

Development of sulfonated polysulfone composite membranes for ammonium rejection

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Abstract. In the present investigation, were synthesized composite membranes prepared by simultaneous casting of two polymer solutions using the technique of phase inversion by immersion / precipitation. The support layer was prepared using polyethersulfone and polysulfone as base polymer and for the top layer was used sulfonated polysulfone (SPSU) with 50% sulfonation degree. The morphology of the resulting membranes were characterized by scanning electron microscopy (SEM). The final results showed that it is possible to prepare composite membranes by simultaneous casting of two polymer solutions with adherence between the two layers. Regarding the permeation tests, the developed membranes presented values of hydraulic permeability within the range of commercial nanofiltration (NF) membranes. Values rejection of 80% ammonium ions can be increased by using a SPSU with a greater degree of sulfonation.

Keywords: polysulfone sulfonated; composite membrane; ammonium rejection

1. Introduction

Polysulfone is one of the materials which has been most widely used in the manufacture of synthetic polymer membranes due to its excellent mechanical, thermal and chemical stability (Bowen *et al.* 2001, Lufrano *et al.* 2001, Blanco *et al.* 2002, Bowen *et al.* 2002). Polysulfones (PSU) have a high glass transition temperature and good mechanical properties and chemical resistances and it is widely used to prepare asymmetric membranes with different pore sizes for ultrafiltration (UF) and microfiltration (MF) applications (Liou *et al.* 2011). Despite of these positive characteristics, their hydrophobic nature makes them less desirable than hydrophilic membranes for the application in aqueous media and leads low water flux through the membrane pores (Genova-Dimitrova *et al.* 2001, Chen *et al.* 2009). Several researchers have been reported the use of sulfonation reaction of polysulfones for increase its affinity for water (Noshay and Robeson 1976, Lufrano *et al.* 2000).

Sulfonated polysulfones (SPSU) seems to be the most interesting polymer materials for the preparation of high flux and anti-fouling membranes due to the excellent properties of the

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backbone, allied to the hydrophilicity of the sulfonate groups (Blanco *et al.* 2001, Blanco *et al.* 2002, Bowen *et al.* 2002).

Recently, several researchers used trimethylsilyl chlorosulfonate to obtain sulfonated polysulfone. The silyl-protected reagent reportedly minimized chain scission, as determined by viscosity experiments (Devrim *et al.* 2009, Chen *et al.* 2009). This reaction mixture remains perfectly homogeneous and the chain scission was minimized (Baradie *et al.* 1998, Bastos 2006, Lufrano *et al.* 2006). The sulfonated polysulfones have been used as ion-exchange membranes, reverse osmosis and ultrafiltration membranes according to the sulfonation degree. Membranes made with a polymer of 50% sulfonation degree exhibited a high salt rejection with good permeate flux (Bowen *et al.* 2001).

Nanofiltration (NF) and reverse osmosis (RO), as novel and powerful pressure-driven separation technology, are widely used to separate or concentrate aqueous solutions containing organics or salts. Nanofiltration (NF) is a membrane process with separation characteristics between reverse osmosis (RO) and ultrafiltration (UF) membranes. The transfer mechanism of NF involves both pore-flow as in ultrafiltration (UF) and solution-diffusion as in reverse osmosis (RO). These advantages lead to a growing list of applications, such as, removal of hardness, pesticides, and natural organic matter in the drinking water industry, recovery of valuable pharmaceutical products, and removal of heavy metals (Li *et al.* 2009). The NF membranes are constituted of two layers, a support layer and a top layer which is responsible for the selectivity of the membrane. Usually, composite membranes are obtained in at least two stages: initially the preparation of the porous support and afterwards the deposition of the top layer.

In the present work, it was investigated the preparation of composite membranes by phase inversion process, using simultaneous casting of two different polymer solutions to form the top and support layers of the membrane. Polyethersulfone and polysulfone were used as base polymer. In order to form the top layer, it was used sulfonated polysulfone with 50% sulfonation degree. All the membranes were characterized by scanning electron microscopy and by permeation experiments: hydraulic permeability, permeate flux and rejection of ammonium ion. The selectivity experiments are carried out using a solution of 100 mgL⁻¹ of ammonium chloride (NH₄Cl) and a solution of ammonium sulphate ((NH₄)₂SO₄) with the same concentration. Ammonia (NH₃) ion was chosen because this ion has been recognized as a major pollutant in both municipal and industrial wastewater (Mashallah *et al.* 2012).

2. Experimental

Flat membranes were obtained by simultaneous casting of two polymer solutions. The polymer solutions used for obtaining the support and the top layers were referred to as the solutions A and B respectively. The membrane was obtained using simultaneous casting solutions A and B. The components of each solution are described as follows:

2.1 Solution A (support layer)

Different solutions were selected using polyethersulfone (PES) (ULTRASON E 6020) from Basf or polysulfone (PSU) (UDEL 3500) from Solvay Advanced Polymer as base polymer; polyvinylpyrrolidone (PVP- K30 e PVP- K90), from Aldrich, as additive, and dimethylacetamide (DMA) as solvent. The composition is presented in Table 1.

Table 1 Composition of the polymer systems used as solution A

Support	PES (%p/p)	PSU (%p/p)	SPSU (%p/p)	PVP K-30 (%p/p)	PVP K-90 (%p/p)	DMA (%p/p)
S-01	15	-	-	-	6	79
S-02				1.5	4.5	
S-03	16	-	4	-	-	80
S-04	-	15	-	1.5	4.5	79

Table 2 Composition of the solutions used for the preparation of the composite membranes

Code membrane	Solution A (support)						Solution B (top layer)
	PES (%p/p)	PSU (%p/p)	SPSU (%p/p)	PVP K-30 (%p/p)	PVP K-90 (%p/p)	DMA (%p/p)	% (p/p) SPSU/DMA
M-12	15	-	-	-	6	79	15
M-15				1.5	4.5		15
M-22	16	-	4	-	-	80	15
M-23	-	15	-	1.5	4.5	79	15
M-30	15	-	-	1.5	4.5		8
M-32				-	6		8

The supports were obtained by single casting of solution A, at room temperature (25°C), on a glass plate, and then immersed into the precipitation bath, which consisted of methanol (S-01 and S-02) or pure water (S-03 and S-04). The exposure time of the polymer solution to the environment, before immersion into precipitation bath was 1 min. After precipitation, the membranes were kept immersed in water overnight for residual solvent extraction.

2.2 Solution B (top layer)

The top layer of the membrane was synthesized using a solution of sulfonated polysulfone (SPSU) with a 50% sulfonation degree using as solvent DMA. The sulfonated polysulfone, with degree of sulfonation of 50%, was prepared from the direct sulfonation method by adding trimethylsilyl chlorosulfonate acid according to a procedure described by Bastos (2006). Before solution preparation, SPSU is pre-dried in a vacuum oven at 30°C for 1 week. SPSU solutions are prepared by dissolving a certain amount of polymer in DMA at room temperature.

The polymer solutions (A and B) were simultaneously cast by using a double casting knife, at room temperature (25°C), on a glass plate, and then immersed into the precipitation bath, which consisted of pure water. The glass plate was constituted of two levels, which allowed solution A to be placed on a lower level (0.4 mm of difference) by using a double casting knife. The exposure time of the polymer solution to the environment, before immersion into water was 1 min. After precipitation, the membranes were kept immersed in water overnight for residual solvent extraction.

2.3 Transport properties of the membranes

2.3.1 Permeate flow and hydraulic permeability

All tests were performed in the permeation system comprising a 350 mL dead-end permeation cell and a magnetic stirring was used. The maximum operating pressure was 5 bar. The system was pressurized by dry compressed air, to carry the solution of the feed tank into the cell and permeating through the membrane. The effective area of membrane was 41.8 cm². The permeation cell used in this work has been described elsewhere (Ding and Bikson 2010).

Cuppons (circular membranes, diameter 76 mm) were used. Initially, the membrane was placed in water for an hour before being placed in the cell. The cell membrane was filled with distilled water at 5 bar to compact the membrane.

Compaction is the accommodation of the structure at the operating pressure. Compaction is achieved when three readings of the permeate flow at 20 min intervals are identical. The same procedure was carried at pressures of 4, 3, 2 and 1 bar. The value of permeated flow (J_p) of the membrane was calculated through Eq. (1) (Mulder 2000).

$$J_p(L\ m^{-2}\ h^{-1}) = \frac{Flow(L\ s^{-1}) \times 3600(s/h)}{membrane\ area\ (m^2)} \quad (1)$$

Data obtained were used to build a curve of permeate flow versus pressure to determine the hydraulic permeability of the membrane, which is the slope of Eq. (1).

2.3.2 Selectivity for ammonium chloride and ammonium sulphate

The selectivity of the membranes was estimated by the rejection factor (R). It is defined as the fraction of solute retained by the membrane to a given concentration of feed solution, according to Eq. (2) (Mulder 2000, Schäfer et al. 2005).

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100 \quad (2)$$

where C_f is the solute concentration in the feed and C_p is the solute concentration in the permeate.

For the selectivity experiments two solutions of feeding had been prepared: a solution of 100 mgL⁻¹ of ammonium chloride (NH₄Cl) and a solution of ammonium sulphate ((NH₄)₂SO₄) with the same concentration. These concentrations had been chosen with the intention to evaluate the rejection of ions ammonium in the range of concentration of the urban and industrial rejects. The determination of ions ammonium in the permeates solutions of feeding had been analyzed by the Nessler method (ASTM 1995).

2.4 Scanning electron microscopy (SEM)

The morphology of the resulting support, obtained by single casting of solution A, or by simultaneous casting of polymer solutions A and B were characterized by scanning electron microscopy (SEM) (JEOL JSM 5610 LV). Samples were prepared by cryogenic breaking and coated with a thin gold layer.

Table 3 Permeate flux values that and hydraulic permeability of the supports

Support code	Transport properties	
	Permeate flux (L/m ² . h)	Hydraulic permeability (L/m ² h. bar)
S-01	147	22
S-02	289	37
S-03	364	56
S-04	302	45

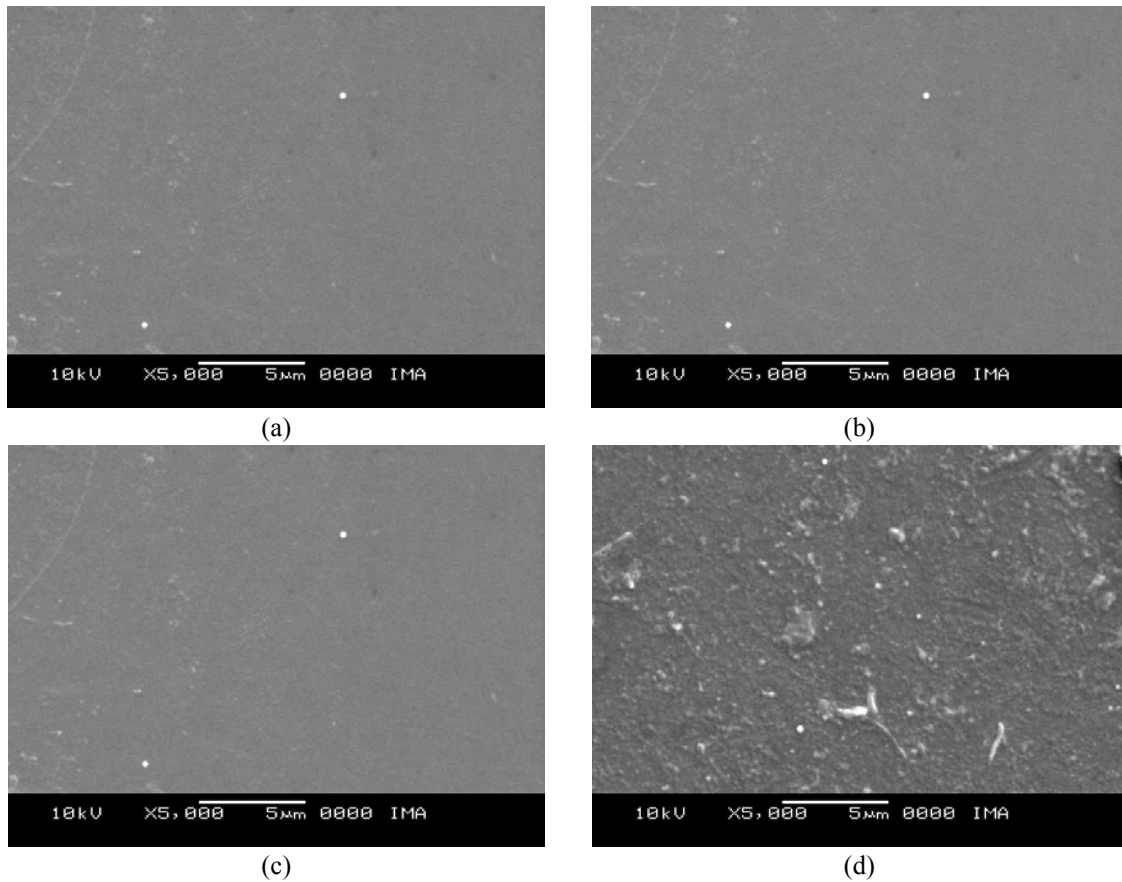


Fig. 1 Surface of the membranes obtained by the single casting of solution A

3. Results and discussion

In order to make the results discussion clearer, this section was separated in two items: the results obtained by simple casting of polymer solution A (support layer) and by simultaneous casting of solutions A and B (composite membrane). The results of permeation measurements and SEM of the membranes obtained by single casting may give information about the solutions and precipitation conditions that lead to obtain suitable supports to the deposition of the top layer.

3.1 Support layer

Table 3 presents permeate flux and hydraulic permeability values of the supports synthesized. Permeate flow and hydraulic permeability was determined for three coupons of each support. The slope is the hydraulic permeability of each coupon, and the values fall in the range found in the literature for ultrafiltration membranes (10-100 L m⁻² h⁻¹ bar⁻¹). (Mulder 2000, Schäfer *et al.* 2005).

The S-01 and S-02 supports presented lower values of flux and permeability than the S-03 support. This fact can be correlated to the use of sulfonated polymer (SPSU) as additive where the sulfonic groups of this polymer increase the polar character of the membrane and, thereby increase the permeability of support S-03.

The supports S-04 presented high values of the permeate flux, indicating that the change of precipitation bath of methanol to pure water caused significant change on the porosity of the support.

Through the photomicrographs of the surface of the supports (Fig. 1), the influence of the precipitation conditions of the polymeric film in the formation of the membrane can be observed. The supports S-03 and S-04, precipitated in water, presented structure roughened in the surface what it indicates porosity; already the supports S-01 and S-02, precipitated in methanol, presented smooth surface total, not being possible to observe superficial porosity in the increase used in the microscopy analyses.

The cross-sections of the membranes obtained by the single casting of solution can be visualized in Fig. 2. It can be noticed that the membranes present structure with interconnected pores in their cross-section when in the solutions that contain PVP as additive. The S-03 support that does not have PVP in its composition only presented macropores in the cross section.

It can be observed also, that the variation of the composition of the precipitation bath modified the morphology of the cross section of the membranes. As shown in the photomicrographs the S-02 support is seen that presented structure of interconnected pores that was precipitated using methanol bath and the S-04 that presents macropores, was precipitated in pure water.

3.2 Composite membranes

In this work were used commercial NF membranes with selective layer based on polyamide containing carboxylate ions (DL and DK/Osmonics), because it was not possible to buy commercial NF membranes containing sulfonic acid groups.

The comparison between the two types of membranes was carried out to obtain initial estimate, since it is known that the type of ionic groups inserted in the selective layer of the membrane that has a significant effect in the performance.

The results of the properties of transport, permeate flux, hydraulic permeability and selectivity of the composite membranes synthesized and commercial nanofiltration membranes are presented in Table 4.

Initially were determined permeate flux and hydraulic permeability. After that was determined the selectivity of the composite membrane, the two saline solutions were added separately for the selectivity test. The first 50 mL of the permeate solution was discarded and the following 50 mL was collected to determine the concentration of ions NH₄⁺.

To study the selectivity of the membranes obtained in this work was chosen as the ammonium ion in the form of ammonium chloride (NH₄Cl) and ammonium sulphate ((NH₄)₂SO₄) that have differences in size and charge of the counter-ion. The mechanism of separation of NF membranes

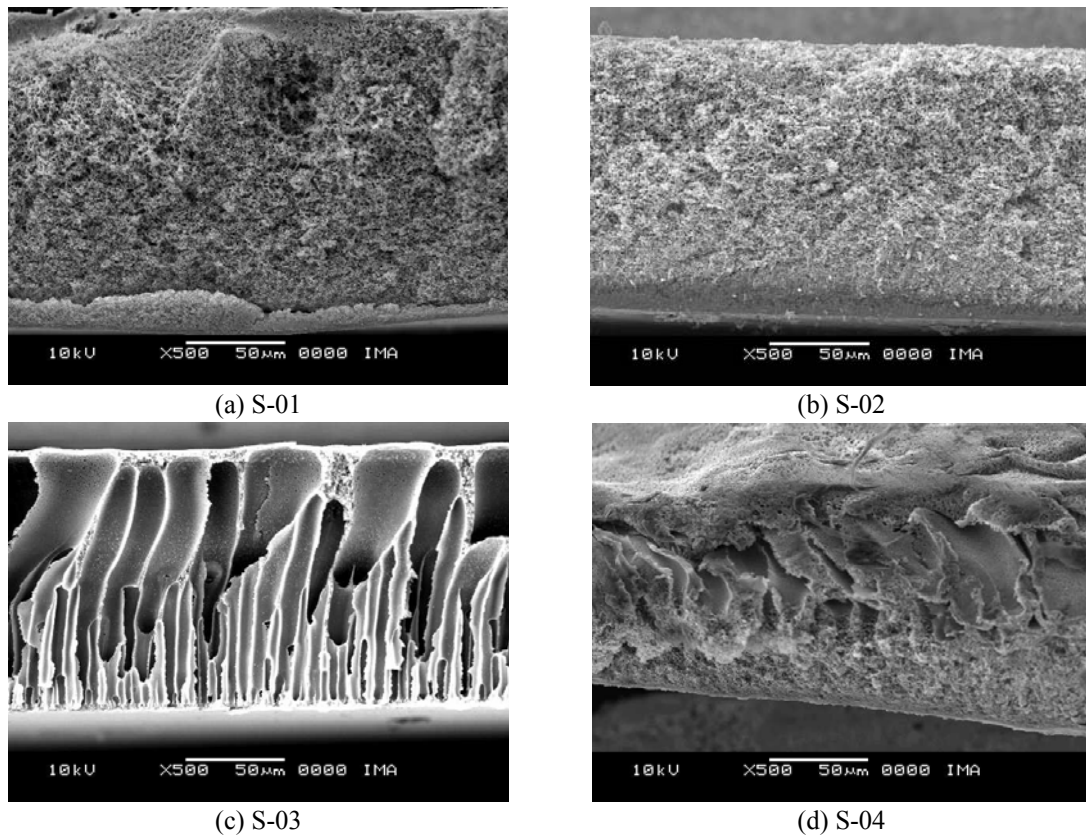


Fig. 2 Cross-sections of the membranes obtained by the single casting of solution A

Table 4 Transport Properties of the composite membranes synthesized and commercial

Code membrane	Permeate flux (L/m ² . h)	Hydraulic permeability (L/m ² h. bar)	(%) $R_{NH_4^+}$	
			(NH ₄) ₂ SO ₄	NH ₄ Cl
M-12	18	2.0	71	4
M-15	2	1.2	80	4
M-22	24	4.1	78	5
M-23	29	8.0	15	3
M-30	131	22.1	< 1	< 1
M-32	123	19.1	< 1	< 1
DK	12	2.4	99	3
DL	11	2.0	92	3

takes place through a combination of two factors: ion size exclusion and ion charge exclusion. Ion charge exclusion depends on the membrane surface charge, ionic strength and ion valence. The pore size of nanofiltration membranes is in the range of 10 Å which reject all ions and particles bigger than 10 Å (Schäfer *et al.* 2005). (Mulder 2000).

Through the results of Table 4, we can also observe that the commercial membranes had presented a rejection to ion ammonium superior than the synthesized membranes. On the other hand, the majority of the synthesized membranes presented greater permeability than the commercial membranes, this can be consequence of the insertion of the sulfonic groups in the top layer of the membrane, modifying the molecular structure of the polymeric chains, spacing them, creating a bigger volume, facilitating the passage of water.

The values found for the hydraulic permeability of the synthesized membranes, were in the range $1.2\text{--}8.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. These values fall in the range found in the literature for nanofiltration membranes ($1.0\text{--}6.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), therefore these membranes can be classified as nanofiltration membranes. (Mulder 2000, Schäfer *et al.* 2005).

The results obtained in the permeation of salts selected (Table 4) showed that the rejection of the membranes in the ammonium sulfate ions is greater than the corresponding ammonium chloride. This confirms that the rejection of ions depends on the associated anion. Chlorine ions, presents ionic diameter of $1.8 \text{ \AA}$ and passes freely through the pores of the membrane, whereas sulphate ions that has ionic diameter of $2.4 \text{ \AA}$ is rejected by the membrane. The difference in the values of rejection of the ion ammonium can also be explained by the load, that is, how much bigger the load of the anion biggest will be the effect of shield in the surface of the membrane, preventing the passage of cations.

In Table 4, it is observed that between all the conditions investigated in the preparation of the composite membranes, the M-15 membrane was the one that presented the biggest rejection to ammonium ions ($R = 80\%$) and the lesser permeate flow indicating raised resistance to the water transport. It is interesting to observe that the M-22 ($R = 78\%$) membrane compared with the M-15 presented increase in the permeated flow without showing to significant fall in the values of rejection to ammonium ions.

The Fig. 3 shows photomicrographs of the cross section of the membranes M-15 and M-22 obtained by simultaneous casting of solutions A and B. One may observe that there was a perfect adhesion, which should be formed by solutions A and B (15 wt.% SPSU). It can be concluded that the double-scattering did not significantly change the morphology of the membranes obtained by this technique, yielding similar structures to those in the single scattering of solution A.

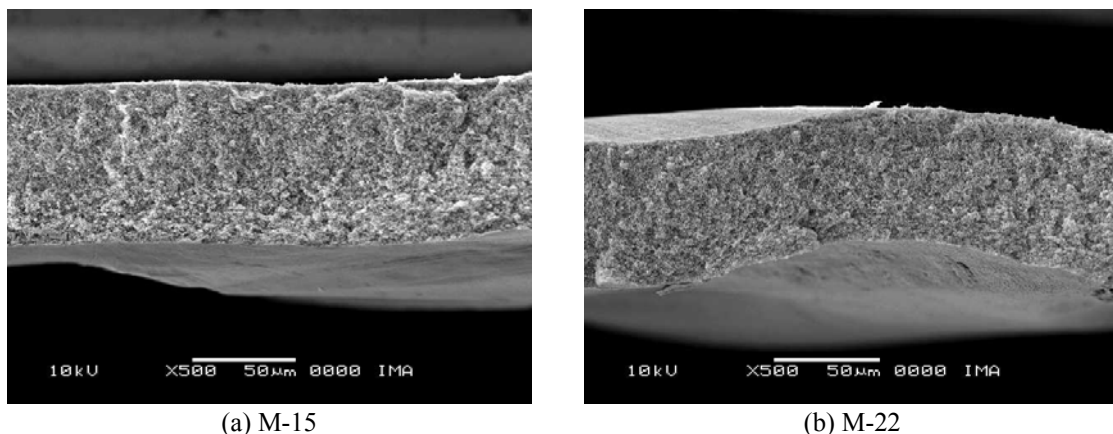
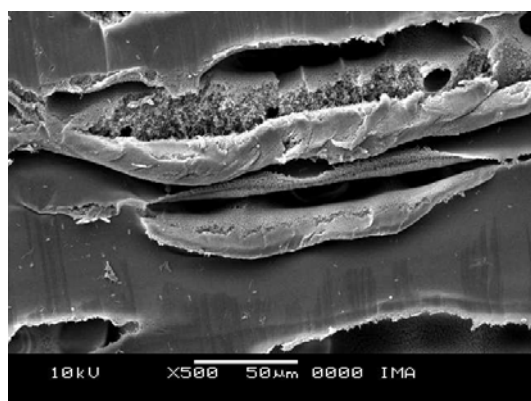


Fig. 3 Cross-sections of the membranes M-15 and M-22 obtained by simultaneous casting of solutions A and B

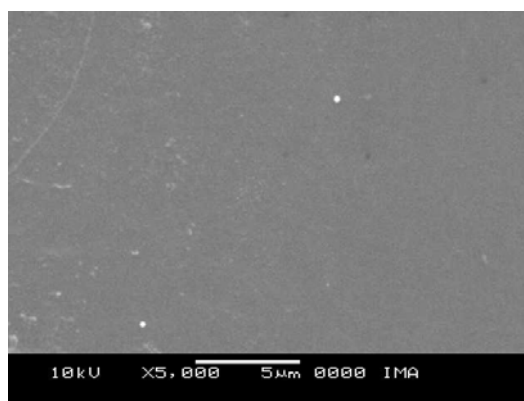
On the other hand the membranes M-30 and M-32, synthesized using solution B with 8 wt.% SPSU, presented increase in the permeate flow and the hydraulic permeability and low value of rejection indicating the presence of defects in the top layer (Fig. 4). With low concentrations of SPSU (8 wt.%) in the coating solution, the top layer is completely separate from the PSU support, as can be seen in Fig. 4(a).

The double-layer casting of flat membranes reveals that an increase of the SPSU concentration to 15wt.% results in composite membrane mechanically stable with good adhering coating layer (Fig. 4 (b)).

Fig. 5 shows photomicrographs of the cross section and surface of the membrane M-15, which shows the formation of membranes with similar morphology to obtained in the simple scattering of the solutions of the support S-02 (Fig. 2) having pores interconnected in center of its cross section. One can also observe that the cross section near the selective layer has become denser, reflecting the influence of the solution of the top layer in the support. The selective layer of this membrane was smooth, not being possible to observe superficial porosity in the increase used in the microscopy analyses.

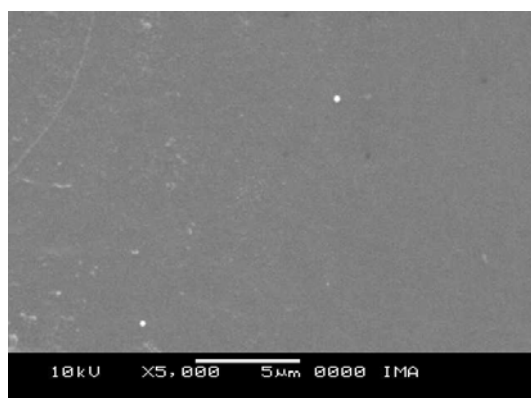


(a) M-15

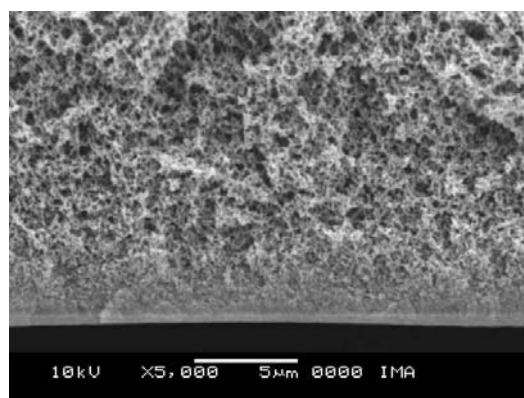


(b) M-22

Fig.4 Surfaces of the membranes M-30 and M-22 obtained by simultaneous casting of solutions A and B



(a) M-30



(b) M-22

Fig.5 Surface and cross section of the membrane M-15

4. Conclusions

In the present work it was demonstrated that it is possible to prepare composite membranes by simultaneous casting of two different polymer solutions to form the top and support layers of the membranes. The support layer was prepared using as base polymers PES or PSU and for the top layer was used SPSU with 50% sulfonation degree.

The membrane morphology analysis indicates that it is possible to obtain composite membranes with adherence between the two layers and that the SPSU concentration in the top layer is of key importance to obtain a composite membrane with dimensional stability. Adhesion of the coating to the PES support is also improved by increasing the SPSU concentration of the coating solutions.

Regarding the permeation tests, the developed membranes presented values of permeated flow of 2-29 L/m²h and hydraulic permeability of 1.2–8.0 Lm-2h-1bar-1 within the range of commercial NF membranes. Values rejection of 80% ammonium ions can be increased by using a SPSU with a greater degree of sulfonation.

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References

- ASTM Manual of water and environmental technology, D1426-93 (1995), "The Nessler Method", American Society for Testing Materials, New York.
- Bastos, E.T.R. (2006), "Development and application of polymeric membranes in the removal ammonium in wastewater", Universidade Federal do Rio de Janeiro, Brazil.
- Baradie, B., Poinsignon, C., Sanchez, J.Y., Piffard, Y., Vitter, G., Bestaoui, N., Foscallo, D., Denoyelle, A., Delabouglise, D. and Vaujany, M. (1998), "Thermostable ionomeric filled membrane for H₂/O₂ fuel cell", *J. Power Sources*, **74**(1), 8-16.
- Blanco, J.F., Nguyen, Q.T. and Schaetzel, P. (2001), "Novel hydrophilic membrane materials sulfonated polyether sulfone Cardo", *J. Membr. Sci.*, **186**(2), 267-279.
- Blanco, J.F., Nguyen, Q.T. and Schaetzel, P. (2002), "Sulfonation of polysulfones: Suitability of the sulfonated materials for asymmetric membrane preparation", *J. Appl. Polym. Sci.*, **84**(13), 2461-2473.
- Bowen, R.W., Doneva, T.A. and Yin, H. (2001), "Polysulfone-sulfonated poly(ether ether) ketone blend membranes: systematic synthesis and characterization", *J. Membr. Sci.*, **181**(2), 253-263.
- Bowen, R.W., Doneva, T.A. and Yin, H. (2002), "The effect of sulfonated poly(ether ether ketone) additive on membrane formation and performance", *Desalination*, **145**(1-3), 39-45.
- Chen, S.H., Liou, R.M., Lin, Y.Y., Lai, C.L. and Lai, J.Y. (2009), "Preparation and characterizations of asymmetric sulfonated polysulfone membranes by wet phase inversion method", *European Polym. J.*, **45**(4), 1293-1301.
- Ding, Y. and Bikson, B. (2010), "Preparation and characterization of semi-crystalline poly(ether ether ketone) hollow fiber membranes", *J. Membr. Sci.*, **357**(1-2), 192-198.
- Genova-Dimitrova, P., Baradie, B., Foscallo, D., Poinsignon, C. and Sanchez, J.Y. (2001), "Ionomeric membranes for proton exchange membrane fuel cell (PEMFC): Sulfonated polysulfone associated with phosphatoantimonic acid" *Membr. Sci.*, **185**(1), 59-71.
- Li, L., Zhang, S. and Zhang, X. (2009), "Preparation and characterization of poly(piperazineamide)

- composite nanofiltration membrane by interfacial polymerization of 3,3',5,5'-biphenyl tetraacyl chloride and piperazine", *J. Membr. Sci.*, **335**(1-2), 133-139.
- Lufrano, F., Squadrito, G., Patti, A. and Passalacqua, E. (2000), "Sulfonated polysulfone as promising membranes for polymer electrolyte fuel cells", *J. Appl. Polym. Sci.*, **77**(6), 1250-1257.
- Lufrano, F., Gatto, I., Staiti, P., Antonucci, V. and Passalacqua, E. (2001), "Sulfonated polysulfone ionomer membranes for fuel cells", *Solid State Ionics*, **145**(1-4), 47-51.
- Lufrano, F., Baglio, V., Staiti, P., Arico, A.S. and Antonucci, V. (2006), "Development and characterization of sulfonated polysulfone membranes for direct methanol fuel cells", *Desalination*, **199**(1-3), 283-285.
- Mashallah, R., Saeed, S. and Sayed, N.A. (2012), "Simulation of ammonia removal from industrial wastewater streams by means of a hollow - fiber membrane contactor", *Desalination*, **285**, 383-392.
- Mulder, M. (2000), *Basic Principles of Membrane Technology*, (2nd Edition) Kluwer Academic Publishers, Dordrecht.
- Noshay, A. and Robeson, L.M. (1976), "Sulfonated polysulfone", *J. Appl. Polym. Sci.*, **20**(7), 1885-1903.
- Liou, R.M., Chen, S.H., Lai, C.L., Hung, M.Y. and Huang, C.H. (2011), "Effect of ammonium groups of sulfonated polysulfone membrane on its pervaporation performance", *Desalination*, **278**(1-3), 91-97.
- Schäfer, A.I., Fane, A.G. and Waite, T.D. (2005), *Nanofiltration: Principles and Applications*, Elsevier, Oxford.
- Devrim, Y., Erkan, S., Baç, N. and Eroğlu, I. (2009) "Preparation and characterization of sulfonated polysulfone/titanium dioxide composite membranes for proton exchange membrane fuel cells", *Int. J. Hydro. Energy*, **34**(8), 3467-3475.