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Preparation, structural and functional characterization of modified porous PVDF membranes by γ-irradiation

M.A. Masuelli[a], M. Grasselli[b], J. Marchese[a], N.A. Ochoa[a,*]

[a] Instituto de Física Aplicada- Universidad Nacional de San Luis-CONICET-FONCYT, Chacabuco 917-CP, 5700 San Luis, Argentina
[b] Dpto. de Ciencia y Tecnología, Universidad Nacional de Quilmes, Roque Saenz Peña 352, (B1876BXD) Bernal, Buenos Aires, Argentina

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ABSTRACT

This work describes the synthesis of charged poly(vinylidene fluoride) (PVDF) membranes. Cationic membranes were prepared by graft modification using radiation-induced polymerization. Glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EDMA) were used as monomers and after graft polymerization the former was sulfonized with sodium sulfite. Membrane characterizations were carried out by FTIR-ATR, SEM-EDS, ionic exchange capacity, hydraulic permeability and liquid–liquid displacement. FTIR-ATR and SEM-EDS analysis revealed that increasing grafting degree increased the amount of the sulfonic group in the membranes. Sulfonated membranes showed smaller pore sizes and higher pore density than the original PVDF membrane. Oil/water ultrafiltration tests with the charged PVDF membranes showed interesting permselectivity performance; high oil retention values ($R > 98\%$), low chemical oxygen demand in the permeate solution ($\mathrm{COD} < 59\,\mathrm{mg\,L^{-1}}$). In addition, low fouling (<16.6%) and negligible irreversible fouling of the charged membranes was observed during the ultrafiltration tests.

1. Introduction

The treatment of exhausted oil emulsions is a great environmental problem due to its high content of non-degradable hydrocarbons and its high chemical oxygen demand (COD). In the last two decades, membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are increasingly been applied for treating oily wastewater [1–4]. Cheryan and Rajagopalan [5] described several studies of membrane applications in a hybrid system when combined with conventional chemical treatment systems to concentrate sludge. In their work the potential of applying membranes to the treatment of oily wastes was also discussed. Although the UF process has been successfully used in oil reduction and chemical oxygen demand, the use in oil/water emulsion treatment applications has remained limited as a result of low permeate fluxes due to membrane fouling. A rapid diminution of the permeate flux reduces the competitiveness of the process. It is well known that the fouling is caused by two main factors, the hydrodynamics of the process and the physicochemical properties of membrane and feed solution. Several approaches to solve this problem have been attempted, among them, back pulsing, vibratory or centrifugal devices to enhance shear at the membrane surface, pretreatment of feed, and modification of membrane surfaces to increase hydrophilicity and/or its surface charge. This paper is focused on the latter of these approaches.

Ulbricht [6] has presented a complete outline on the development of polymeric membranes having advanced or novel function in the various membrane separation processes. Fouling-resistant surface functional membrane could be obtained by various methods to improve the membrane hydrophilicity. Charged membranes offer the advantage that in addition to solute retention by size exclusion mechanism, an electrostatic repulsion effect is added [7,8]. The poly(vinylidene fluoride) (PVDF) polymer has widely been studied and reported as a material to tailor polymeric membrane for many different applications and as candidate for surface modification. It is due to its good thermal stability, chemical resistance, excellent process facility, and handiness in controlling structural and morphological characteristics. However, the strong fouling tendency generated from its intrinsic hydrophobicity limits the application of PVDF membranes in aqueous mixtures filtration. Several techniques to synthesize charged PVDF membranes have been reported in the literature, such as blends or base polymer modifications by a chemical or physical process. Hester and Mayes [9] prepared immersion precipitated membranes with enhanced fouling resistance from blends of PVDF and a free-radically synthesized amphiphilic comb polymer having a methacrylate backbone and poly(ethylene oxide) side chains. Hydrophilic PVDF–PVP

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* Corresponding author. Tel.: +54 2652 446211; fax: +54 2652 430224.
E-mail address: aochoa@unsl.edu.ar (N.A. Ochoa).

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ultrafiltration membrane was achieved by using $KMnO_4$ and KOH as oxidant and strong base to facilitate the HF-elimination from PVDF chain, and polyvinylpyrrolidone aqueous solution as a coating media [10]. Wei et al. [11] described the properties of surface-modified PVDF membranes. These membranes were created by coating hydrophilic polymers on the support PVDF membrane to reduce the tendency to protein fouling. Baroña et al. [12] prepared negatively charged PVDF microfiltration membranes using simple and direct sulfonation with chlorosulfonic acid without grafting or irradiation techniques.

Graft polymerization of specific functionalities or polymer layers has been employed as a route to tailor PVDF polymeric membrane surfaces for many different applications, particularly for proteins separation and purification processes. Considerable attention has been directed at modifications using irradiation source as a way to reduce fouling, for example: grafting process along the ion track of irradiated PVDF films to obtain an inhomogeneous composite material of polystyrene-PVDF [13]; covalent bonding of amino-terminated molecules onto acrylic acid by radiation induced grafting PVDF [14]; post-radiation-induced-graft polymerization of poly(acrylic acid) onto PVDF using reversible addition-fragmentation transfer (RAFT) mechanism [15]; modifying the pore surface and inner part of polymeric material by plasma method [16]; grafting PVDF porous membrane with poly(ethylene glycol) methyl ether methacrylate by the pre-irradiation method with high energy electron beam [17]; grafting the zwitterionic sulfobetaine methacrylate on the surface of PVDF membrane via ozone surface activation and surface-initiated atom transfer radical polymerization [18]; grafting polymerization of N-vinyl-2-pyrrolidinone onto the PVDF-based microporous membrane containing a small quantity of poly-ethersulfone under UV irradiation [19]; and irradiating PVDF powder in air using a ^{60}Co γ-ray source, and then grafting hydrophilic monomers of acrylic acid (AAc) or methyl acrylic (MAA) [20].

As it was above mentioned the PVDF modifications were usually focused on improving the membrane antifouling performance for protein concentration or separation from aqueous solutions. The research which our group is undertaken examines the effects of membrane morphologies and surface modifications on fouling behavior during oily wastewater treatment. In previous work blend membranes with different degrees of hydrophilicity were prepared from PVDF and poly(methyl methacrylate) (PMMA) [21]. Oily emulsion tests showed that membranes with higher PMMA content lead to lower fouling. Charged ion exchange resin-polymer composite membranes to treat oily suspension were performed [22]. It was found a high electrostatic oil repulsion at 20% (w/w) resin content resulting in membrane no fouling and low oil concentration in the permeate solution. More recently, new membranes based on sulfonated polycarbonate (SPC) and PVDF were prepared [23]. SPC was obtained by treating polycarbonate with acetyl sulfate. Membrane performance was assessed using an oil–water emulsion. Results indicated that the membranes containing 20% of SPC did not present an appreciable irreversible fouling.

As a continuance of our previous published papers on emulsified oily wastewater treatment [21–23], in this work, an alternative method to surface modification techniques to obtain PVDF graft charged membranes to improve the oily emulsion fouling resistance is proposed. The technique involves the use of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EDMA) monomers in the grafting polymerization step followed by sulfonated with sodium sulfite. Data of FTIR-ATR, SEM-EDS, ionic exchange capacity, hydraulic permeability and liquid–liquid displacement are included in order to carry out a physicochemical characterization. Finally, the fouling behavior of the synthesized membranes is analyzed by permeation tests with an oil emulsion solution.

2. Experimental

2.1. Materials

PVDF Solef® 1015 high viscosity was provided Solvay Belgium and polyvinylpyrrolidone (PVP) K30 was supplied from Fluka. Glycidyl methacrylate (GMA) and ethylenglycol dimethacrylate (EDMA) were purchased at Sigma–Aldrich Co., St. Louis, USA, and used as provided. Sodium sulfite, isopropanol, isobuthanol, methanol, *N*,*N*-dimethylacetamide (DMAc), natrium hydroxyde (NaOH), natrium chloride (NaCl) and chlorhydric acid (HCl) were provided by Merck. Viledon 2431 non-woven support (thickness: 0.14 mm; air permeability at 200 Pa: 500 L/m^2 h) was kindly provided by Carl Freudenberg, Germany.

Commercial emulsive oil (Insignia® oil) was purchased from JyM Lubricantes S.A. (Argentina). Oily/water emulsion was prepared mixing 1 g of Insignia® oil in 1 L of distilled water (0.1% (w/v) oil concentration) by stirring with an UltraTurrax-T50 stirrer at 500 rpm. The emulsion had the following characteristics: pH 7, viscosity $\eta = 1.058 \times 10^{-3}$ Pa s, average oil droplet diameter of 2.5 μm (optical microscopy) and chemical oxygen demand (COD) of 1700 mg L^{-1} [22].

2.2. Membrane preparation

The general procedure for membrane preparation was as follows: 12% of PVDF and 10% of PVP were dissolved in DMAc at 50 °C by stirring with a magnetic bar during 10 h. The final mixture was cast onto the non-woven support using a film extensor at 25 °C. Then, the supported polymeric film solution was coagulated in bi-distilled water at 25 °C. Afterwards membrane was introduced in a 5 L water bath during 12 h.

2.3. Grafting GMA and GMA-EDMA

GMA and EDMA were used as monomers (reactive and cross-linker monomer respectively) in the grafting polymerization step. In a 1 L vessel PVDF porous membrane (membrane surface = 374 cm^2) was soaked in a monomer solution. Monomer solution was prepared in distilled water and methanol 1:1 degassed by N_2 bubbling. GMA and EDMA monomer concentrations (w/w %) are informed in Table 1. The samples were irradiated at room temperature in a ^{60}Co PISI semi industrial irradiation source (CNEA, Ezeiza, Argentina) at a dose rate of 0.9 KGy/h and a total dose of 7 KGy. The irradiated membranes were washed first with a methanol/water solution (1/1), and then with pure methanol. Finally, they were dried at 60 °C during 24 h. The grafting degree (GD) of GMA was determined from:

$$\mathrm{GD}[\%] = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

where W_0 and W_1 are the weights (g) of the PVDF film and GMA grafted film, respectively.

Table 1
Monomer concentrations, grafting degrees and conversions.

Membrane	GMA (w/w %)	EDMA (w/w %)	GD (%)	*X* (%)
PVDF	–	–	0	0
G1-PVDF	0.10	–	0.8	99
G1X-PVDF	0.10	0.01	0.6	95
G5-PVDF	0.5	–	3.2	99
G5X-PVDF	0.5	0.05	3.1	95

2.4. Sulfonation

Grafted-irradiated membranes were sulfonated by soaking in a solution of sodium sulfite/water/isopropanol (wt%, 10/75/15) at 40 °C during 24 h in order to ensure the major conversion of epoxy group to sulfonic group [24,25]. Sulfonated membranes were labeled with an additional letter (S). The conversion from epoxy to sulfonic group was calculated from the GMA weight (W_1) change as follows:

$$X[\%] = \frac{(W_2 - W_1)/103}{(W_1 - W_0)/142} \times 100 \qquad (2)$$

where W_2 is the weight of sulfonated film. The values 142 and 103 correspond to the molecular weights of GMA and sodium sulfite, respectively. The PVDF grafting and sulfonation reactions are schematized in Figs. 1 and 2.

2.5. Pore size measurements by liquid–liquid displacement porosimetry

Three liquids (mixture of isobutanol/methanol/water; 15/7/25, v/v/v) (surface tension, $\gamma = 0.35$ mN/m) are used to pores analysis by applying relatively low pressures [26]. Procedure consists on filling the membrane with a liquid (wetting liquid, aqueous phase) and then displacing it from pores with the organic phase (isobutanol saturated with water and methanol). Flux through the membrane is obtained by using a syringe pump (ISCO 500D) to gradually increment the flux on the organic-phase side. Simultaneously, equilibrium pressure is measured in each incremental stage using a pressure transducer (OMEGA DP200). When the applied pressure and flux through the membrane were monitored, then the radii of opened pores at each applied pressure can be calculated from Cantor's equation [27]. This equation is valid if it is assumes the liquid effectively wets the membrane (i.e. with null contact angle).

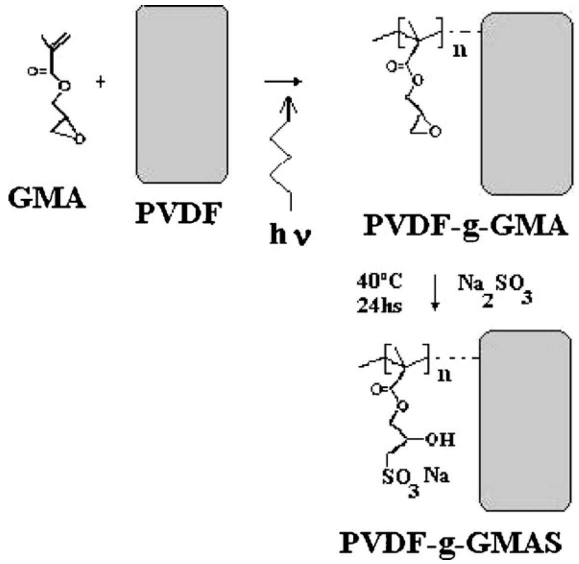

Fig. 1. Scheme of GMA insertion in PVDF and sulfonation reaction.

$$r_p = \frac{2\gamma}{\Delta p} \qquad (3)$$

where Δp is the applied pressure, γ is the interfacial tension and r_p is the pore equivalent radius. Assuming cylindrical pores, Hagen–Poiseuille relationship can be used to correlate volumetric flux density J_{vi} to a given pore radius r_p. In each stage of incremental volumetric flux density, the corresponding pressure (Δp_i) was

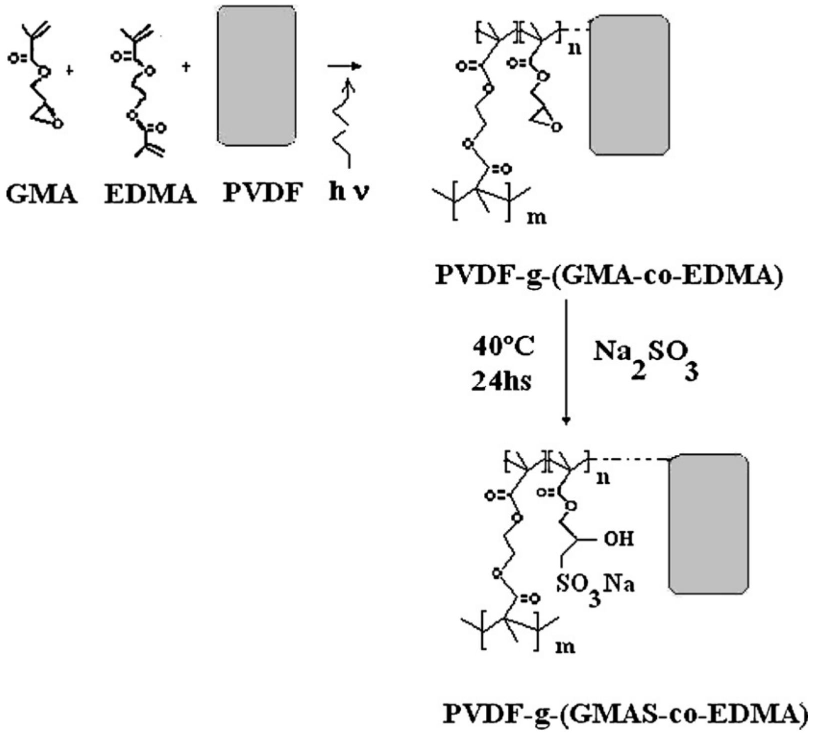

Fig. 2. Scheme of GMA + EDMA grafting onto PVDF and sulfonation reaction.

measured. From these data the distribution of the number of pores (n_i) versus pore radius were calculated according to:

$$\frac{dn_i}{dr_{pi}} = -\frac{\eta\tau\ell\Delta p_i^6}{16\pi\gamma^6}\frac{d^2 J_{vi}}{d\Delta p_i^2} \tag{4}$$

where η is the dynamic viscosity, τ is the tortuosity, and ℓ is the pore length which corresponds to the active layer thickness of the membrane. The membrane surface porosity (ε) can be evaluated from

$$\varepsilon = \frac{\pi\sum_i^n n_i r_{pi}^2}{A_m} \tag{5}$$

where A_m is the membrane surface area ($A_m = 2.46 \times 10^{-3}\ m^2$).

2.6. Ion exchange capacity

Data on ion exchange capacity (IEC) gives information regarding ionizable groups available on the membrane. The ion exchange capacity – with units mequiv./g of dry polymer – of the original and sulfonated PVDF membranes was measured using the standard experimental method according to Taeger et al. [28] as follows: membrane was immersed in 1 N HCl for 24 h, rinsed in distilled water; subsequently, membrane samples were soaked for 24 h in 1 N NaCl solution (exchange of H^+ by Na^+ within the film) and titrated with 0.01 N NaOH to determine the concentration of the exchanged protons. The IEC values was calculated from

$$\mathrm{IEC} = \frac{(VN)_M - (VN)_b}{m} \tag{6}$$

where V and N are the volume and normality of the NaOH spent on the membranes (M) and blank (b), and m is the mass of the membrane sample.

2.7. FTIR-ATR spectroscopy

Membranes IR spectra were recorded by Impact 410 – Nicolet FT-IR Spectrometer. ATR technique was performed on multiple reflection system using a vertical variable angle (fixed to 45°) with a KRS-5 crystal (thallium bromide–iodide).

2.8. SEM-EDS microscopy

The morphologies of PVDF and charged membranes were observed using a scanning electron microscope (SEM) LEO 1450VP, and energy dispersion X-ray analysis was carried out using an EDS Genesis 2000 (EDAX). For the SEM morphological cross-sections analysis, samples were prepared by fracturing the membranes after immersion in liquid nitrogen and afterward coated with carbon. They were observed under high vacuum and EDS spectrums were obtained applying an acceleration voltage of 120 kV.

2.9. Filtration experiments

All filtration experiments were carried out with a Minitan-S ultrafiltration device (Millipore Corp), with an effective membrane transfer area of $3 \times 10^{-3}\ m^2$. The experimental protocol was: first, the membrane was compacted at 100 kPa pressure of transmembrane during 30 min [29]. Then, the hydraulic permeability of the original membrane was determined from measurements of pure-water fluxes at different pressures (100–20 kPa). Fouling test experiments with 0.1 wt% of oil emulsion were performed during 2 h at 67 kPa and feed flow of 1 L/min. After that, the membrane was cleaned with pure water during 1 h at the same operational conditions that fouling test. Finally, in order to determine the irreversible fouling resistance, pure-water flux was measured under the same hydraulic permeability conditions (100–20 kPa). All permeation trials were carried out in duplicate.

2.10. Chemical oxygen demand (COD)

Permeate samples were refluxed in strongly acid solution with a predetermined excess of potassium dichromate. The consumed oxygen was measured against standards at 600 nm by U-2001 UV–visible Hitachi spectrophotometer according to the 5220D Standard Method for the Examination of Water and Wastewater [30].

2.11. Oil retention

Oil content was evaluated by UV–vis spectroscopy at 220 nm. The oil retention coefficient R (%) was calculated from [22]

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{7}$$

where C_p and C_f are the oil concentration in permeate and feed, respectively.

3. Results and discussion

3.1. Grafting and sulfonation

The grafting degree of GMA grafted on to the irradiated membrane is shown in Table 1. The GD increase as the monomer GMA concentration increases and it slightly decrease in presence of the EDMA crosslinker. Similar results were reported in (GMA/DVB or GMA/EDMA) cografting of polyethylene [31,32]. Conversion degree of GMA epoxy group into the sulfonic group is also shown in Table 1. The results indicated that the epoxy groups of grafted membrane were satisfactorily functionalized (X between 95 and 99%).

Membranes modification can be qualitatively verified by FTIR. Fig. 3 shows the resulting spectrum of PVDF, G5 PVDF, and G5 PVDF (S) membranes. The bands at 3400 cm^{-1} and at 3600 cm^{-1} of the PVDF spectrum are due to the stretching of the antisymmetric C–H bond and to the symmetric stretching, respectively. The amide carbonyl band at 1688 cm^{-1} [33] indicates the presence of PVP coming from casting dope. At 1200 cm^{-1} the predominant vibrations are C–H, C–C and C–F deflections. Within the range of 1020–1330 cm^{-1}, band is produced by overlapped elongation of C–H and C–F. In 505 and 880 cm^{-1}, the signals are due to torsion, bending and stretching of atoms C, H and F [34]. The characteristic signals of GMA grafted membrane previous to sulfonation (spectrum G5-PVDF) are: C=O at 1720 cm^{-1} and C=O wag at 630 cm^{-1}, –O– (oxirane) presents absorption bands at 848, 908 and 990 cm^{-1} [35,36] being the last band the only one not overlapped, C–O–C at 1100 cm^{-1}, $-CH_2$ at 2970 cm^{-1}, –OH and –OH wag at 3420 and 2400 cm^{-1}, respectively. The spectrum corresponding to G5-PVDF(S) shows visible characteristic peaks for SO_3^- with absorption at 1250–1150 and 1060–1030 cm^{-1} [37,38]. The strong band of frequency 1250–1150 cm^{-1} can be ascribed to stretch vibration for S=O, and the absorption band at 1060–1030 cm^{-1} is assigned to the symmetric stretching band. However, the C–O–C for asymmetric stretching band is 1290–1180 cm^{-1}, and the O–C–O peak is 645–575 cm^{-1}. After sulphite reaction absorption peak at 990 cm^{-1} disappears (oxirane ring of GMA). The spectra of G1-PVDF, G1-PVDF(S) and crosslinked membranes (G1X-PVDF and G5X-PVDF) showed similar signals than G5-PVDF, and G5-PVDF (S) membranes (spectra are not shown).

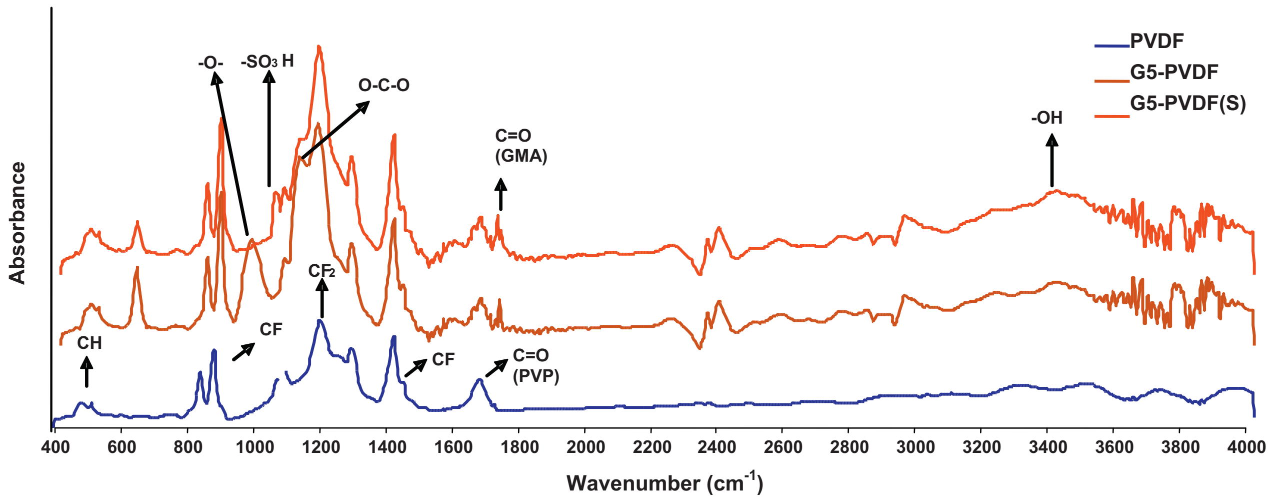

Fig. 3. ATR-FTIR spectrum of PVDF, G5-PVDF, and G5-PVDF(S) membranes.

3.2. SEM-EDS microscopy

Fig. 4 illustrates the images obtained by backscattered electrons of the surface as well as the data obtained by EDS for PVDF and the sulfonated G5-PVDF(S) and G5X-PVDF(S) membranes. From the EDS results, it can be observed that the PVDF membrane shows signals corresponding to C, F and O. PVP presence in PVDF membrane can be observed by low O/C ratio. Membrane G5-PVDF(S) have two kind of phases: (i) mainly grafted and sulfonated phase showing a comparable C, F, Na, S and O signals, and (ii) small regions (clearly shown in the micrograph) where C and F are the main signals respect to Na, S and O signals.

Table 2 shows changes in ratios of the elemental components of grafted membranes (F/C, O/C, S/C, and S/O). The elemental ratio of the original PVDF membrane was included as reference. It can be noticed that radiation-induced grafting of GMA/EDMA onto PVDF membrane causes a drastic decrease in the F/C ratio compare to the original membrane. This can be ascribed to the fact that the grafting process mainly occurs at the membrane surface, as it can be noticed from the very low mass incorporated in the grafting process (GD less than 3.5% in all cases). On the other hand, the observed decreasing trend in the F/C ratio with the increasing grafting degree

Table 2
Membrane elemental analysis from EDS measurements.

Membrane	F/C (w/w)	O/C (w/w)	S/C (w/w)	S/O (w/w)
PVDF	0.480	0.004	0	0
G1-PVDF(S)	0.410	0.032	0.021	0.652
G1X-PVDF(S)	0.440	0.030	0.018	0.597
G5-PVDF(S)	0.237	0.155	0.098	0.621
G5X-PVDF(S)	0.350	0.108	0.034	0.570

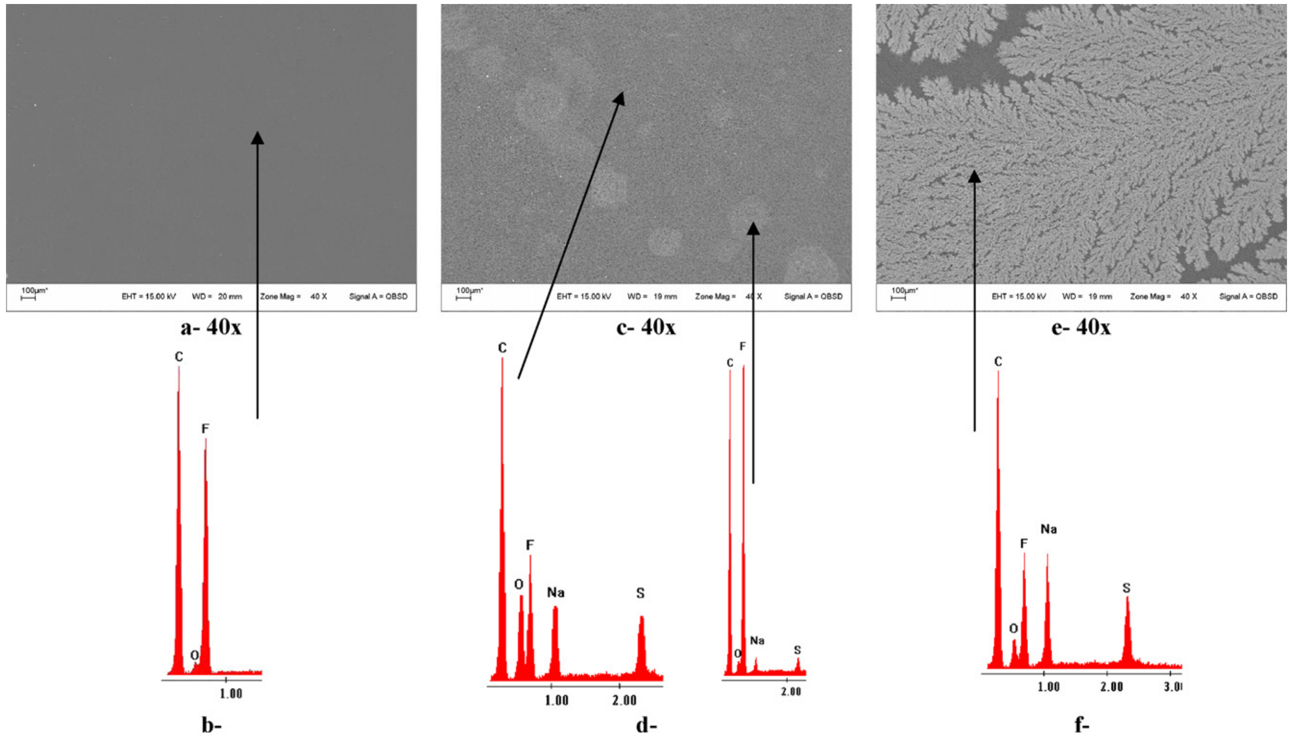

Fig. 4. SEM membrane surface images and EDS spectra: (a and b) PVDF; (c and d) G5-PVDF(S); (e and f) G5X-PVDF (S).

Table 3
Ionic and structural parameters of the membranes.

Membrane	IEC (μequiv./g)	r_{pLLDP} (nm)	ε (%)
PVDF	0	43.84	24.03
G1-PVDF(S)	6.60	7.22	15.63
G1X-PVDF(S)	5.78	7.35	15.89
G5-PVDF(S)	9.88	4.18	4.16
G5X-PVDF(S)	8.65	2.23	8.50

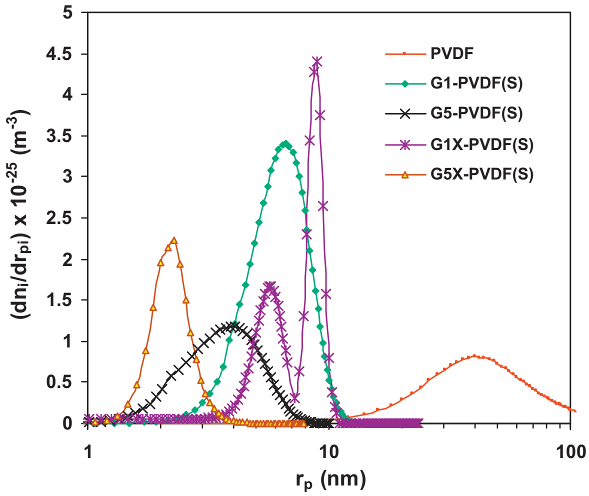

Fig. 5. Pore size distribution of the membranes from LLDP measurements.

can be attributed to an increase in the thickness of the grafted GMA layer. The third and fourth columns in Table 2 show that the S/C as well as O/C ratios increase with the increase of the degree of grafting of the membranes indicating an augment of the sulfonic groups in the membrane.

3.3. *Ion exchange capacity*

Table 3 shows the ion exchange capacity of the sulfonated membranes. The results indicated that all modified membranes had higher ion exchange capacity than PVDF membrane. This capacity increased with GMA content and decreased when the crosslinker was included in the grafted polymer. The crosslinking reaction produces a more closed structure of the grafted polymer decreasing the amount of oxirane groups available to generate sulfonic groups in presence of sodium sulphite.

3.4. *Measurements of pore size distribution*

Structural characteristics of the prepared membranes were analyzed using the LLDP technique. Fig. 5 shows the results of pore size distribution of the studied membranes, indicating that there was a noticeable diminution in the pore size of the sulfonated membranes compared with those of the original PVDF membrane. Only G1X-PVDF(S) membrane presented a bimodal distribution of pore radius with maximum at 5 nm and 9 nm. Table 3 shows the mean pore radii data determined from the pore size distribution, evidencing a reduction on pore size from 43.84 nm for the unmodified membrane to 4.18 nm for sulfonated membrane with 0.5% GMA (G5-PVDF(S)). The presence of crosslinker leaded to a major decrease of mean pore size reaching a minimum value of 2.23 nm for the membrane with 0.05% of EDMA (G5X-PVDF(S)). The general tendency indicated grafted-sulfonated technique generated membranes with lower porosity and higher number of pores of smaller size than those of the unmodified membrane.

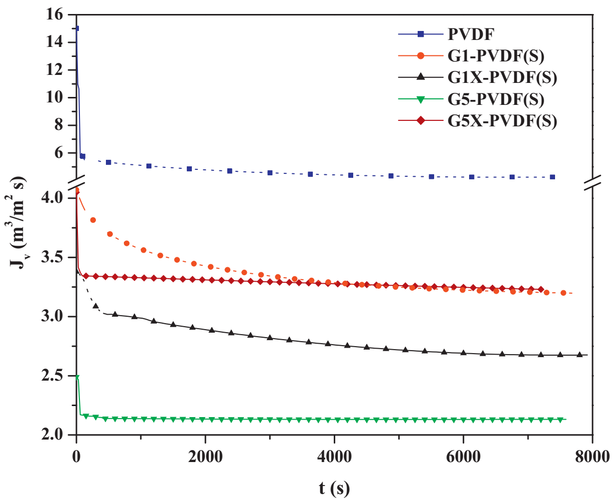

Fig. 6. Membrane permeated fluxes versus filtration time.

3.5. *Functional characterization*

Table 4 shows the main results obtained from pure water flux measurements through the prepared membranes, i.e.: hydraulic permeabilities of the virgin membranes (L_h), hydraulic permeability of the membranes after cleaning procedure (L_{hc}). The initial permeate flux (J_{v0}) can be obtained from hydraulic permeability of the membranes at $\Delta p = 67$ kPa. Good reproducibility of water permeability of the charged membranes after cleaning was obtained indicating there was a very low irreversible fouling during the filtration tests. Charged membranes reduced notably the hydraulic permeability compared with the PVDF membrane in concurrence with their mean pore size and porosity decrease. Membrane G5X-PVDF(S) showed the smallest pore size (2.23 nm), however its L_h value was higher than the G5-PVDF(S) ($r_{\mathrm{pLLDP}} = 4.18$ nm) probably as a consequence of its highest porosity ($\varepsilon = 8.5\%$).

The oil retention and COD values are also informed in Table 4. The grafted-sulfonated G5-PVDF(S) and G5X-PVDF(S) membranes showed the highest oil retention (*R*%) in total agreement with their highest IEC and smallest pore size. The water permeate from the filtration with sulfonated membrane has appropriate characteristics (COD < 100 mg L^{-1}) for direct discharge into municipal wastewater treatment plant and river ditches, according to the current legislation in Argentina [39].

Fig. 6 shows the normalized permeate flux (J_v/J_{v0}) as a function of time for original and modified PVDF membranes. It shows the variation of normalized flux with time during the permeation

Table 4
Hydraulic permeability, initial and limiting fluxes, oil retention, and COD data.

Membrane	$L_h \pm \Delta\varepsilon$ ($\times 10^{10}$ ms^{-1} Pa^{-1})	$J_{v\infty} \pm \Delta\varepsilon$ ($\times 10^5$ ms^{-1})	$L_{hc} \pm \Delta\varepsilon$ ($\times 10^{10}$ ms^{-1} Pa^{-1})	*R* (%)	COD (mg L^{-1})
PVDF	22.38 ± 1.8	4.25 ± 0.40	7.49 ± 0.72	82.90	230.6
G1-PVDF(S)	6.08 ± 0.52	3.21 ± 0.29	5.91 ± 0.55	98.24	49.6
G1X-PVDF(S)	5.07 ± 0.41	2.68 ± 0.23	5.11 ± 0.48	97.78	54.7
G5-PVDF(S)	3.71 ± 0.27	2.13 ± 0.21	3.81 ± 0.37	98.75	43.9
G5X-PVDF(S)	6.04 ± 0.54	3.23 ± 0.30	5.86 ± 0.57	99.20	39.0

Table 5
Resistances (m^{-1}) of original and charged PVDF membranes.

Membrane	$R_m \pm \Delta\varepsilon \times 10^{-11}$	$R_T \pm \Delta\varepsilon \times 10^{-11}$	$R_F \times 10^{-11}$	$R_{iF} \times 10^{-11}$	R_F/R_T (%)
PVDF	4.47 ± 0.40	14.90 ± 1.1	10.43	8.87	70.0
G1-PVDF(S)	16.46 ± 1.2	19.73 ± 1.3	3.27	0.45	16.6
G1X-PVDF(S)	19.82 ± 1.4	23.63 ± 1.9	3.81	−0.25	16.1
G5-PVDF(S)	26.90 ± 2.1	29.73 ± 2.3	2.83	−0.63	9.5
G5X-PVDF(S)	16.54 ± 1.2	19.60 ± 1.5	3.10	0.52	15.8

experiences, where there was a drop in permeate flux and afterward it remained essentially constant during the rest of the test reaching a pseudo-steady state (limiting flux, $J_{v\infty}$). Flux decay is a measure of the fouling phenomenon, which it was more evident in PVDF membrane. Grafted membranes with sulfonic groups result in a significant reduction in the flux drop under emulsion ultrafiltration. The electrostatic exclusion plays an important role during the oil emulsion filtration process. Due to the emulsion droplets at pH 7 [22] have the same charge sign as the fixed charge in the grafted membrane surface (negative), the emulsion droplets were rejected from the membrane surface diminishing the fouling phenomena. The permeation flux during filtration can be expressed in terms of the resistance model [22] as

$$J_v = \frac{dV}{Adt} = \frac{\Delta p}{\eta(R_m + R_F)} = \frac{\Delta p}{\eta R_T} \tag{8}$$

where J_v is the permeate flux ($m^3/m^2\,s$), R_T the total resistance of permeation (m^{-1}), and η is the permeate viscosity (Pa s). R_T involves the intrinsic resistance of membrane, R_m, and the fouling resistance, R_F. The osmotic, concentration polarization and others fouling effects are included in R_F, which can be subdivided into reversible fouling (R_{rF}) and irreversible fouling (R_{iF}),

$$R_F = R_{rF} + R_{iF} \tag{9}$$

The limiting flux values after $t = 120$ min ($J_{v\infty}$ in Table 4), were used as a reference fluxes to evaluate the total resistance. The irreversible fouling resistances were obtained from the hydraulic permeabilities after membrane cleaning with water (L_{hc} in Table 4). Table 5 shows the resistance data that quantify the fouling phenomenon. The original PVDF membrane has a higher hydraulic permeability as mentioned above, resulting in a lower intrinsic membrane resistance. However, PVDF membrane showed the highest R_F and R_{iF} fouling which represent a 70% and 60% respectively of the total resistance. On the other hand, the grafted-sulfonated membranes possessed higher R_m (lower L_h) and lower R_F values than the PVDF membrane. The case of membranes with high IEC values (G5-PVDF(S) and G5X-PVDF(S)) was the most noticeable. GMA-EDMA grafted membranes had a lower fouling resistance contribution to total membrane resistance when they were compared with GMA grafted membrane. As it can be noted, the irreversible fouling values obtained from ($L_{hc} - L_h$) were within the L_h experimental error, so it can be considered negligible compared to the intrinsic membrane resistance. As general result, the incorporation of ionizable groups by means of irradiation-induced polymerization produced membranes with low fouling feature.

4. Conclusions

PVDF membrane was modified with glycidyl methacrylate (GMA) by gamma-rays induced graft polymerization method. In order to obtain charged membranes the oxirane ring of grafted membranes was efficiently sulfonated by reaction with sodium sulphite. These results were confirmed by FTIR-ATR and SEM-EDS measurements. The characterization results indicated that the modified membranes had higher ion exchange capacity, smaller pore size and lower porosity than the unmodified PVDF membrane. Charged membranes presented a very low irreversible fouling, high oil retention and low COD values in the permeate stream. Results obtained demonstrated that the synthesized grafted-sulfonated PVDF membranes have promising permselectivity properties to separate oil from oily wastewater with adequate COD characteristics, showing a potential for industrial wastewater treatment.

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