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Hydrophilic surface modification of microporous poly(tetrafluoroethylene) membranes through defluorination and sulfonation

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Abstract. Poly(tetrafluoroethylene) (PTFE) microfiltration membranes were chemically modified with a two-step chemical reaction. The membranes were defluorinated through controlled etching with sodium-naphthalene solution, and then sulfonated using chlorosulfonic acid. The effects of surface modification on the morphology, pore size and distribution, ion-exchange capacity (IEC), hydrophilicity, pure water flux, and fouling of the membrane were investigated. Using X-ray photoelectron spectroscopy (XPS), the surface composition of the sulfonic acid groups on the modified PEFE membranes was analyzed. As the degree of sulfonation increased, the IEC and hydrophilicity of the membranes increased without any deformation of the morphology or pore size, as observed by scanning electron microscopy (SEM) and capillary flow porometry under controlled reaction conditions. It was also observed that the flux of pure water increased with decreasing intrinsic resistance as the degree of sulfonation increased. Membrane fouling with humic acid was suppressed with an increasing degree of sulfonation, because of enhanced electrostatic repulsion between the negatively charged surface and negative charged humic acid.

Keywords: hydrophilicity; microfiltration; microporous and porous membranes; morphology; surface modification

1. Introduction

Owing to the complexity of wastewater with hazardous substances and stringent requirements for purity of drinking water, numerous membrane technologies for water treatment have been extensively investigated (Ariono *et al*. 2018). Progress in research on membranes for water treatment, from reverse osmosis to microfiltration, has been made by varying the size of pores, controlling the morphology, enhancing mechanical properties, and reducing fouling on the surface of the membrane (Wang and Zhang 2022). The study of techniques for surface modification of membranes is essential because membrane fouling is inevitable, and the interaction between foulants and membrane surfaces needs be reduced to enable longer-lasting filtration operations.

With respect to membrane materials, a number of engineering polymer materials such as polysulfone (PSF), polyethylene (PE), and polyvinylidene fluoride (PVDF) have been extensively used for commercialized membranes. In terms of chemical stability and mechanical durability, one potential candidate as an excellent membrane material is polytetrafluoroethylene (PTFE). However, owing to its low surface energy and hydrophobic nature, versatile commercial applications of water treatment and membrane manufacturing have been hindered. In order for hydrophobic PTFE to become hydrophilic, many studies have been conducted to modify the surface characteristics of PTFE materials, including UV lasers (Katan *et al*. 1998), electron and ion beam irradiation (Matienozo *et al*. 1994), plasma modification (Svorcik *et al*. 1998), and chemical etching (Zhao *et al*. 1999). All of the aforementioned treatments lead to improvement in adhesion and wettability because hydrophilic groups such as hydroxyl, carboxyl, and sulfonic acid on the surface are introduced. Among the above techniques of surface modification, plasma and high beam irradiation require sophisticated facilities, including vacuum lines, and are too expensive be utilized in industrial applications. However, surface modification by chemical etching is generally considered a desirable process in terms of cost-effective mass production while conserving the separation properties of membranes (Woo *et al*. 2021).

Although chemical etching of PTFE has been known to improve bondability with other substrates, the highly reactive chemical reaction of an etchant prepared with sodium metal and naphthalene in polar aprotic solvents with PTFE has not yet been fully explored. It is known that the etchant can defluorinate the C-F bonds of PTFE and can produce unsaturated carbons in polymer chains as well as chain cleavage at a high concentration of sodium naphthalene solution. Several studies have reported the modification of PTFE materials using a sodium naphthalene solution with the formation of unsaturated carbon bonds and

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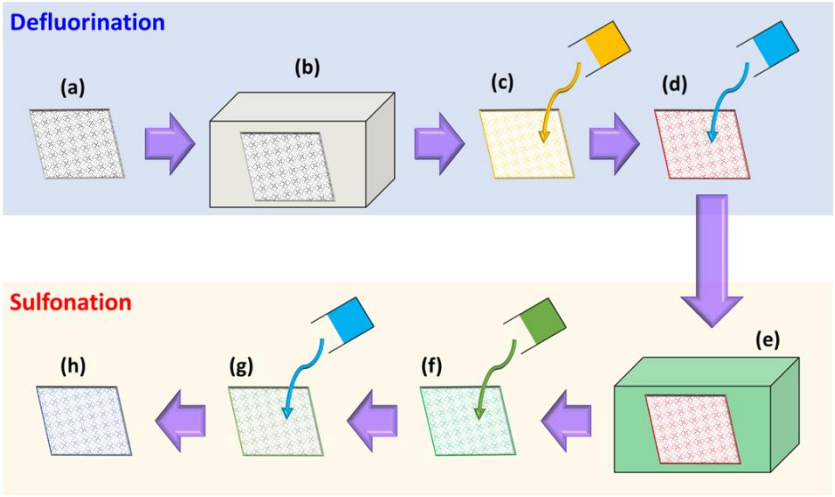

Fig. 1 Graphical illustration for the modification by defluorination and sulfonation: (a) a commercial hydrophobic PTFE membrane, (b) sodium naphthalene 0.1 M in tetrahydrofuran (THF) at room temperature for reaction times of 1, 3, or 5 min, (c) washed several times with THF, (d) rinsed several times with DI water to remove excess sodium naphthalene solution, (e) defluorinated membranes in 15 % (v/v) chlorosulfonic acid solution of 1,4-dioxane at 60℃ for 2 h, (f) washed several times with 1,4-dioxane, (g) rinsed with DI water to wash off the excess chlorosulfonic acid, and (h) the modified membranes

other functional groups such as hydroxyl and even carbonyl groups, depending on reaction conditions such as the concentration of sodium naphthalene and water, reaction temperature, and time (Noh *et al*. 1997). It was also reported that an increase in the sodium naphthalene solution concentration results in an increase in defluorination, as evidenced by a color change of the membrane from yellowish to intense dark tan. Thus, it is possible that such an inert and microporous hydrophobic PTFE membrane can be chemically modified as long as the reaction can be well controlled without any alteration of pores or deterioration of the polymer by means of mild reaction conditions.

In this study, we have illustrated the introduction of hydrophilic functional groups such as -SO_3, which is sulfonation, through a two-step modification in a controlled reaction. It will be shown here how the negative charges of sulfonic acid groups play a role in microfiltration in addressing the anti-fouling effect. The effect of surface modification on microfiltration membranes, such as ion exchange capacity, morphology, and hydrophilicity, has been characterized. Membrane performance, such as enhanced water flux and anti-fouling, has been evaluated. A further objective of this work is to develop a modified porous membrane using a simple and applicable method to facilitate the manufacture of PTFE membranes, and to decrease the fouling phenomenon by means of electrostatic repulsion between the negatively charged surface of membranes and negatively charged foulants.

2. Experimental

2.1 Materials

Poly(tetrafluoroethylene) (PTFE) hydrophobic membranes with a pore size of 0.22 μm were procured from Millipore, USA. Sodium-naphthalene complex solution (2.5 wt.% sodium, 7.5% wt. naphthalene, 90% wt. tetrahydrofuran, Seoil Tech., Korea) was used for defluorination. Tetrahydrofuran (THF, 99.5%), chlorosulfonic acid (99%), and 1,4-dioxane (99%), from Showa Chemical Co. Ltd., Japan, were used without further purification. Ethyl alcohol (≥99.9%) was purchased from Merck KGaA, Germany. Humic acid (H16752) with a weight-averaged molecular weight of 4000–20,000 Dalton was purchased from Sigma-Aldrich, USA. All chemicals were used as received.

2.2 Method of modification

2.2.1 Defluorination of PTFE membranes

Hydrophobic PTFE membranes were defluorinated by immersion in a 0.1 M concentration of sodium naphthalene solution in THF at room temperature. The PTFE membranes were treated for reaction times of 1, 3, or 5 min and then washed several times with THF and deionized water in sequence to remove excess sodium naphthalene solution. Finally, the tan-brown membranes were stored in aqueous ethyl alcohol solutions before the sulfonation reaction.

2.2.2 Sulfonation of PTFE membranes

The defluorinated membranes were soaked in 1,4-dioxane for several hours to allow chlorosulfonic acid to penetrate into the inner pores. The pre-wetted defluorinated membranes were then instantaneously transferred to a 15% (v/v) chlorosulfonic acid solution in 1,4-dioxane at 60 °C for 2 h for sulfonation. After the reaction, the modified membranes were gently transferred into a 1,4-dioxane bath in order to wash off the excess chlorosulfonic acid. Finally, the modified membranes were rinsed with deionized water and stored in deionized water prior to use.

2.3 Characterization measurements

2.3.1 X-ray Photoelectron Spectroscopy analysis

The surface composition of chemical functional groups on the modified membranes was analyzed using X-ray

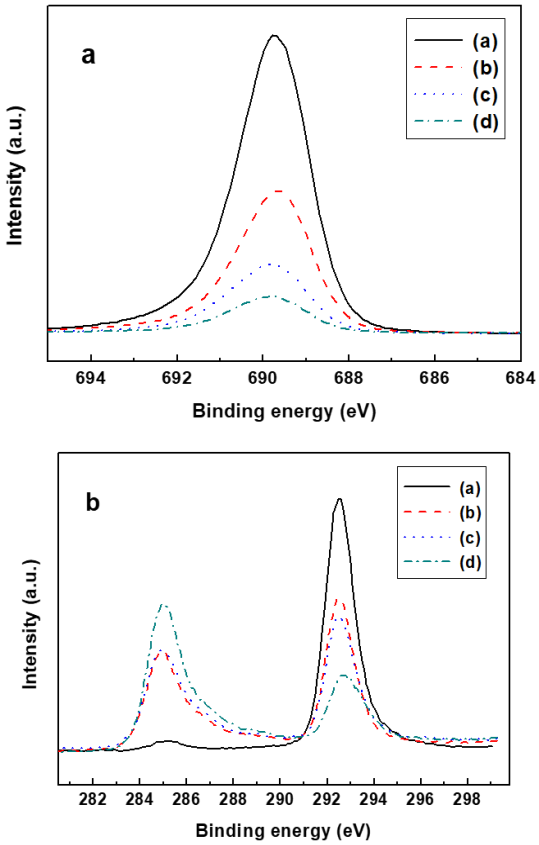

Fig. 2 XPS narrow scan for F 1s(a) and C 1s(b) spectra of the defluorinated-sulfonated PTFE membranes with different defluorination time (*t*) in minutes: (a) *t* = 0; (b) *t* = 1; (c) *t* = 3; (d) *t* = 5

photoelectron spectroscopy (XPS, Thermo Election, K-Alpha System spectrometer) equipped with a Kα (1486.6 eV) anode (72 W, 12 kV, 6 mA) source. The spectra were obtained at a sampling depth of less than 10 nm using a concentric hemispherical energy electron analyzer.

2.3.2 Scanning electron microscopy and pore size distribution

The membrane morphology of the samples was obtained by scanning electron microscopy (Hitachi, S-3500NThe pore size and distribution of the membranes were determined using a capillary flow porometer (Porous Materials Inc., CFP-1200AE), and Galwick (15.9 dyne/cm) was used as a pre-wetting liquid (Woo *et al*. 2018).

2.3.3 Ion exchange capacity, water uptake measurements and contact angle measurement

Ion-exchange capacity (IEC) was evaluated by titration, and the water uptake of the membranes was determined as reported by our group (Han *et al*. 2011). The static contact angles of the membranes were measured using a Phoenix 150 apparatus (SEO Instruments, Korea), and contact angles were analyzed from images of 0.05 mL droplets using an image analysis program (Surfaceware ver. 1.3). The measurement was carried out at 23 °C, and the value of the contact angle was an average of five measurements at different locations on the surface.

2.3.4 Liquid entry pressure

The membranes were mounted on a homemade cell with a diameter of 52 mm. Pressurized water measured with a digital pressure gauge (from 0 to 10 bar, Keller, PY-21Y) was supplied to the upper side of the membrane. A dry membrane was mounted on the grid cell supporter, and the bottom part of the membrane cell was filled with distilled water as the permeating liquid. The liquid entry pressure (LEP) value was measured as a function of the applied pressure at which the liquid started to flow from the membrane. The liquid entry pressure was determined using Eq. (3) (Garc´ıa-Payo *et al*. 2000):

$$\Delta P = -\frac{2\gamma \cos\theta}{r} \quad (1)$$

where ΔP is the pressure difference at the liquid-vapor interface (psi), γ is the liquid-vapor surface tension (dynes/cm), θ is the contact angle (degree), and *r* is the pore radius (μm). At least three measurements were taken for each sample and the average LEP was recorded.

2.3.5 Water flux experiments

Using a stirred filtration cell (Amicon Co., Ltd., Type 8050), filtration experiments were carried out. Pure water fluxes for the membrane were measured as a function of transmembrane pressure from 0.2 to 1.2 kg/cm^2. An electronic balance (Mettler Toledo PB1502-S) was used to monitor the cumulative mass of permeated water over time. Before measuring the pure water flux, all the membranes were pre-wetted with methanol and then washed with deionized water several times. Using flux results, the membrane hydraulic resistance (R_m) was evaluated in accordance with Eq. (2) (Mulder 1999):

$$J_W = \frac{\Delta P}{\mu \cdot R_m} \quad (2)$$

where J_w is the pure water flux (L·m^{-2}·h^{-1}), ΔP is the transmembrane pressure (kg·cm^{-2}), and μ is the viscosity of water (kg·m^{-2}·h^{-1}).

3. Results and discussion

3.1 Surface modification: defluorination / sulfonation

Hydrophobic PTFE microfiltration membranes were modified using a two-step chemical process: defluorination and sulfonation. Prior to sulfonation, PTFE membranes were defluorinated with a sodium naphthalene solution. By changing the reaction time, the degree of defluorination could be controlled.

To quantitatively evaluate the amount of defluorinated carbons and the formation of unsaturated carbon bonds, surface analysis was performed using X-ray photoelectron spectroscopy (XPS).

XPS narrow scan spectra of F 1s and C 1s were analyzed for the unmodified and defluorinated membranes, respectively. Fig. 2(A) shows a decrease in the intensity of the F 1s peak at a binding energy of 689.7 eV with increasing reaction time in the sodium naphthalene solution,

Table 1 Effective thermal conductivity (k_e) and tortuosity (τ) models

Sample name	F / C	C=C / C	S / C	DS(%)
Unmodified PTFE	2.00	0.00	0.000	0.00
PTFE-DF1	0.98	0.121	0.000	0.00
PTFE-DF2	0.82	0.165	0.000	0.00
PTFE-DF3	0.60	0.272	0.000	0.00
PTFE-DS1	0.97	0.108	0.026	5.2
PTFE-DS2	0.80	0.141	0.040	8.1
PTFE-DS3	0.63	0.214	0.051	10.2

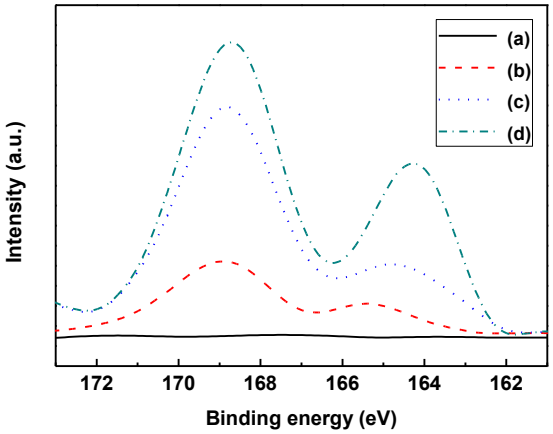

Fig. 3 XPS narrow scan for S 2p spectra of the defluorinated-sulfonated PTFE membranes with different defluorination time (t) in minutes: (a) t = 0; (b) t = 1; (c) t = 3; (d) t = 5

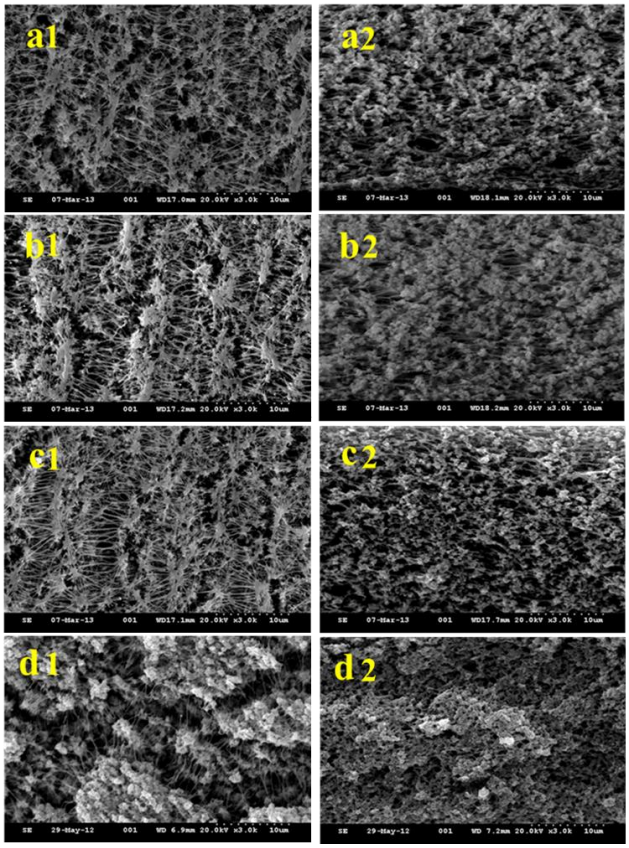

Fig. 4 Surface (a1-d1) and cross-sectional SEM (a2-d2) images of unmodified PTFE (0.22μm) membrane and modified membranes: (a) unmodified, (b) with 5.3% DS, (c) with 10.2% DS and (d) damaged sample (Magnification 3K)

owing to defluorination of the PTFE. As seen in Fig. 2(B), two peaks are observed in the C 1s spectrum. The peak at 291.2 eV is attributed to C 1s of the CF_2 species, which is only observed for the unmodified PTFE membrane. As the reaction time increases, however, another peak appears at 284.3 eV and the peak at 291.2 eV decreases in intensity, which indicates defluorination and the formation of CF=CF species on the treated PTFE membrane surface taking place at the same time (Hubert *et al*. 2012). The atomic ratio of fluorine to carbon (F/C) for the defluorinated PTFE membranes (PTFE-DF) decreased from 2.00 to 0.60 over the reaction period. The concentration of unsaturated carbons increased as the reaction time in the sodium naphthalene solution increased, as listed in Table 1. Thus, as reported by McCarthy *et al*., it is obvious that the chemical structure of PTFE (-CF_2–CF_2-) is modified to -CF=CF- (Shoichet *et al*. 1991).

Using three different concentrations of unsaturated carbon samples listed in Table 1, the second step, that is, sulfonation, was performed using chlorosulfonic acid. In order to control the degree of sulfonation with different numbers of unsaturated carbons in PTFE-DF membranes, the sulfonation reaction was carried out under finite reaction conditions, as mentioned in section 2.2.2. Fig. 3 shows the S 2p spectra of the PTFE membranes after sulfonation with different defluorination reaction times. The membranes exhibit two characteristic peaks corresponding to S $2p_{(3/2)}$ and S $2p_{(1/2)}$ at binding energies of 164.5 and 168.8 eV. As can be seen, the atomic concentration of sulfur increases with the concentration of unsaturated carbons. A quantitative determination of the concentration of sulfonic groups in the defluorinated-sulfonated PTFE membranes (PTFE-DS) was calculated, and the concentration of carbon obtained from the peak area of the XPS spectrum was divided by 2 because PTFE has two carbons in a monomer unit. Thus, the degree of sulfonation (DS) on the membrane surface listed in Table 1 is defined as the number of sulfonic acid groups divided by the total number of monomer units of PTFE in percent, as follows: 0, 5.3%, 8.1%, and 10.2% for defluorination reaction times of 0, 1, 3, and 5 min, respectively.

3.2 SEM analysis and pore size distribution

The effects of defluorination and sulfonation on the morphology of both the unmodified and modified PTFE microfiltration membranes was investigated by using SEM to observe the cross-section and top surface of the membranes. It can be seen that the top surface of the unmodified PTFE membrane has a porous fibrous microstructure characterized by nodes that are well interconnected by fibrils throughout the membrane surface, and the cross-section shows a tortuous pore structure, as can

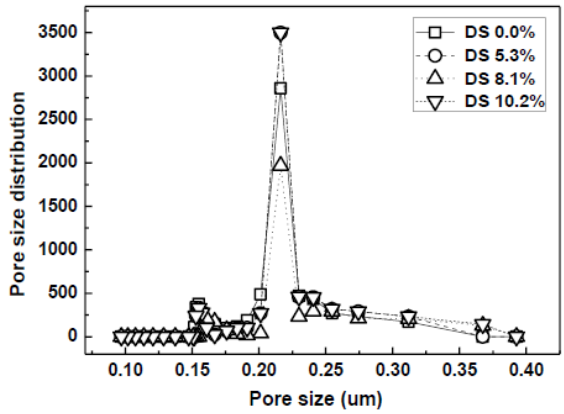

Fig. 5 Pore size distribution (PSD) with respect to its average pore diameter for the unmodified and sulfonated membranes with the different degrees of sulfonation

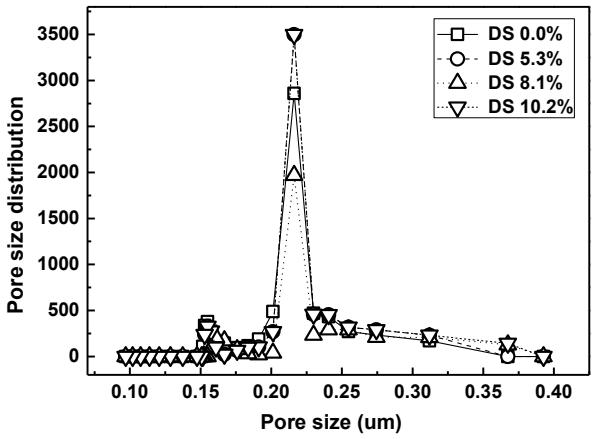

Fig. 6 Pore size distribution (PSD) with respect to its average pore diameter for the unmodified and sulfonated membranes with the different degrees of sulfonation

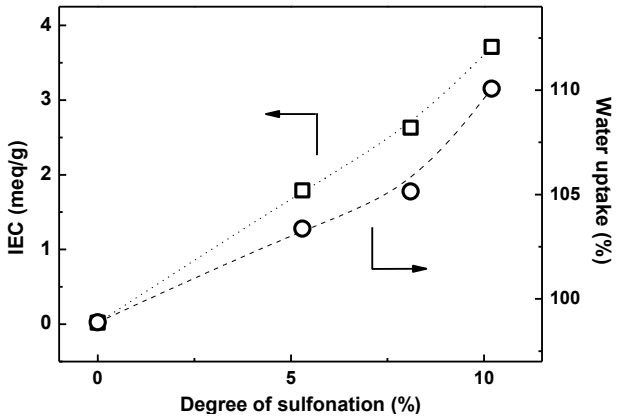

Fig. 7 Ionic exchange capacity (IEC) and water uptake of sulfonated PTFE membrane as a degree of sulfonation

be seen in Fig. 4a. The other two sets of images (Fig. 4b and 4c) illustrate that the modified membranes of 5.3% DS and 10.2% DS, respectively, appear quite similar to the unmodified ones. However, it should be noted that morphological deformation, as shown in Fig. 4d, can take place at defluorination times of over 15 min.

Since SEM images only provide morphological information regarding surface porosity, it is necessary to determine whether the pore size and porosity change during the two-step modification. Thus, compared with the unmodified membrane, flow porometry was performed. As can be seen in Fig. 5, the mean size of the pores did not vary after the modification, and the distribution of pore size did not change within experimental error (d_p = 0.22 μm ± 0.0132). Thus, modification only occurred on the surface of the membrane as well as the walls of the pores without deterioration of the microporous structure of the PTFE membranes within 5 min.

3.3 Degree of hydrophilicity

When membranes have hydrophilic functional groups on their surface, it is important to understand the water flux and physical properties of the membrane surface and micropore walls. As shown in Fig. 6, ion exchange capacity (IEC) and water uptake were measured as a function of the degree of sulfonation. As the concentration of sulfonic acids on the membrane surface, DS, increases, both the IEC value and the water uptake increase. It is well known that water uptake depends on the concentration of incorporated sulfonic acids on the membrane surface, which have a strong attraction for water owing to bound water (Hodge *et al*. 1996). Therefore, it can be expected that the wettability would be enhanced with IEC values or the degree of sulfonation on the surface and wall of the membrane.

In order to show direct evidence of the hydrophilic nature of the modified membranes, the contact angle and liquid entry pressure were measured. These are simple and available methods to characterize the hydrophobic or hydrophilic nature of functional groups attached to the surface of membranes (Huang *et al*. 2011). As shown in Fig. 6, the contact angle of the unmodified membrane (129°) was dramatically reduced as the degree of sulfonation increased, down to 35° for the 10.2% DS sulfonated membrane. Likewise, the liquid entry pressure (LEP), defined as the pressure difference from which the liquid penetrates into the pores of the hydrophobic membrane, decreased as a function of DS. In particular, for PTFE-DS3 (DS = 10.2%) water can permeate through the membrane under less than 1.6 bars of transmembrane pressure because the top surface and the surface of the pore walls are the most hydrophilic.

3.4 Water flux experiments

The relationship between the water flux and transmembrane pressure for the unmodified and sulfonated membranes was explored, as illustrated in Fig. 7a. The unsulfonated membrane is hydrophobic in nature, with a flux as low as 1969.2 LMH at 1.0 kg/cm^2. As more sulfonic acids are introduced into the membrane, there is a steeper slope in the water permeance. Thus, as the membranes become more hydrophilic owing to the introduction of sulfonic acid groups, the permeability of water increases. In particular, the slope of permeance for the modified membrane with a DS = 10.2% is five times the value of that for the unmodified membrane.

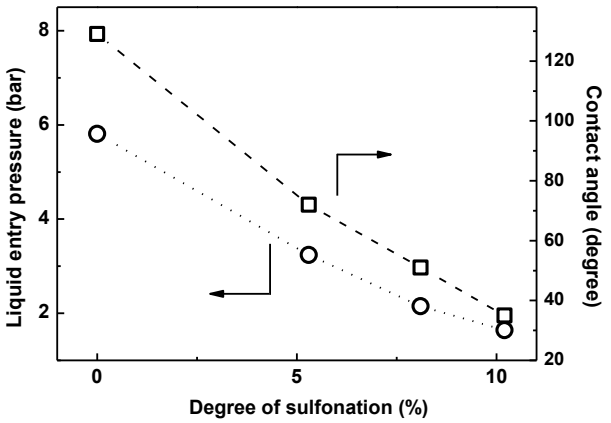

Fig. 8 Liquid entry pressure (LEP) and contact angles of unmodified and sulfonated PTFE microfiltration membranes with as a degree of sulfonation

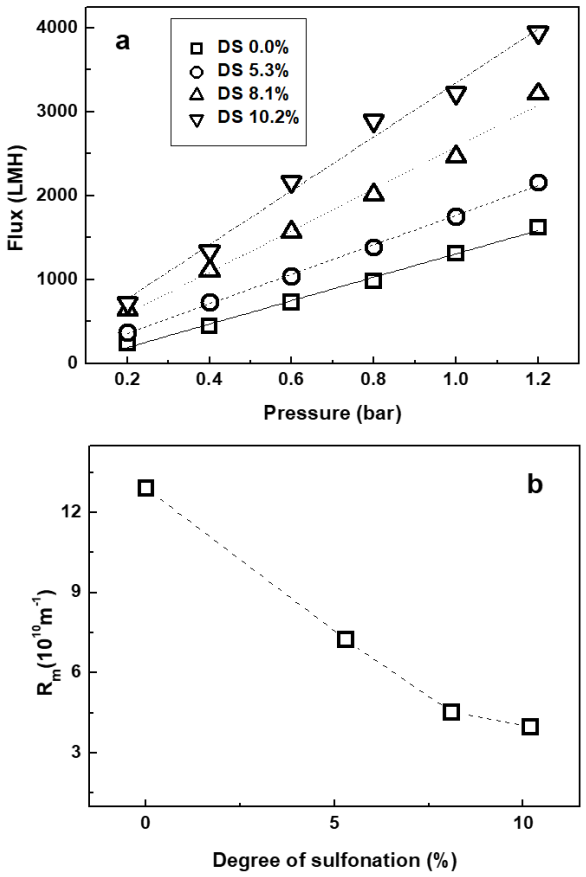

Fig. 9 (a) The relationship of pure water flux with respect to trans-membrane pressures for the unmodified and sulfonated PTFE membranes. (b) The intrinsic membrane resistance (R_m) of the unmodified and sulfonated PTFE membranes as a function of the degree of sulfonation

From the slopes in Fig. 8, the intrinsic resistance of the membranes (R_m), which is the inverse values of slope of water flux with respect to transmembrane pressure, was estimated. As shown in the inset of Fig. 8, the intrinsic resistance of the membrane decreases with an increasing degree of sulfonation, and the R_m value for DS = 10.2% is three times less than that of the unmodified membrane.

3.5 Fouling and rejection experiments

It is important to estimate membrane properties for practical applications, such as fouling phenomena, as the membrane surfaces have hydrophilic and charged functional groups. HA was chosen as a well-known standard foulant. It is a heterogeneous mixture with both aromatic and aliphatic components and contains three main functional groups: carboxylic acids (COOH), phenolic alcohols (OH), and carbonyl groups (C=O) (Lumsdon *et al.* 2005). As mentioned in section 2.3.6, using the fractionated humic acid solution, the fouling effect on modified membranes was investigated. With the introduction of sulfonic acid groups on the membrane, one would expect electrostatic repulsion between the membrane surface and the HA during filtration. Fig. 8 shows normalized flux (J/J_0) values measured as a function of filtration time.

The normalized flux was measured as a function of time at a fixed flux (1000 $Lm^{-2}h^{-1}$). It can be seen that the flux decreases with time during microfiltration due to typical fouling. However, the rates of flux decay are reduced in the case of the modified membranes, as they have more negative charges on the surface.

According to the pore blockage-cake filtration model developed by Ho and Zydney (2000), the filtrate flux through a fouled membrane is equal to the sum of the flow rate through open and blocked pores, and the normalized flux can be expressed as follows:

$$\frac{J}{J_o} = \exp\left(-\frac{\alpha \Delta P C_b}{\mu R_m} t\right) + \frac{R_m}{R_m + R_c}\left(1 - \exp\left(\frac{-\alpha \Delta P C_b}{\mu R_m}\right)\right) \quad (2)$$

membrane, α is the pore blockage parameter (m^2/kg), ΔP is the applied transmembrane pressure [Pa], C_b is the bulk concentration of the feed solution [kg/m^3], μ is the viscosity of water [Pa·s], R_m is the intrinsic membrane resistance [m^{-1}], which is evaluated in Fig. 8, t is the filtration time [s], R_c is the initial resistance of the deposit [m^{-1}], and R_c is the resistance of the deposit cake that forms on the membrane surface [m^{-1}].

The first term in eqn. 3 accounts for the classic pore blocking model, which usually dominates early in the filtration process, and shows a simple exponential decay in volumetric flow rate, whereas the second term is the cake filtration model, which is proportional to the ratio of the membrane resistance to the total resistance later in the filtration process. Thus, using the initial exponential decay of flux, pore blockage parameters (α) for the modified membranes were calculated. As shown in the inset of Fig. 9, the pore blockage parameter decreases with the degree of sulfonation. Compared with the unmodified membrane (α = 200 m^2/Kg), the PTFE-DS3 membrane (DS = 10.2%) has a value that is four times smaller (52 m^2/Kg), as listed in Table 2.

Therefore, the interesting result can be explained by the Donnan electrostatic effect, which excludes the permeation of negatively charged solutes such as HA through the negatively charged membrane, even though the particulates are smaller than the size of the pore openings. In other words, as the concentration of sulfonic acids on the membrane surface increases, the membrane surface has a

Table 2 Transmembrane pressure (Δp), intrinsic membrane resistance (R_m), the pore blockage parameter (α) and rejections (R) for unmodified and defluorinated-sulfonated membrane (PTFE-DS)

Sample name	Δp (kPa)	R_m (x10^{10}) (m^{-1})	α (m^2/kg)	R (%)
Unmodified PTFE	78	12	200	19
PTFE-DS1	56.3	7.2	115	26
PTFE-DS2	37.1	4.53	61.05	28
PTFE-DS3	27	3.98	51.59	32

higher charge density, which causes a stronger repulsion between HA and the membrane surface as well as the pore walls. As reported by Baroña (2007) and Shao (2013), the water flux and the solute rejection of charged membranes depend not only on the size of the pores, but also depend on charge repulsion between the membrane and negatively charged solutes. In addition, it was pointed out that a modified negatively charged membrane with strongly acidic (sulfonic acid) functional groups has better rejection of humic acid and less membrane fouling than that with weakly acidic functional groups such as carboxylic acids because of the difference in intrinsic charge density. Likewise, the greater the charge on the membrane modified by the strongly acidic functional groups, the larger the electrostatic repulsion of HA from the membrane, which could also lead to a higher rejection of HA and less flux decline on fouling during microfiltration, as listed in Table 2. Therefore, the existence of electrostatic charge repulsion between the negatively charged membrane and negatively charged foulants reduces the initial fouling effect of humic acid.

4. Conclusions

Hydrophobic PTFE membranes were modified to become hydrophilic through a simple and reliable chemical modification consisting of defluorination and sulfonation steps. Different degrees of sulfonation with respect to defluorination were controlled by means of the reaction time with sodium naphthalene solution in THF. Within this controlled reaction, the morphology and size of the pores did not vary. It was also observed that the membranes were more hydrophilic as more sulfonic acid groups were incorporated onto the membrane surface, based on the results of analysis by contact angle, water uptake, and LEP. Finally, it was shown that water flux increased, whereas fouling decreased with the degree of sulfonation owing to electrostatic repulsion between the negative charges on the pore walls and membrane surface and the negative charges on humic acid.

Acknowledgments

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References

Ariono, D., Aryanti, P.T., Wardani, A.K. and Wenten, I.G. (2018), "Fouling characteristics of humic substances on tight polysulfone-based ultrafiltration membrane", *Membr. Water Treat.*, **9**(5), 353-361. https://doi.org/10.12989/mwt.2018.9.5.353.

Baroña, G.N.B., Cha, B.J. and Jung, B. (2007), "Negatively charged poly(vinylidene fluoride) microfiltration membranes by sulfonation", *J. Membr. Sci.* 290, 46-54. https://doi.org/10.1016/j.memsci.2006.12.013.

Childress, A.E. and Elimelech, M. (1996), "Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes", *J. Membr. Sci.*, **119**, 253-268. https://doi.org/10.1016/0376-7388(96)00127-5.

García-Payo, M.D.C., Izquierdo-Gil, M.A. and Fernández-Pineda, C. (2000), "Wetting study of hydrophobic membranes via liquid entry pressure measurements with aqueous alcohol solutions", *J. Colloid Interf. Sci.*, **230**, 420. https://doi.org/10.1006/jcis.2000.7106.

Han, M.J., Baroña, G.N.B. and Jung, B. (2011), "Effect of surface charge on hydrophilically modified poly(vinylidene fluoride) membrane for microfiltration", *Desalination*, **270**, 76-83. https://doi.org/10.1016/j.desal.2010.11.024.

Ho, C.C. and Zydney, A.L. (2000), "A combined pore blockage and cake filtration model for protein fouling during microfiltration", *J. Colloid Interf. Sci.*, **232**, 389-399. https://doi.org/10.1006/jcis.2000.7231.

Hodge, R.M., Bastow, T.J., Edward, G.H., Simon, G.P. and Hill, A.J. (1996), "Free volume and the mechanism of plasticization in water-swollen poly(vinyl alcohol)", *Macromolecules*, **29**, 8137-8143. https://doi.org/10.1021/ma951073j.

Huang, Q.L., Xiao, C.F., Hu, X.Y. and Li, X.F. (2011), "Study on the effects and properties of hydrophobic poly(tetrafluoro-ethylene) membrane", *Desalination*, **277**, 187-192. https://doi.org/10.1016/j.desal.2011.04.027.

Hubert, J., Dufour, T., Vandencasteele, N., Desbief, S., Lazzaroni, R. and Reniers, F. (2012), "Etching processes of polytetra-fluoroethylene surfaces exposed to He and He−O_2 atmospheric post-discharges", *Langmuir*, **28**, 9466-9474. https://doi.org/10.1021/la300822j.

Katan, E., Narkis, M. and Siegmann, A (1998), "The effect of some fluoropolymers' structures on their response to UV irradiation", *J. Appl. Polym. Sci.*, **70**, 1471-1481. https://doi.org/10.1002/(SICI)1097-4628(19981121)70:8<1471::AID-APP6>3.0.CO;2-A.

Lumsdon, D.G. and Fraser, A.R. (2005), "Infrared spectroscopic evidence supporting heterogeneous site binding models for humic substances", *Environ. Sci. Technol.*, **39**, 6624-6631. https://doi.org/10.1021/es050180i.

Matienzo, L.J., Zimmerman, J.A. and Egitto, F.D. (1994), "Surface modification of fluoropolymers with vacuum ultraviolet irradiation", *J. Vac. Sci. Technol. A*, **12**, 2662-2671. https://doi.org/10.1116/1.579086.

Mian, W. and Yongbin, Z. (2022), "Water transport through hydrophobic micro/nanoporous filtration membranes on different scales", *Membr. Water Treat.*, **13**(6), 313-320. https://doi.org/10.12989/.2022.13.6.313.

Mulder, M. (1996), *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, London, U.K.

Noh, I. and Hubbell, J.A. (1997), "Photograft polymerization of acrylate monomers and macromonomers on photochemically reduced PTFE films", *J. Polym. Sci. Part A Polym. Chem.*, **35**,

3467-3482. https://doi.org/10.1002/(SICI)1099-0518(19971130)35:16<3467::AID-POLA14>3.0.CO;2-D.

Shao, J., Zhao, L., Chen, X. and He, Y. (2013), "Humic acid rejection and flux decline with negatively charged membranes of different spacer arm lengths and charge groups", *J. Membr. Sci*. **435**, 38-45. https://doi.org/10.1016/j.memsci.2013.01.063.

Shoichet, M.S. and McCarthy, T.J. (1991), "Convenient syntheses of carboxylic acid functionalized fluoropolymer surfaces", *Macromolecules* 24, 982-986. https://doi.org/10.1021/ma00005a003.

Švorčík, V., Miček, I., Rybka, V., Palmetshofer, L. and Hnatowicz, V. (1998), "Ion beam ablation of polytetrafluoroethylene", *J. Appl. Polym. Sci*. **69**, 1257-1261. https://doi.org/10.1002/(SICI)1097-4628(19980808)69:6<1257::AID-APP21>3.0.CO;2-O.

Tang, C.Y., Kwon, Y.N. and Leckie, J.O. (2007), "Fouling of reverse osmosis and nanofiltration membranes by humic acids effects of solution composition and hydrodynamic conditions", *J. Membr. Sci*., **290**, 86-94. https://doi.org/10.1016/j.memsci.2006.12.017.

Woo, Y.C., Kim, Y., Yao, M., Tijing, L.D., Choi, J.S., Lee, S., Kim, S. and Shon, H.K. (2018), "Hierarchical composite membranes with robust omniphobic surface using layer-by-layer assembly technique", *Environ. Sci. Technol*., **52**, 2186-2196. https://doi.org/10.1021/acs.est.7b05450

Woo, Y.C., Yao, M., Shim, W.G., Kim, Y., Tijing, L.D., Jung, B., Kim, S.H. and Shon, H.K. (2021), "Co-axially electrospun superhydrophobic nanofiber membranes with 3D-hierarchically structured surface for desalination by long-term membrane distillation", *J. Membr. Sci*., **623**, 119028. https://doi.org/10.1016/j.memsci.2020.119028

Zhao, B., Brittain, W.J. and Vogler, E.A. (1999), "Trichlorosilane chemisorption on surface-modified poly(tetrafluoroethylene)", *Macromolecules*, **32**, 796-800. https://doi.org/10.1021/ma9811526.

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