pump the liquid from the feed beaker through the cell. The speed is controlled with a speed drive system. Because of this peristaltic pump the flow is not perfectly smooth. A pulse dampener is added in the line to reduce the fluctuations of the flow. The two cell compartments are connected to a Capsuhelic differential pressure gage (0-5psi, accuracy ± 0.05 psi). The voltage is measured with a Fluke 45 dual display multimeter (resolution 0.001mV, accuracy 0.02%).

The solution is circulated under no differential pressure until the difference in potential between the two half cells remain constant (about 30 min). The conductivity of the solution is measured and the pressure is increased up to 4.5psi by touching valve 2. The resulting difference in potential is measured. The pressure is decreased of 0.5psi until 1psi and the potential is measured each time. At the end of the series the conductivity of the solution is checked and the pressure is released. The cells are emptied and the solution is replaced by Milli-Q water. The system is flushed with the water before any other measurement.

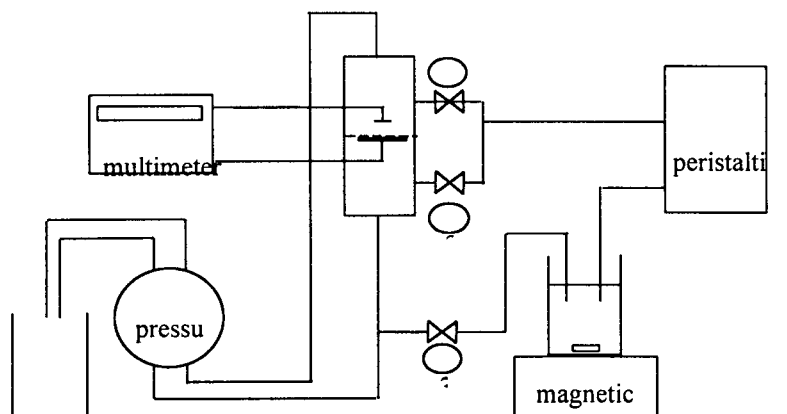


Figure 4 Experimental set-up for zeta potential measurement

The Helmholtz-Smoluchowski equation was used to calculate the zeta potential from these measurements:

$$\xi = \frac{\eta \kappa \Delta E}{\varepsilon_0 \varepsilon_r \Delta P} \quad (6)$$

with: $T = 20^\circ \text{C} \pm 1^\circ \text{C}$ $\Delta E = \text{potential difference (mV)}$
 $\eta = 1.002 \cdot 10^{-3} \text{ (kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}\text{)}$ $\Delta P = \text{pressure difference (psi)}$
 $\varepsilon_0 \varepsilon_r = 80.37$ $\kappa = \text{conductivity (mS} \cdot \text{cm}^{-1}\text{)}$
 $\xi = \text{zeta potential (mV)}$

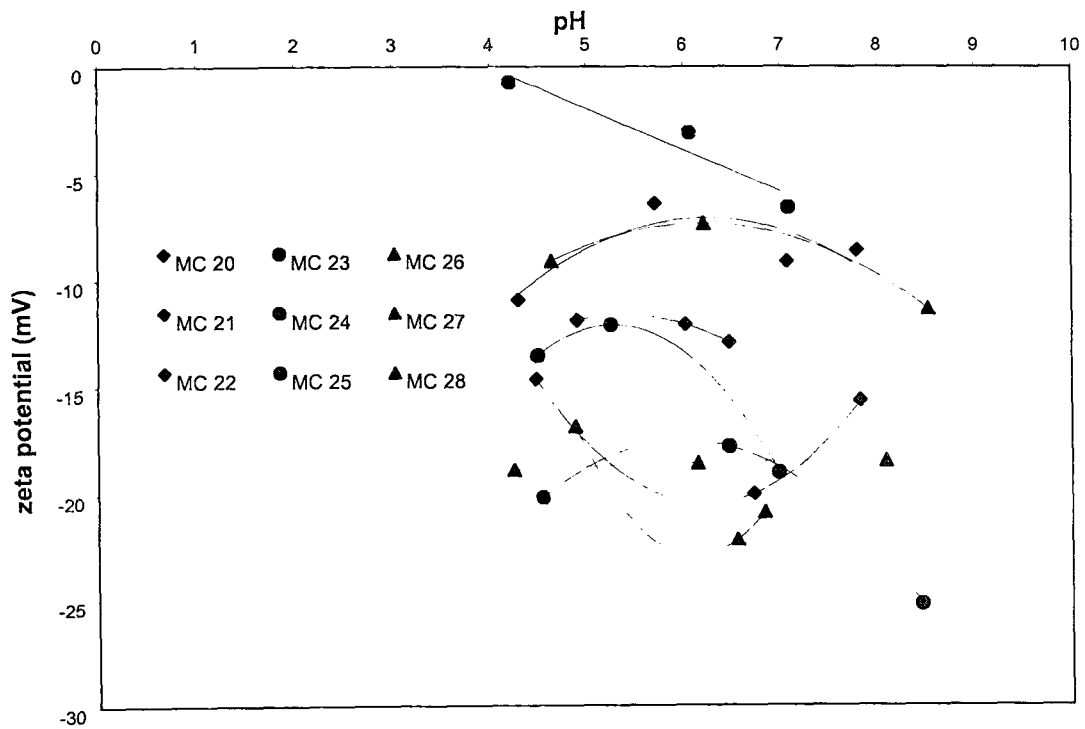


Figure 5 Zeta potential measurements ($[\text{NaCl}] = 0.01\text{M}$ and $[\text{Na}_2\text{HPO}_4] = 0.0005\text{M}$)

ADSORPTION EXPERIMENTS

First membrane water permeability was measured. In these experiments the organic matter was Suwannee River reference humic acid purchased from the International Humic Substances Society. A solution of this humic acid was placed in a glass jar with the membrane on the top, the skin side facing the interior of the jar. A Teflon sheet covered by one sheet of Parafilm and three sheets of aluminum foil was then placed on the membrane. The jar was closed and turned upside down, in order to contact the solution and membrane. The aluminum sheets were required to avoid any leakage from the jar. The jar was then placed on a gyrator shaker in the dark at $22 \pm 2^\circ\text{C}$ and it was shaken during the time of the experiment.

After the adsorption period the membrane was removed from the jar. The humic acid concentration of the supernatant was measured by UV absorption (254nm) and the percent of mass adsorbed was calculated by:

$$\% \text{ mass adsorbed} = 100 * \frac{UV_0 - UV_f}{UV_0} \quad (7)$$

with UV_0 : UV measurement of feed solution before adsorption

UV_f : UV measurement of supernatant after adsorption

Water permeability was measured and compared with the value obtained with the clean membrane. The membrane resistances were calculated and the adsorptive resistance, i.e. the resistance due to the adsorbed humic acid is obtained by:

$$R_a = R_t - R_m \quad (8)$$

with R_a : membrane adsorptive resistance

R_t : total membrane resistance after adsorption

R_m : clean membrane resistance

Clark and Lucas (1998) proposed a model based on diffusion and adsorption of humic acid materials from a mixed solution into a one-dimensional porous medium. They introduced a interaction parameter, Km , given by:

$$Km = \frac{h}{\alpha} \quad (9)$$

where K = the partition coefficient, h = solution depth (in the jar), m = membrane thickness, and where α is calculated from

$$\frac{UV_0 - UV_f}{UV_0} = \frac{1}{1 + \alpha} \quad (10)$$

For a given membrane, K_m characterizes the strength of interaction between the humic acid and the membrane. The main benefit of the parameter K_m over simply presenting the fractional uptake is that K_m takes into account the solution volume.

Table 7 Interaction parameter (K_m)

MC20 $K_m = 0.7$	MC23 $K_m = 0.59$	MC26 $K_m = 0.43$
MC21 $K_m = 0.14$	MC24 $K_m = 0.25$	MC27 $K_m = 0.26$
MC22 $K_m = 0.04$	MC25 $K_m = 0.04$	MC28 $K_m = 0.04$

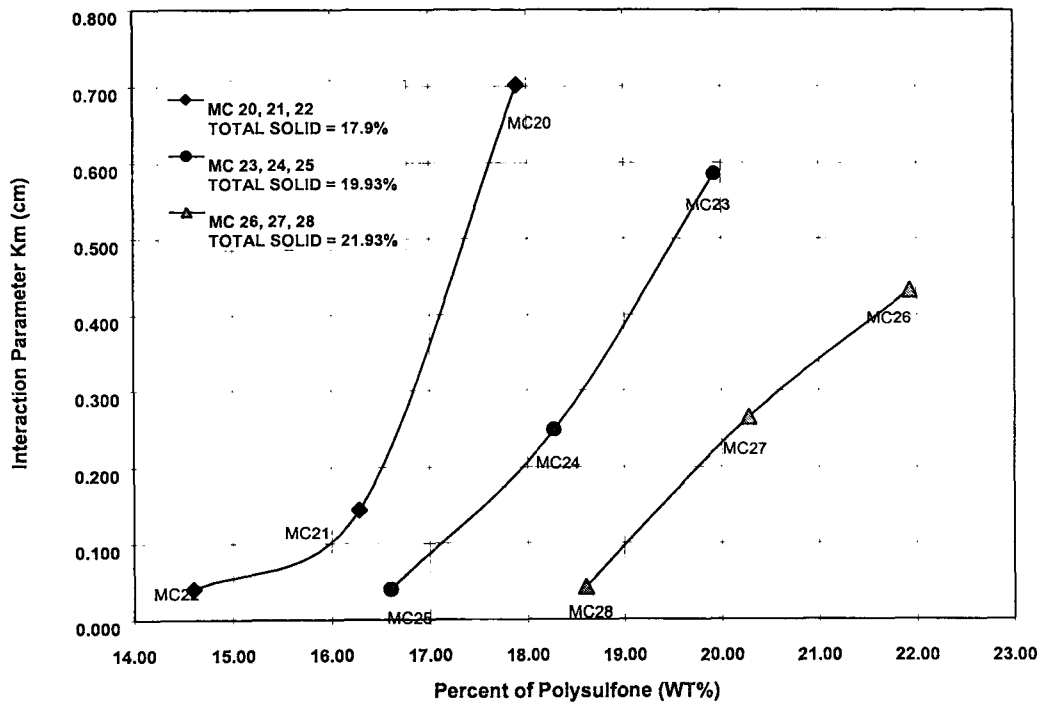


Figure 6 Effect of SPEES/PES content on interaction parameter

CROSSFLOW FILTRATION EXPERIMENTS

A channel-type crossflow UF/MF membrane filtration unit (Model SEPA CF System, Osmonics Inc., Minnetonka, MN) was used for crossflow filtration tests. A schematic diagram of the crossflow membrane filtration system is shown in Figure 2.12. A 12 liter glass jar served as a feed tank, and a large magnetic stirrer was used for mixing the feed tank. A Masterflex peristaltic pump (Model H-07017-00, Cole-Palmer Instruments Co., Chicago, IL) was used to drive the feed water to the membrane cell. The pump was driven by an adjustable speed gearmotor (Model Type 42DSBEPM-E1, Bodine Electric Company, Chicago, IL) and a permanent magnet control with analog interface board (Model Type FPM 856, Bodine Electric Company, Chicago, IL). Two pulsation dampeners (Model H-07596-20, Cole-Palmer Instruments Co., Chicago, IL) were installed serially close to the pump to reduce the pulsations created by the peristaltic pump. This provided almost pulsation-free feed to the channel-type crossflow UF/MF membrane filtration unit.

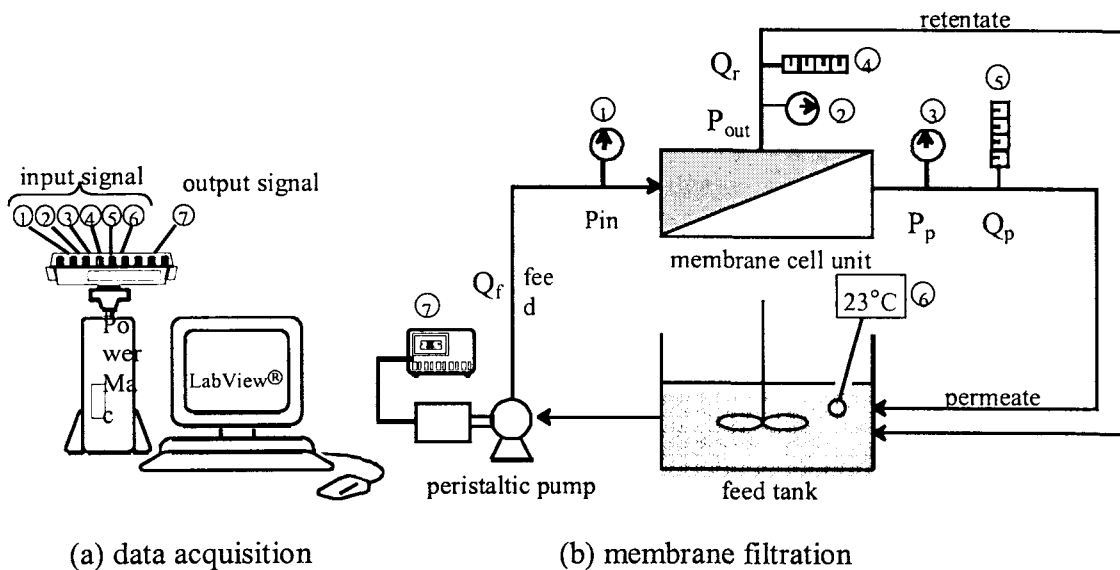


Figure 7 Schematic diagram of cross-flow filtration experimental set-up

A general-purpose programming system called LabView was employed to control the system as well as to continuously log data onto a computer during filtration tests. All measurement instruments in the system generate analog signals, which could be logged onto a computer. Inlet, outlet, and permeate pressures were measured by digital pressure transmitters (Model PG-4/20, PSI-Tronix, Tulare, CA). Permeate and retentate flowrate were measured by

150 mm variable area flowmeters (Model H-03229-31 and H-03229-35, respectively, Cole-Palmer Instruments Co., Chicago, IL) equipped with flowmeter electronic conversion modules (Model H-03298 00, Cole-Palmer Instruments Co., Chicago, IL). Temperature was measured by an RTD probe (Model DD93560-02, Cole-Palmer Instruments Co., Chicago, IL), which was inserted into the permeate tube line. The temperature probe was connected to an RTD indicator-transmitter (Model H-08099-00, Cole-Palmer Instruments Co., Chicago, IL).

The membrane was cut and soaked in Milli-Q water for at least four hours, and the water was changed every half hour up to two hours. The membrane was then pre-compacted by filtration of Milli-Q water under the operating transmembrane pressure of 20 psi for 24 hours or until a constant flux was established. The variation of water flux with pressure was then measured to check the linearity.

Crossflow filtration tests were carried out in the constant transmembrane pressure mode. The humic acid solutions were filtered for 24 hours. Samples were taken from the feed, retentate and permeate during this period.

The cleaning procedure involved several steps. After humic acid filtration, the membrane was flushed for 5 minutes with clean water, in order to measure the resistance due to concentration polarization (surface wash). The membrane was then taken out of the cell and its surface was rinsed with clean water as thoroughly as possible. Then, the membrane was put back in the filtration cell with its skin side facing the permeate spacer, and the system was flushed with clean water for about 5 minutes under the same transmembrane pressure (backflush). After backflushing, the clean water flux was measured again under the same operating conditions. The last step of the cleaning procedure was to put the fouled membrane into 0.1 M NaOH solution for about 5 hours (chemical cleaning). The chemical cleaning was to remove most of the adsorbed matter in membrane pores and surface. After rinse the water permeability was measured again.

In order to prevent any bacterial growth in the system during down times, it was filled with 0.01 % NaN₃ solution after each filtration test. With this procedure, we were able to get reproducible and coherent results of filtration with humic acid.

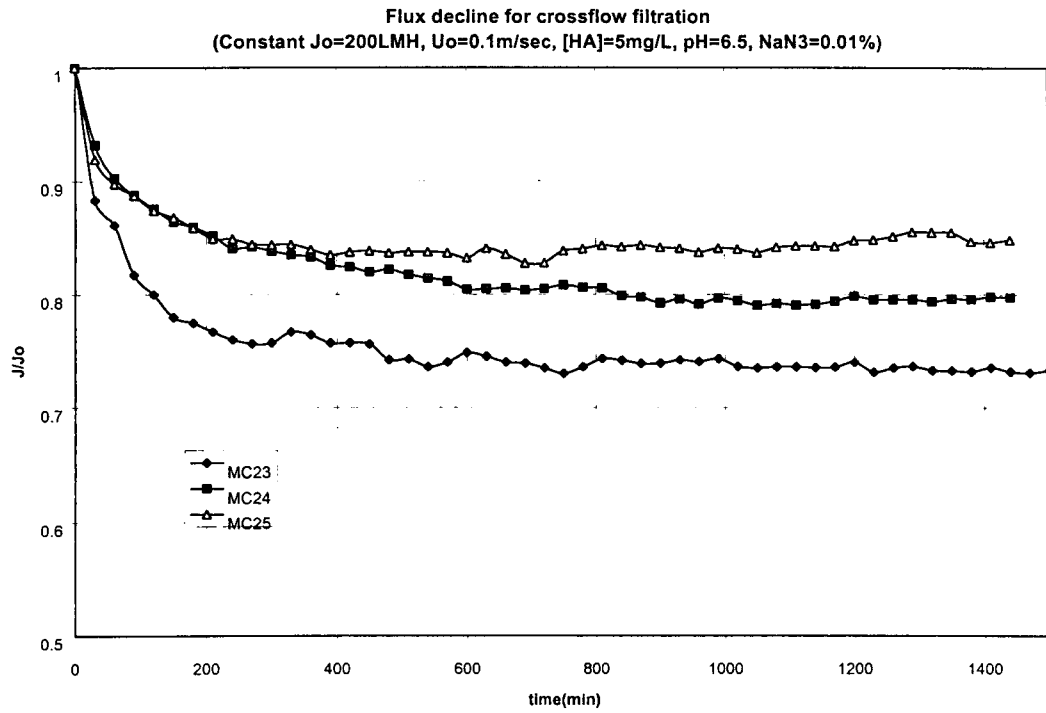


Figure 8 Effect of SPEES/PES contents on flux decline during crossflow filtration

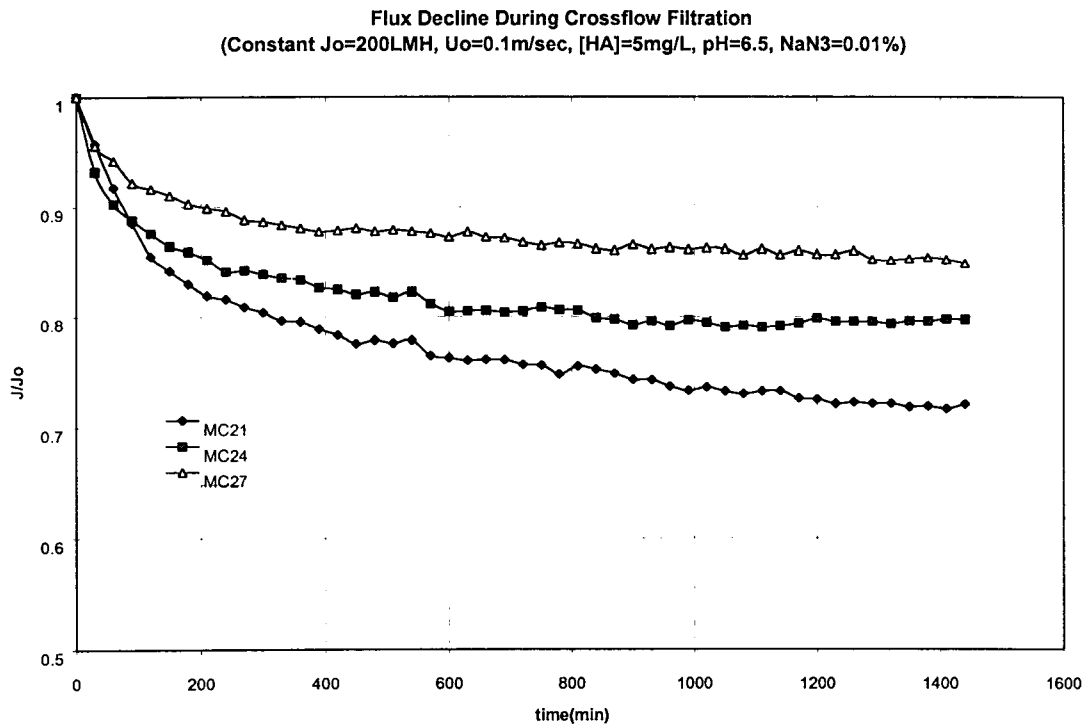


Figure 9 Effect of solid contents on flux decline during crossflow filtration

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