

Synthesis Polysulfone-Acetyethanol Ultrafiltration Membranes. Application to Oily Wastewater Treatment

Martin Alberto Masuelli*

Instituto de Física Aplicada-CONICET, Cátedra de Química Física II, Facultad de Química Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco, San Luis, Argentina

*Corresponding author: masuelli@unsl.edu.ar

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Abstract Chemical functionalization of polymers after the synthesis of membranes has great importance for various applications separative processes of industrial or environmental interest. Polysulfone (PSf) is one of the most applied polymers for separative processes used especially in membrane technology, due to its excellent chemical, mechanical and thermal properties. The functionalization of PSf makes it very attractive to give special characteristics due to their high hydrophobicity and membrane fouling fast. In this work PSf perform functionalization by the method of Friedel-Crafts with choroethyl chloroacetate and subsequent hydrolysis of chloroethyl group (-OH). After synthesizing the membrane is characterized by FT-IR ATR spectroscopy, ¹HNMR, contact angle measurements, retention of polydisperse solutes and hydraulic permeability. Finally, the membranes tests fouling are performed with an oily wastewater emulsion. The fouling tests showed that the functionalized PSf membrane demonstrated significant anti-fouling property, suggesting the remarkable benefit for long-term operation in practical applications. Specifically, all the functionalized membranes reached almost 60% water flux recovery and were able to maintain the constant initial fluxes in filtration test, whereas the raw membrane only recovered 70.27% and suffered continuous decline. This promotion might be related to the increase of membrane surface hydrophilicity.

Keywords: polysulfone-COEtOH, membrane, characterization, oily wastewater

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1. Introduction

A cutting emulsion is a complex mixture, which at first glance is apparently homogeneous, and is highly stable over time. Contains the anionic surfactants (such as sodium dodecyl sulfate, SDS, or sodium dodecylbenzenesulfonate, SDBS) has a hydrocarbon chain of 8 to 22 carbons (oils and fats, O & G), germicides, antioxidants, sodium carbonate and sodium hydroxide. This emulsion is purchased commercially and used in cutting the metal industry, machining, milling, turning and grinding. The preparation is performed by mixing the emulsified oil in water with the range of 4 to 10% (vol.). Due to the addition of wash water, the oil content in the final effluent is between 1-0.1%. The end result is a highly stable effluent in time and very expensive treatment. The great stability over time makes this type of oily effluents are high environmental pollutant degradation period so their treatment is truly essential to improve environmental quality in the places where it is consumed in large volumes. The great ecological and toxicological problems of oily emulsions lies in the environmental impact of the billions of liters of oil/water emulsion produced by the metalworking industry, causing a negative impact on local and regional level, both in human and in the environment.

The most common diseases are caused by oil dermatitis, respiratory, and different types of cancers such as liver, kidney, skin and intestine [1].

Higuchi et al. 1991-92 performed various modifications in polysulfone by the technique known Friedel-Crafts [2,3]. These authors modified the PSf after separation studies conducted bovine serum albumin (BSA, 67.5kDa) and polyethylene glycol (PEG, 6kDa) getting rejections from 91-96% to 99.9% for PEG and BSA.

Authors that evaluated anti-fouling properties are Kumar et al. [4] prepared PSf-chitosan blend; Peeva et al. [5,6] crosslinked hydrogel polyethersulfone composite membranes; Abdulgader et al. [7] realized a review in processes of hybrid ion exchange membranes for water treatment. Chen et al. [8] and Xing et al. [9] worked in membrane technology for oily wastewater.

Membrane technology is used with stable emulsions, particularly oil in water wastewater. The advantages of this technology over other methods are that they are applicable to various industrial aqueous wastes highly stable over time. Energy costs are low compared to thermal or electrothermal treatment. The chemical nature of the membrane may have a greater effect on the flow, such as a hydrophilic membrane draws more water to the oil, giving a greater flow of water in the permeate [10]. Fouling of an ultrafiltration membrane is manifest as decreased permeate flow that occurs when all the

operation parameters such as pressure, flow rate, temperature and feed concentration are kept constant. The effect of contamination is characterized by irreversible decrease flow. The fouling of the membrane is due to deposition and accumulation of particles on the surface or within the pores of the membrane as a result of interactions between the membrane and the solutes in the feed stream so that it is difficult to make general rules or theories about the nature and extent of contamination that are of universal application. A significant reduction in the rate of permeation is caused by the effect of concentration polarization (concentration gradient generated by the accumulation of solute at the membrane-solution), which leads to a decrease in the apparent permeability of the membrane. The application of membrane technology in the water treatment includes sterilization, removal of natural organic matter (NOM) and treating oil emulsions [11,12]. The use of membrane processes has long been a prominent, especially in ultrafiltration for the effluents treatment. However, the fundamental point of both the economy and the speed of the process is the membrane itself as it determines the limiting phenomenon of this Application: soiling. This phenomenon can be minimized in three ways: a) by operating conditions, varying the pressure of the feed flow or b) by pretreatment, which includes the addition of flocculants, and c) the modification of the chemical properties of the membrane surface minimize solute-membrane interaction. In general membrane functionalization can be accomplished by inserting (grafting), produced by various methods: ionizing radiation, plasma, oxidizing systems, UV radiation, and consists mainly incorporated into a hydrophilic membrane or a ligand group electrostatically charged.

Among the materials commonly used in the preparation of membranes are polymers, inorganic powders and mixtures thereof. The fundamental characteristics of the polymers responsible for the structural and permselective membrane are the average of large macromolecules, the size distribution thereof, the architecture, the specific nature of the chemical groups and the disposition of these groups in the chains, and the state of aggregation of the macromolecules. The main factors which should be for the synthesis of polymers of the membranes are: heat resistance, chemical and mechanical. The polymer chosen for this work is polysulfone (PSf) having a high thermal stability ($T_g = 195\text{ }^\circ\text{C}$), good resistance to pH between 1 and 13 and can be molded into various configurations of membranes, and in a wide range of sizes pores. The combination of the phenyl ring attached to sulfone groups results in a high resonance stabilization justified. Sulfone group acts as an electron emitter given in the aromatic groups oxidative and thermal resistance. Polysulfone is a Lewis base and is soluble in polar solvents such as dichloromethane, tetrahydrofuran, N,N-dimethylformamide, N,N-dimethylacetamide and dimethylsulfoxide [13,14].

This study is aimed at the synthesis of polysulfone ultrafiltration membrane (PSf), incorporating the same group chloroethyl-chloroacetate, then replace by hydrolysis by chloroethyl groups, in order to confer greater hydrophilicity and reduce the fouling effect. The performance of the membranes obtained is analyzed by permeation measurements of emulsified oily wastewater.

2. Material and Methods

2.1. Polysulfone Functionalization

The chloroacetylation of polysulfone (UDEL 3500P) is performed in methylene chloride solution (provided by Tetrahedron) in a ratio of 3% weight of PSf, then 10 ml of solution are added chloroethyl chloroacetate (BDH) of 3 and 5% vol. containing 10 mg of AlCl_3 anhydrous (Fluka). All reagents are under anhydrous conditions. After 48 hours of stirring at 28°C the polymer is precipitated with 50 ml of isopropanol (Tetrahedron). The precipitate is washed several times with ethanol and dried under vacuum at 50°C for 12 hours. The hydrolysis is performed with 0.5 M NaOH (Biofarm) solution for 12 hours, and then is washed with 0.01 M HCl (Alkemir) solution for 12 hours and finally with ethanol. The hydrolyzed polymer is dried under vacuum at 50°C for 24 hours. This modified method is accorded with references [2,3].

2.2. Membrane Synthesis

The polymer with 17% weight is dissolved in N, N-dimethylformamide (Sigma) containing 2% of PEG (Fluka) of molecular weight of 35kDa [15]. Casting solutions were cast on a Viledon 2430 (Carl Freudenberg, Germany) non woven support and immersed in bi-distilled water at $25\text{ }^\circ\text{C}$ for 24 hours and then is washed with bi-distilled water and stored wet until used. The membranes obtained are: PSf17 (unmodified), PSf-COEtOH (3% vol. of chloroethyl chloroacetate hydrolyzed) and PSf-COEtOH1 (5% of chloroethyl chloroacetate hydrolyzed).

2.3. FT-IR ATR Spectroscopy

From PSf powder with/without functionalization KBr tablets were prepared, and these were analyzed on a Varian 640 FT-IR ATR spectrophotometer.

2.4. $^1\text{H-NMR}$ Determination

$^1\text{H-NMR}$ spectra were recorded on a Bruker AC-200 NMR spectrometer at room temperature. Polymers were dissolved in CDCl_3 . Chemical shifts δ are expressed in parts per million (ppm).

2.5. SEM Microscopy

Scanning electron microscopy images were obtained using an EVO40 Carl Zeiss microscope (Cambridge, London). Membrane samples were freeze-fractured and then coated by sputtering a thin gold layer. They were observed under high vacuum.

2.6. Contact Angle

Contact angle θ , between water and the membrane surface was measured in a 1501 Micromeritics contact angrometer. Each value was obtained 3 min after dropping water on the membrane surface, and consists of adding 1 mL of water drop on the membrane, and the angle to the surface this is θ . The average contact angles (θ) with a standard deviation of ± 2 were determined using the following expression:

$$\cos \theta = 1 - \frac{Bh^2}{\sqrt{\left(1 - \frac{Bh^2}{2}\right)}} \quad (1)$$

where $B = \rho g/2\gamma$, with “g” being gravity acceleration (980 cm/s²), “ ρ ” the density of bi-distilled water (0.9971 g/cm³), “ γ ” the interfacial tension of bi-distilled water (71.97 erg/cm²), and “h” the height of the liquid drop.

2.7. Retention of Polydisperse Solutes

Determinations pore size distribution were made using dextrans whereas retention is due to sieving mechanisms such that each molecular weight fraction is a retaining pores completely polydisperse solute while the other allows the molecules to happen. It is assumed that no friction effects in the pores. Dextrans were used for this at a concentration of 1 g/l with molecular weights of 8.8 kDa to 500kDa. Determining the concentration in permeate was evaluated by HPLC-Gilson using a refractive index detector and PoliSec-GFC-5000P column, with bi-distilled water as mobile phase.

Determinations of pore size distribution were made using dextrans whereas retention is due to sieving mechanisms such that each molecular weight fraction is a retaining pores completely polydisperse solute while the other allows the molecules to pass. It is assumed that no friction effects in the pores and can establish a mass balance for each molecular weight as:

$$J_v c_p = J_{v,t} c_m \quad (2)$$

where $J_{v,t}$ is the flux transmitted through the fraction of pores that can not retained (cm). Furthermore, the flow ratio of water flow transmitted considering Darcy's law can be expressed as:

$$\frac{J_{v,t}}{J_{w,t}} = \frac{\eta}{\eta_0} \quad (3)$$

where η and η_0 are the viscosities of the solution and solvent respectively. Low concentrations but this relationship can be approximated to 1 so that:

$$J_{w,t} = J_v (1 - R) \quad (4)$$

R is the coefficient of solute retention which is defined as $R = (1 - C_d/C_p)$, where C_a and C_p are the solute concentrations in the feed and permeate respectively. Again using mass balance can be established:

$$J_v c_p = J_s$$

and

$$J_w = J_v - J_s \quad (5)$$

allowing J_w know if C_p is known. Consequently $J_{w,t}/J_w$ can be calculated for each C_p and R , i.e. for each molecular weight. The cumulative fraction of flow passing through the pores that can retain for each molecular size (which can be taken as equivalent to the pore size, r_p , if the contributions to hydration volume and adsorption are not considered), while its derivative should provide flow through the pores of a given radius that allows passing solutes. The distribution of pore radius can be summarized as follows:

$$f_d = \frac{d\left(\frac{J_{w,t}}{J_w}\right)}{dr_p} \quad (6)$$

The porous radius r_p can be related to the molecular size of dextran molecule by

$$r_p = 0.4253(MW)^{0.452} \quad (7)$$

So a plot of $d(J_{w,t}/J_w)/d(r_p)$ vs. r_p can be obtained, and whose area can be determinate the average pore radius (r_{pa} in nm). Dextrans were used at a concentration of 0.20 g/l.

2.8. Hydraulic Permeability and Fouling Test

The membrane was placed in permeation cell at a constant feed flow 1L/min (see Figure 1). In the first 1.0 h of pure water permeation stage, the relative fluxes for all these membranes behaved similarly and decreased only slightly since the membranes were compacted at high pressure prior to measurement (100kPa). Hydraulic permeability (L_H in (m³/m²sPa)) is performed by measuring the permeate flow to different transmembrane pressures 25-89 kPa. The L_H is given by the equation:

$$L_H = \frac{J_{ve}}{\Delta p} \quad (8)$$

where J_{ve} is the permeate flux density (m³/m²s), and Δp is the transmembrane pressure (Pa). Then he proceeded to fouling of the membranes at 67 kPa with a 0.1% oil emulsion (soluble oil Tutela K2P, Argentina), with the following characteristics: pH=10 and COD=2100ppm. L_H is measured with pure water after fouling (L_{H0}), and then fouling the membrane is water washing (L_{Hwa}). Rejection oil content ($R_{CA\%}$) is defined as the amount of solute which retains the membrane and is given by the following equation:

$$R_{CA\%} = 100(1 - c_{pe}/c_{ae}) \quad (9)$$

where C_{ae} is the concentration of emulsion feeding, while C_{pe} is the concentration in the permeate, both measurement of C_{ae} and C_{pe} in a spectrophotometer at 220nm.

The Membrane fouling is a complex phenomenon where permeate flux declines drastically due to phenomena involving chemical and physical factors [15,16,17]. The flux drop can be summarized as follow:

$$J_{vf} = \frac{1}{A} \frac{dV}{dt} = J_{v0} (1 + Kt)^n \quad (10)$$

where J_{vf} is the permeate flux, A the effective area of membrane, V the permeate total volume, t time, K the fouling constant, J_{v0} initial flux of the resulting dynamic membrane after the blocking of initial pores [18,19,20]. For the cake model, $n = 2$ and

$$K = 2K_{cf} J_{v0}^2$$

with

$$K_{cf} = C_{cf} \frac{\rho_c \eta_e}{\Delta p} \quad (11)$$

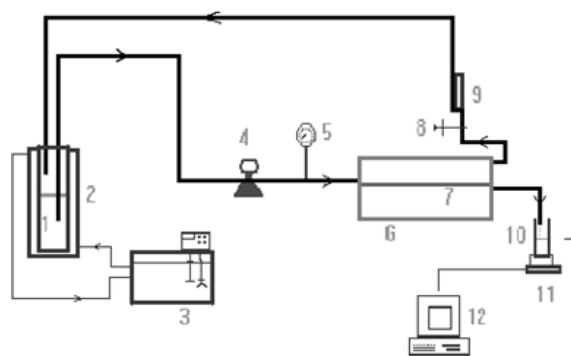


Figure 1. Graph of the filtration system: (1-2) feeding reservoir-retained, (3) thermostatic bath, (4) pump, (5) pressure sensor, (6) cell Minitan-S, (7) membrane, (8) valve, (9) flowmeter, (10) permeate reservoir, (11) analytical balance, (12) Computer

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where ρ_c is the cake mass per unit of permeate volume, η_e is the feed solution viscosity ($\eta_e = 1.0362 \times 10^{-3}$ Pa. s) and C_{cf} is the apparent specific resistance of the cake. To calculate C_{cf} , it has been assumed that the deposited mass per unit of filtered volume, ρ_c , is equal to the feed oil/water concentration. In fact it is strictly true only for dilute concentrations. An integration of Eq. (9) leads to:

$$\frac{t}{V} = K_{cf} V + \frac{1}{J_{v0}} \quad (14)$$

3. Results and Discussion

The Figure 2 show Friedel-Craft mechanism of acetylation of PSf, where R is Chloromethyl group. In a simple mechanistic view, the first step consists of dissociation of a chloride ion to form an acylium ion (acylium ion). In some cases, the Lewis acid binds to the oxygen of the acyl chloride to form adduct. Regardless, the resulting acylium ion or a related adduct is subject to nucleophilic attack by the arene. Finally, chloride anion (or AlCl_4^-) deprotonates the ring (an arenium ion) to form HCl, and the AlCl_3 catalyst is regenerated.

Haloacyles are reactive towards nucleophiles. They are polar molecules: the carbon to which the halogen is attached is slightly electropositive where the halogen is slightly electronegative. This result in an electron deficient (electrophilic) carbon, which inevitably, attracts

nucleophiles. Substitution reactions involve the replacement of the halogen with another molecule thus leaving saturated hydrocarbons, as well as the halogenated product. Alkyl halides behave as the $-\text{COEt}^+$ synthon, and readily react with nucleophiles. Hydrolysis, a reaction in which water breaks a bond, is a good example of the nucleophilic nature of halogeno-alkanes. The polar bond attracts a hydroxide ion, OH^- (NaOH aq.) being a common source of this ion). This OH^- is a nucleophile with a clearly negative charge, as it has excess electrons it donates them to the carbon, which results in a covalent bond between the two. Thus $\text{C}-\text{Cl}$ is broken by heterolytic fission resulting in a halide ion, Cl^- . As can be seen, the OH is now attached to the alkyl group, creating an alcohol.

PSf FTIR-ATR spectrum shows a band at 1240 cm^{-1} corresponding to the C-O-C vibration, the vibration of the aromatic ring has a band at 1488 cm^{-1} , the band is between $873-852 \text{ cm}^{-1}$ is a deformation in the vibration aromatic C-H, the band is at 1170 cm^{-1} is the vibration of the $\text{C}(\text{CH}_3)_2$. The IR spectrum of the hydrophylized polysulfone membrane shown O-C stretching band at 1187 cm^{-1} , -OH band between $3400-3600 \text{ cm}^{-1}$ and a typical signal $\text{C}=\text{O}$ at 1716 cm^{-1} (Figure 3). Grafted degree calculated from FTIR-ATR spectra is 3.4%, respect to $\text{C}=\text{O}$ signal.

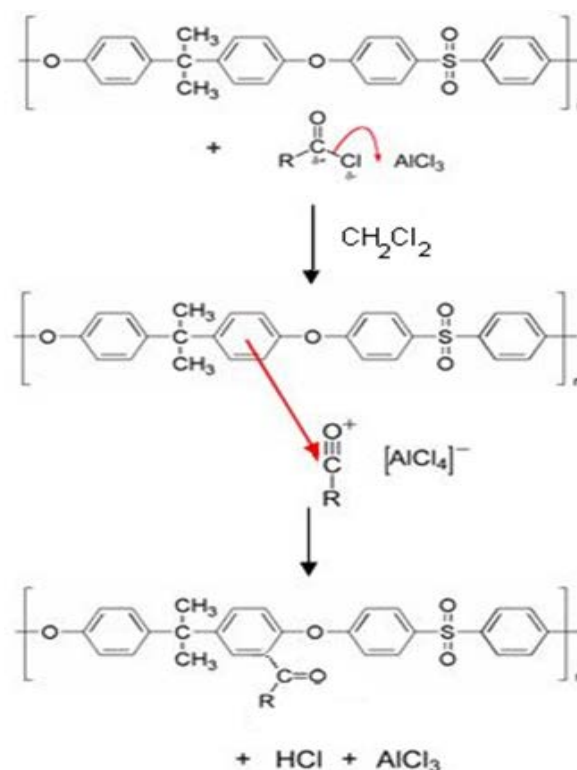


Figure 2. Schematic diagram of Polysulfone functionalization

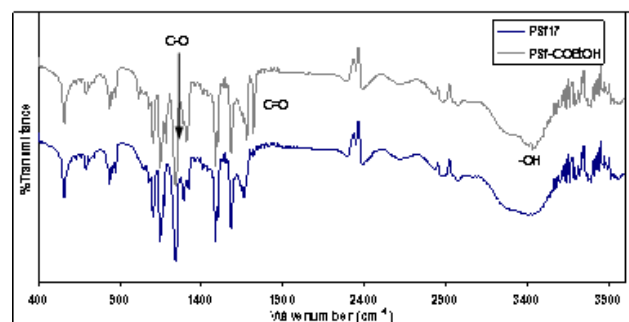


Figure 3. FTIR-ATR spectra of the membranes

Figure 4 shows the $^1\text{H-NMR}$ spectra for polysulfone and chloroacetylated polysulfone as well as the effect of reaction time on chloroacetylation. The chemical shifts of the polysulfone were found as follows (ppm): a: 6.90–7.86 (multi Hs on phenyl groups) and b: 1.72 (CH_3). ($^1\text{H-NMR}$ spectral data of Udel polysulfone: $\delta = 7.85$ H-d (4H d); $\delta = 7.24$ H-b (4Hd); $\delta = 7.00$ H-c (4Hd); $\delta = 6.94$ H-a (4Hd); $\delta = 1.69$ CMe, (6Hs).). The chemical shifts of the chloroacetylated polysulfone are listed below (ppm): 6.85–7.86 (multi Hs on phenyl groups), 4.71 (CH_2OH) and 1.58 ($-\text{OH}$). The chemical shift characteristic at 4.71 confirmed the formation of the chloroacetylated polysulfone. The most important step in preparing functionalized membrane is chloroacetylation, because the chloroacetylated polymer is readily further modified due to the high reactivity of the tethered chloroacetyl

group [21]. The successful chloromethylation also determines how many functional groups on the polymer chain can be directly substituted to further transfer to conductive hydroxyl groups, which in turn determines the hydrophilic characteristic. On the other hand, we noticed that the chloroacetylation could easily cause gelation, leading to a lower yield of the chloroacetylated polymer. It has been reported that crosslinking often takes place rapidly during chloroacetylation of polystyrene resin as the active aromatic ring attacks the chloroacetyl group in a Friedel–Crafts acylation fashion, which in turn causes inter-polymer or intra-polymer crosslinking or gel formation [22,23]. All the numbers of the chloroacetyl groups were obtained by integration of chemical shifts exhibited by chloroacetyl and phenyl groups.

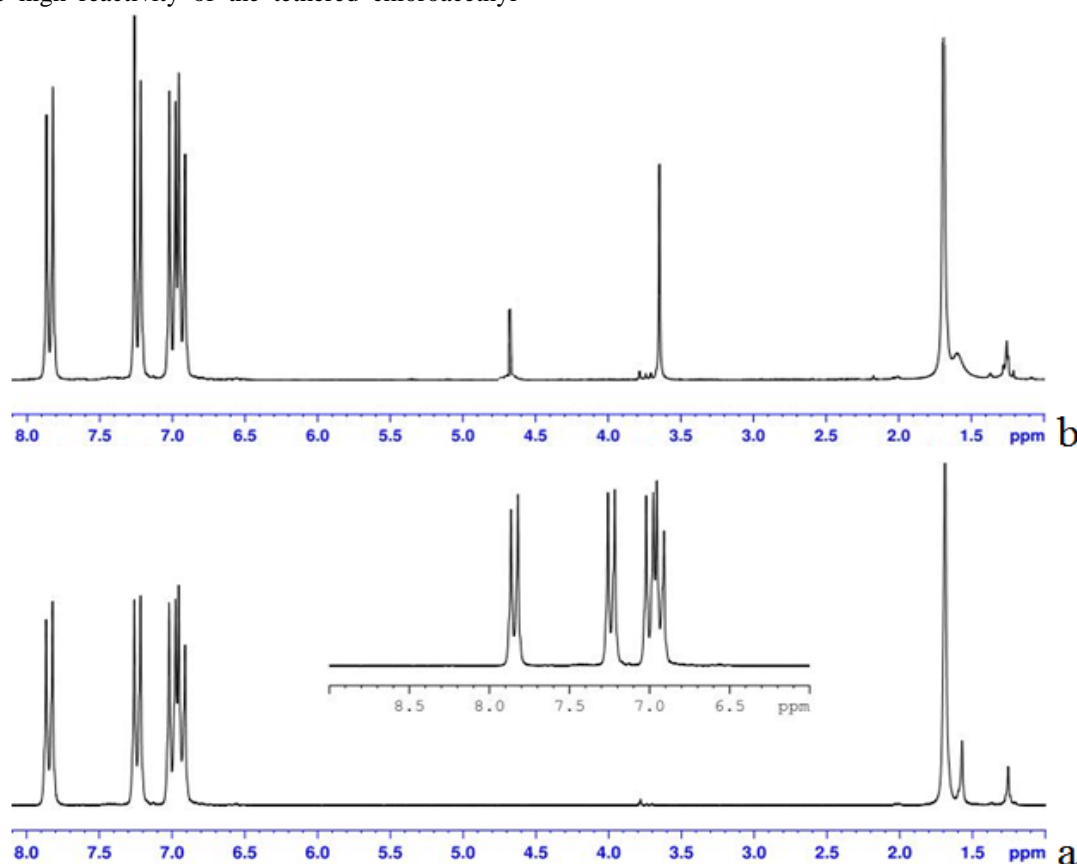


Figure 4. $^1\text{H-NMR}$ of a- PSf, and b- PSf-COEtOH

Table 1. Data obtained from the membranes

| Membranes | θ | r_{pa} (nm) | $L_{Ho} \times 10^{10}$ ($\text{m}^3/\text{m}^2 \text{ s Pa}$) | $R_{CA\%}$ | $L_{Hla} \times 10^{10}$ ($\text{m}^3/\text{m}^2 \text{ s Pa}$) |
|-------------|----------|------------------|---|------------|--|
| PSf17 | 77.9 | 28.02 | 6.11 | 95.25 | 1.52 |
| PSf-COOEtCl | 78.5 | 25.35 | 6.38 | - | - |
| PSf-COEtOH | 74.6 | 22.18 | 7.42 | 97.17 | 4.85 |
| PSf-COEtOH1 | 73.7 | 21.39 | 7.68 | 97.62 | 5.12 |

Figure 5 shows SEM images of membrane cross-sections. There is a noticeable variation in the membrane structure from a finger-like morphology for a non-resin membrane (PSf) to a more densified structure for PSfCOEtOH membrane. This effect causes a low a decrease of macrovoids in the porous substructure was obtained by adding water to casting solution. This also seems to be our case since $-\text{COEtOH}$ group adsorbed easily water from the air during their storage. The

adsorbed water in the PSf-COEtOH would produce an increase of the casting solution viscosity causing a decrease of the mass transfer rate during coagulation and consequently, a low decrease in the macrovoid formation.

The pore size distribution shows that the membranes are in a range similar pore sizes (Figure 6a). In the hydrolyzed membrane is the characteristic $-\text{OH}$ band at 3400cm^{-1} . The contact angle measurements and hydraulic permeability demonstrate an increased hydrophilicity of the membrane which has been hydrolyzed respect to polysulfone (Table 1). Fouling tests (Figure 4b), there are no large changes in flow falls membranes with rejections greater than 96% (Table 1). The PSf-COEtCl membrane fouling test not realized, because hydrolyze $-\text{COEtOH}$ to the pH in the oil/water emulsion used. Phenomenon demonstrated low decrease in pore size of the membranes functionalized.

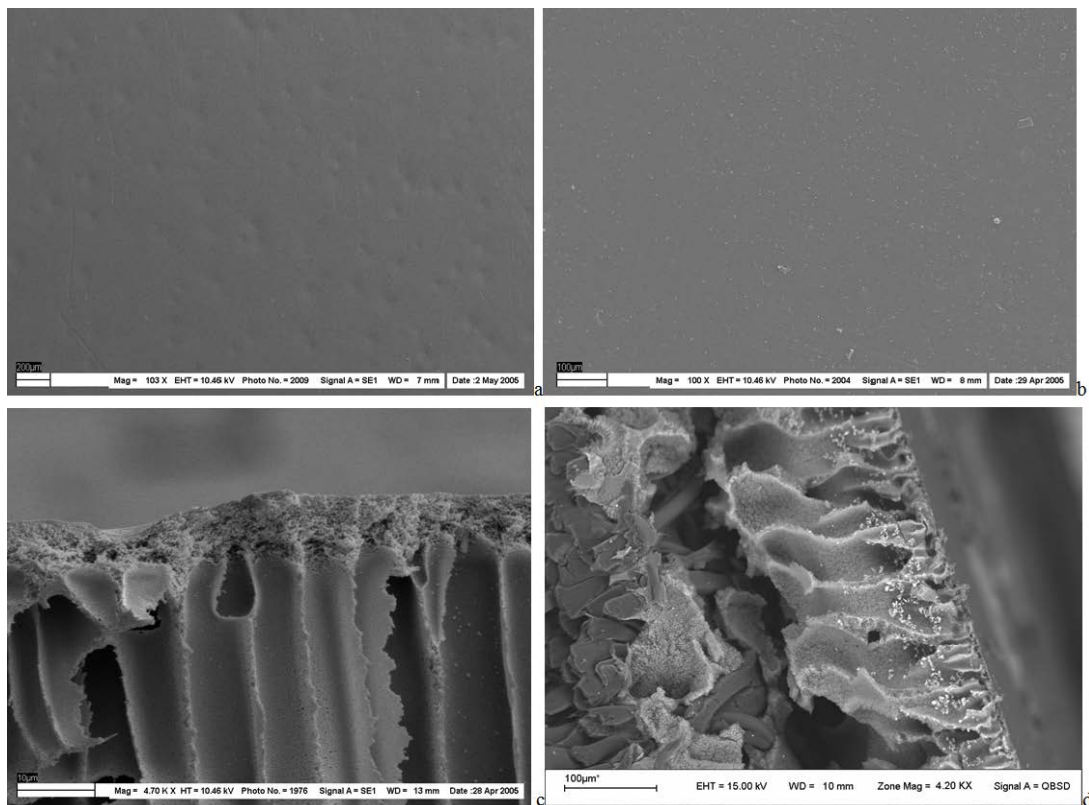


Figure 5. SEM image of membranes. Surface a- 17PSf, b- PSf-COEtOH. Cross Section c- 17PSf, and d- PSfCOEtOH

Table 2. Cake model parameters

| Membranes | $K_{fc} \times 10^5$ (s/m^2) | $C_{fc} \times 10^{-15}$ (m/g) | $J_{v0} \times 10^5$ ($m^3/m^2 \cdot s$) | $K \times 10^{-3}$ (s^{-1}) |
|-------------|-------------------------------------|---------------------------------------|---|------------------------------------|
| PSf17 | 8.21 | 5.34 | 3.74 | 2.32 |
| PSf-COEtOH | 7.35 | 4.78 | 3.19 | 1.51 |
| PSf-COEtOH1 | 7.10 | 4.62 | 3.03 | 1.33 |

A major problem in oily wastewater separation by membrane ultrafiltration is the deterioration of permeability and selectivity due to membrane fouling. To investigate the anti-fouling properties of the fabricated membranes, fouling operations as described by cake formation were conducted using oil/water emulsion [24,25]. The density of flux was defined as the real-time flux (J_v) to the initial pure water flux (J_{v0}), and the time-dependent relative flux curves for the investigated membranes are shown in Fig. 6b. When the feed liquid was changed to oil/water emulsion, the fluxes decreased sharply due to the filtration cake formation by the deposition and adsorption of oil/water on membrane surface. But the concentration polarization was suppressed by the rigorous feed alimentation on membrane surface. It was worth noting that the surface-hydrophilized membranes had less flux decrease than the untreated membranes (PSf17). The more hydrophilic the membrane was, the less decrease for the flux. From the data of the third step, we can see that higher relative fluxes were recovered after membrane cleaning with water flux for the hydrophilized membranes. Furthermore, the sequence of flux recovery ratio for the investigated membranes was consistent with the surface hydrophilicity [17,18,19]. These results showed the anti-fouling ability of PSf membrane was improved significantly by the PSf hydrophilization.

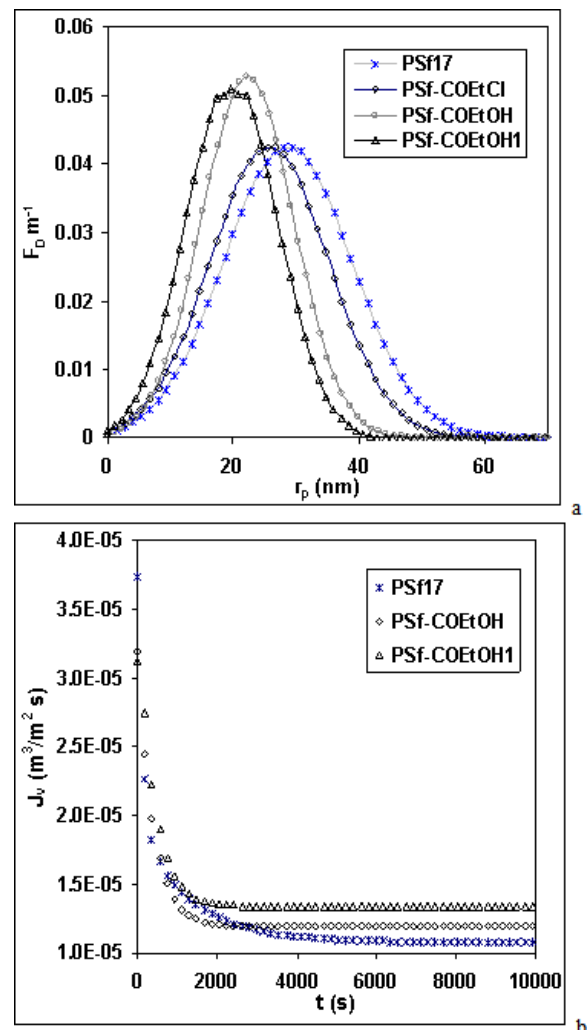


Figure 6. a- Pore size distribution. b- Testing membrane fouling

The measurements of flux decline with the oil/water emulsions are shown in Figure 6b. This figure indicate a sharp decrease of permeate flux as a function of time. Considering the mean pore size of PSf-COEtOH membrane is 22.18 nm and the 2.18 μm average drop size of the emulsion, it can be assumed that the high rejection of particles generates a cake layer in a few minutes (17 minutes for modified membrane and 41 minutes for PSf17). The fall flow is 70.27% to PSf17, 60.94% for PSf-COEtOH and 57.1% for PSf- COEtOH1. The recovery of the initial hydraulic permeability (L_{H1a}/L_{H0}) is 24.88% for PSf17, 65.36% for PSf-COEtOH, and 66.67% for PSf-COEtOH1, respectively.

The effect of hydrophilicity directly related to the presence of -OH group produces a reduction of the fouling rate (K_{cf}). This significant change of flux rate is reflected in the apparent specific cake resistance values determined by Eq. (10). In Table 2, a decrease of C_{cf} as the -OH group content respect to PSf17. These results indicate that a less compact layer cake is formed due to a lower adsorption of oil molecules on the membrane modified according with the growing hydrophilic character of PSf-COEtOH membranes [17,25,26].

4. Conclusions

A novel anti-fouling PSf-COEtOH membrane was successfully obtained using the Friedel-Crafts functionalization of hydrophobic polysulfone. The acetylation, with different dosage ranging from 3% to 5% vol. of chlorethyl chloroacetate, was grafted into the membrane matrix for the functionalization of the internal surfaces and pores of membrane [27,28]. The fouling tests showed that the functionalized PSf membrane demonstrated significant anti-fouling property, suggesting the remarkable benefit for long-term operation in practical applications [29,30]. Specifically, all the functionalized membranes reached almost 60% water flux recovery and were able to maintain the constant initial fluxes in filtration test, whereas the raw membrane only recovered 70.27% of flux and suffered continuous decline. This promotion might be related to the increase of membrane surface hydrophilicity. The physicochemical properties of the PSf membrane change for the presence of -OH group. The functionalized membranes had the highest performance in both the flow and the quality of permeate. The hydrofilyzed PSf membrane while increases hydrophilicity with respect to polysulfone membrane and not fully recover its initial permeate flow, but has high $R_{CA\%}$ (>97%).

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