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Preparation and characterization of organic-inorganic porous membranes: Evaluation of their performance in ultrafiltration

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ABSTRACT

Flat membranes of polysulfone (PSf)/zirconium oxide (ZrO_2) with several oxide percentages were synthesized by the phase inversion process adding ZrO_2 to the casting solution. The effect of inorganic material concentration on the pore mean diameter, on the hydraulic permeability and on the decline of permeate flow in the ultrafiltration of an oil emulsion was analyzed. The results indicate that mean pore radius increases with zirconium oxide content. The presence of zirconium oxide in the casting solution produces membranes with a higher hydraulic permeability. There is an optimum oxide concentration for which the stationary permeate flow is 30% higher than that of an oxide-free membrane.

Keywords: Organic–inorganic membranes; ZrO_2; O/W separation; Fouling

1. Introduction

The UF technique is widely used for purification, fractioning, separation and concentration of solutes soluble or dispersed in water. With the development of synthetic membranes, there has been an increased interest in membrane processes for treating water.

The flux drop due to fouling phenomenon has a negative impact on the feasibility and economy of UF process, and therefore, there is a particular interest in its prevention or minimization. Polymeric membranes less sensitive to fouling can be obtained developing materials by the synthesis of new polymers. Another way of doing this is to alter materials of common use for membrane manufacture by changing the chemical structure of the polymer, e.g. grafting. An alternative to generating modified materials is the addition of other organic or inorganic materials to casting solution in order to obtain membranes with better permeoselective properties. With regard to this, Genné et al. [1] reported the preparation of PSf membranes cast from polymeric solutions with the addition of different amounts of zirconium oxide. Membrane permeability was found to increase for growing amounts of inorganic grains added to casting solution. However, image analysis of surface micrographs did not reveal the corresponding changes in surface porosity and pore dimensions of the skin. The observed flux behavior in protein filtration was attributed to the disturbance of normal phase-inversion process by the presence of inorganic grains.

Doyen et al. [2] analyzed comparatively UF membrane behavior of different materials: polymeric (PSf/PVP), ceramic (ZrO_2) and organ-minerals (ZrO_2/PSf) membranes. These three types of membranes with very similar pore size showed, however, very different water permeability coefficients. This difference was attributed to changes in

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the surface porosity of membranes, according to the field emission scanning electron microscopy studies (FESEM).

Bottino et al. [3] prepared and characterized membranes composed of organic-inorganic material by phase-inversion method. The fabricated membranes were made up of fine particles of silica evenly dispersed in a PVDF polymeric matrix. Increasing amounts of silica added to more diluted PVDF solutions yielded membranes with higher permeate flux and lower retention, while no particular influence on membrane performance was observed by adding silica to concentrated PVDF solutions.

In other work, Bottino et al. [4] prepared membranes composed of PVDF-ZrO_2 by the phase-inversion method of a ternary suspension by adding ZrO_2 particles to PVDF solution. To verify the efficiency of prepared membranes, the ultrafiltration of 40 KD dextran solution was carried out. The results showed that the structure of membrane cross-sections was strongly affected by the presence of ZrO_2. An increase of ZrO_2 concentration led to an increase of permeate flux at the expense of the retention.

Luo et al.[5] prepared TiO_2 nanoparticles (40 nm or less) in anatase crystal structure from the controlled hydrolysis of titanium tetraisopropoxide. The hydrophilic modification of poly(ether sulfone) UF membrane was performed by self-assembly of the hydroxyl group of TiO_2 nanoparticle surface and the sulfone group and ether bond in poly(ether sulfone) structure through coordination and hydrogen bond interaction. The experimental results show that the composite UF membrane has good separation performance and offers a strong potential for possible use as a new type of anti-fouling UF membrane.

Cao et al. [6] analyzed comparatively the performance and morphology between neat PVDF membrane and PVDF composite membranes with nanosized TiO_2 particles of different size. The TiO_2/PVDF membrane with smaller nanoparticles had smaller mean pore size on its surface and more apertures inside the membrane. X-ray diffraction (XRD) experiments also suggested that smaller TiO_2 nanoparticles had stronger effect on the crystallization of PVDF molecules.

This work is aimed at both the study of the impact that the presence of zirconium oxide has on the casting solution constituted by polysulfone/N,N-dimethylformamide in the preparation and structures of membranes, and the analysis of membrane permeoselective characteristics in the filtration of oil emulsions.

2. Experimental

PSf UDEL® P-3500 was provided by Amoco, polyvinylpyrrolidone (PVPK30) was used as pore forming, dextrans: 8.8 KDa, 40 KDa, 70 KDa, 200 KDa, 2000 KDa, 4900 Kda, and ZrO_2 (4.5 mm average particle size) were purchased from Fluka. N, N-dimethylformamide (DMF), KCl were provided by Merck. A commercial emulsive oil (Insignia® oil) was purchased from JyM Lubricantes S.A. (Argentina). A synthetic emulsion was prepared dispersing commercial kerosene, purified, in deionizated water using Triton X-100 as emulsifier and PVA as co-emulsifier. Triton X-100 was provided by J.T. Bakerand, PVA by Fluka. Viledon 2431 non-woven support was kindly provided by Carl Freudenberg, Germany.

2.1. Preparation of membranes

The general preparation procedure was as follows: PSf and PVPK30 were dissolved in DMF, after the oxide was added to the solution under continuous mixing using a magnetic stirring bar. The final mixture was cast onto the non-woven support using a film extensor. The solution was then coagulated with bidistilled water at 25°C. Afterwards, membranes were stored in a water bath until being used. Table 1 shows the different compositions of each membrane.

2.2. Microscopy

Scanning electron microscopy images were obtained using a LEO 1450 VP. Membrane samples were freeze-fractured and then, coated by sputtering a thin gold layer. They were observed under high vacuum.

2.3. Determination of zeta potential from electroviscous effect

Electroviscous effects were determined by measuring water flux at different values of pH and salt concentration. This was done in the same device as the permeability measurements using the protocol described elsewhere [7].

Table 1
Composition of casting solution

Membrane	PSf (wt%)	PVP K30 (wt%)	DMF (wt%)	ZrO_2 (wt%)	ZrO_2/PSf ratio (%)
PSf	15	5	80	0	0
Zr-20	14.56	4.85	77.68	2.91	20
Zr-40	14.14	4.71	75.48	5.66	40
Zr-60	13.75	4.58	73.41	8.25	60
Zr-80	13.39	4.46	71.44	10.71	80

1×10^{-3} M and 0.1 M potassium chloride (KCl) (Merck) solutions was used as the background electrolyte in electroviscous effect measurements. Deionised water was used in the preparation of the KCl solutions. 0.1 M KOH (Fluka) or HCl (Merck) was used for pH adjustment.

In order to calculate zeta potential from electroviscous effect we have used the Levine equation [8]:

$$\frac{\mu_a}{\mu_o} = \left(1 - \frac{8\beta(e\zeta/kT)^2(1-G)F}{(\kappa r)^2}\right)^{-1} \qquad (1)$$

where μ_a is the apparent viscosity, μ_o the bulk viscosity of the electrolyte solution, ζ the zeta-potential of the capillary surface, κ the Debye constant, and r is the pore radius. G and F are dependent on ζ and on κr, and can be determined from graphs given in [8].

2.4. Filtration experiments

All experiments of filtration were carried out in a Minitan–S ultrafiltration device from Millipore Corp and the UF set-up diagram is shown in Fig. 1. Once the compaction and hydraulic permeabilities were determined, measurements of electroviscous effect were done and then, measurements with dextrans were carried out using a dextran molecular weight ranging from 8 KDa to 4900 KDa, according to a method reported elsewhere [9,10]. Dextran concentrations were determined using a HPLC from Gilson coupled to a refraction index. The distribution of pore radius can be summarized as follows with f_d (nm^{-1}):

$$f_d = \frac{d(J_{w,t}/J_w)}{d(r_p)} \qquad (2)$$

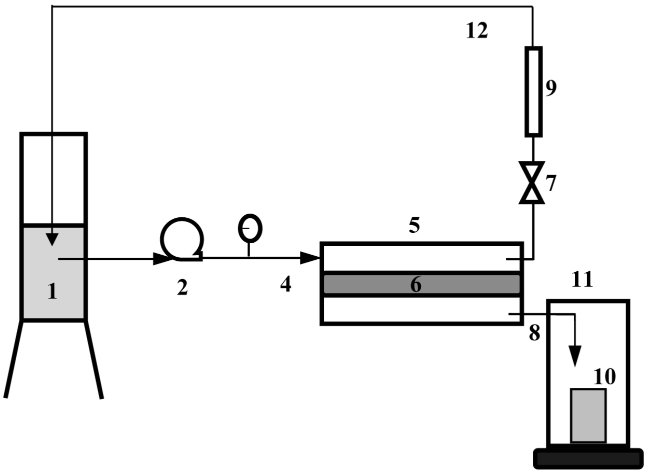


Fig. 1. UF set-up diagram. 1 – Feed temperature controlled reservoir, 2 – Peristaltic pump, 3 –Gauge pressure, 4 – Emulsion feed, 5 – Membrane cell, 6 – Membrane, 7 – Valve, 8 – Permeate, 9 – Rotameter, 10 – Permeate collector, 11 – Balance, 12 – Retentate.

where $J_{w,t} = J_v(1-R)$, J_v is the permeate flux (m/s Pa), R the retention coefficient was evaluated from observed dextran retention coefficients for different low-pressure drops and then extrapolated to a zero pressure. $J_w = J_v - J_s$ with $J_s = J_v C_p$, where C_p has been expressed as volume fraction. The porous radius r_p (nm) can be related to the molecular size of dextran molecule (Dalton) [11] by:

$$r_p = 0.4253\ (\mathrm{MW})^{0.45} \qquad (3)$$

2.5. Emulsion used

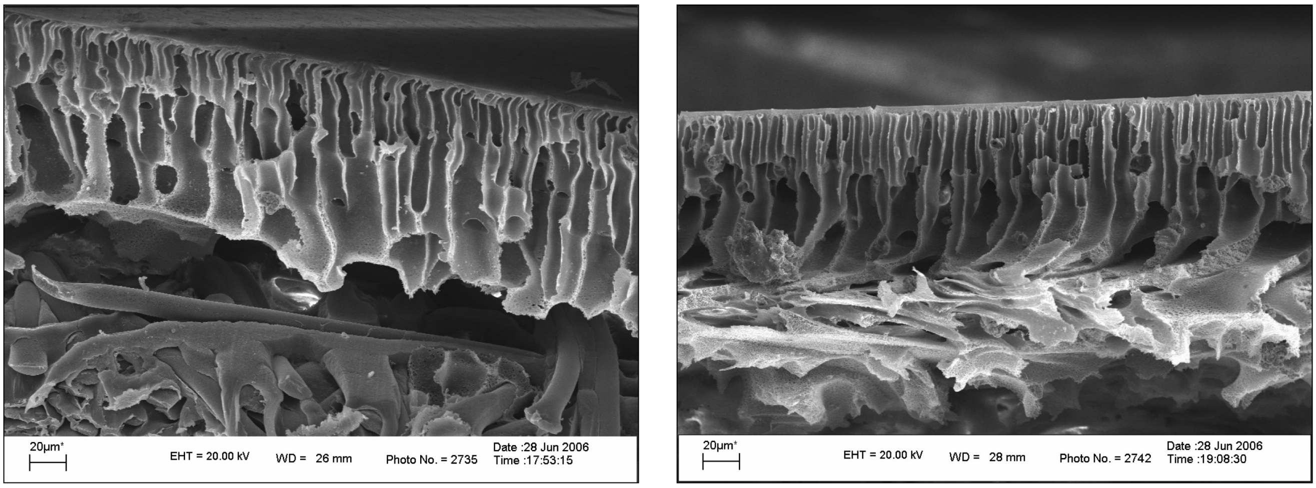
The emulsions used in filtration experiences were synthesized in the laboratory from commercial kerosene dispersed in deionizated water. The hydrocarbon concentration was 250 ppm. During the synthesis of emulsions, a mixture of surfactants (polyvinyl alcohol and Triton X-100) was used to keep their stability, which has been studied by turbidimetric measurements for several weeks with different emulsion concentrations.

Oil content was evaluated using a method described by Cumming et al. [12,13]. A copper–organic complex was dissolved in kerosene. Permeate and retentate samples were treated by ultrasound and measured using atomic absorption. Copper content was proportional to oil content.

3. Results and discussion

Fig. 2 shows SEM images of Zr-20 and Zr-80 membrane cross-sections. In Zr-20 membrane, a finger-like structure is observed while in Zr-80 membrane, there are two zones, namely: a finger-like one in the upper part, and a more densified one nearby the support. The presence of insoluble solids in a liquid solution can increase the casting solution viscosity conducing to diminish the macrovoids formation. Bottino et al. [3] found that an increase in the viscosity values is observed when the silica concentration increase in a PVDF solution, but no change in the membrane substructure is mentioned. Yang et al. [14] reported that the viscosities of PSf casting solutions increase with the increase of TiO_2 content, while the macrovoids are suppressed at high filler concentration.

However, this porous structure densification does not produce a decrease of the pore size. Fig. 3 shows the distributions of pore radius obtained from dextran rejection measurements. In this figure, a shift to larger pore sizes is observed when oxide content increases. In the case of PSf membrane, a pore mean size (rp_m) of 5.78 nm was found, whereas in Zr-80 membrane, a rp_m of 23.70 nm was obtained. Mean radius pores (rp) are shown in Table 2. Inorganic particles create zones of discontinuity in the polymeric solution such as void spaces between particles and the polymeric matrix during the phase inversion process. A low adhesion between particle-polymer phases produces larger pore size.



(a) Zr-20 (b) Zr-80

Fig. 2. Cross-section micrograph of organic–inorganic membranes.

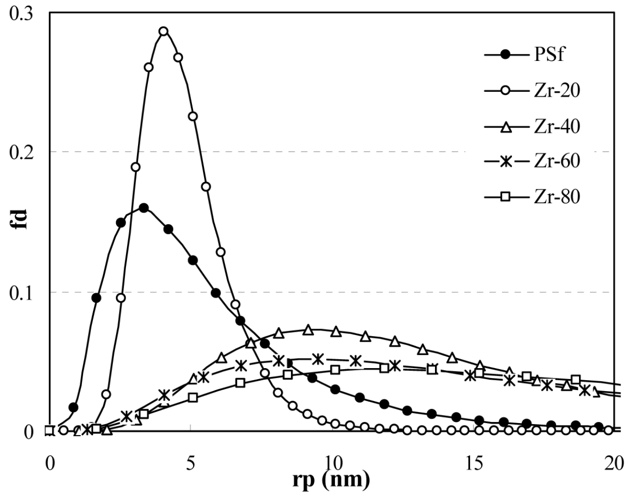


Fig. 3. Pore size distributions, f_d (nm^{-1}) vs. r_p (nm) obtained from dextran permeation.

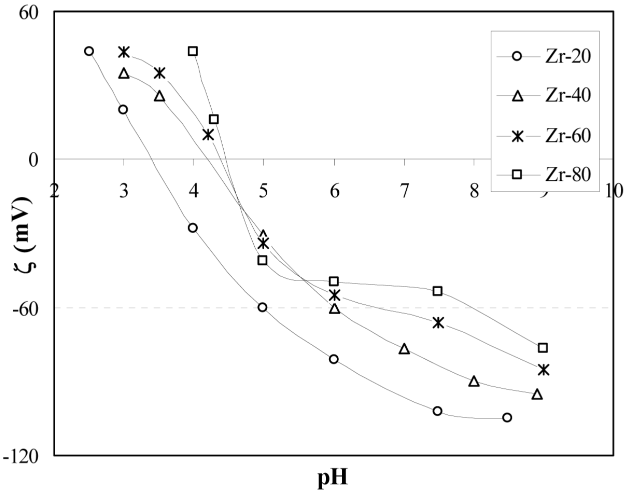


Fig. 4. Zeta potential obtained from electroviscous effect at ΔP = 55.14 KPa.

Table 2 and Fig. 4 show the results obtained from electroviscous effect measurements. In all the cases, there is an isoelectric point (IP) which increases with the zirconium oxide content. Huisman et al. [15] reported an isoelectric point below pH = 3 using the electroviscous effect which is similar to that found in this work for a PSf membrane of 3.78 nm-nominal pore radius. However, ZrO_2 inorganic membranes present an IP value of pH =

Table 2
Characteristics of prepared membranes: mean pore size and standard deviation of porous size distribution, water permeability and isoelectric point

Membrane	PSf	Zr-20	Zr-40	Zr-60	Zr-80
r_p, nm	5.78	4.75	14.13	18.86	23.70
σ, nm	3.99	1.54	7.70	12.50	17.72
Lho, m/s Pa	8.2 e–10	1.31 e–09	1.05 e–09	1.16 e–09	1.14 e–09
I.P. (pH)	<3	3.35	4.15	4.40	4.50

8 [7]. The trend found in this work seems to be within these extreme values.

Table 2 also shows the values of hydraulic permeability (Lho) of compacted membranes. In all the cases, the presence of ZrO_2 leads to membranes with a higher hydraulic permeability, while PSf/ZrO_2 compound membranes are less compactable than those of pure PSf (Fig. 5). Compaction appears when a polymeric membrane undergoes pressure, the polymers are slightly reorganized and the structure is changed, resulting in lowered volume porosity, increased membrane resistance and eventually lowered flux.

The degree of compaction is inversely proportional to the percentage of inorganic material. Organic-inorganic membranes compact between 45 and 60%, while those of PSf compact 90%. The reason for this behavior may be that the addition of inorganic material to the polymeric matrix improves membrane mechanic properties decreasing their sensitivity to compression in comparison with membrane cast from PSf.

3.1. Analysis of fouling in the ultrafiltration of an oil emulsion

Fig. 6 shows the development of permeate flux with filtration aging for membranes with variable amounts of zirconium oxide. In all the cases, the largest declination happens during the first 10 min of the experience, and the flux keeps a constant value for each case, called stationary flux (J_{est}). The presence of inorganic material in membranes improves this parameter — important for a process design — showing that there is an optimum 40% concentration of ZrO_2 (Table 3). This leads to a significant improvement on J_{est}, i.e. 30% higher than that of a PSf membrane. This optimum concentration of ZrO_2 is not only determined by a larger pore size — membranes with concentrations higher than 40% (of ZrO_2) have larger pore sizes but smaller J_{est} — but also by some kind of membrane-emulsion electrostatic interaction.

With regard to permeate quality, the oil apparent retention coefficient (R_o) — oil rejection coefficient — is defined according to Eq. (4):

$$R_0 = 1 - \frac{C_p}{C_o} \tag{4}$$

Concentrations C_o and C_p correspond to oil concentration (mg/L) in feed and permeate streams, respectively. Table 3 shows the results obtained for R_0 of the membranes studied after its use in emulsion filtration. These results show that PSf membranes are highly selective to oil emulsion treatment. There is not a notable difference in membrane emulsion rejection as a function of ZrO_2 percentage since all the membranes show an oil retention

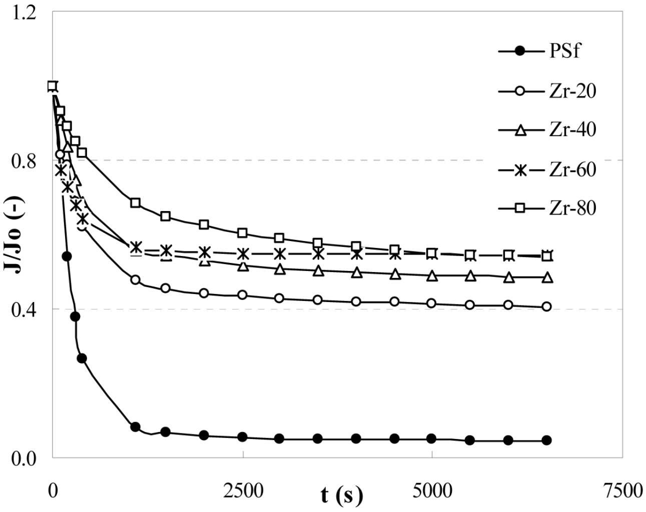


Fig. 5. Normalized flow decline due to water permeation (*J* at time t/J_{est}) at ΔP = 55.14 KPa.

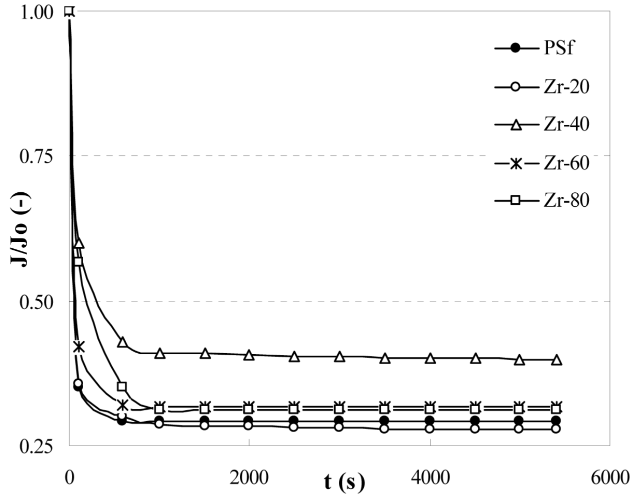


Fig. 6. Normalized flow decline in the emulsion ultrafiltration with the prepared membranes at ΔP = 55.14 KPa.

Table 3
Initial and stationary flux and oil rejection coefficient for the prepared membranes

Membrane	PSf	Zr-20	Zr-40	Zr-60	Zr-80
J_o, m/s	5.95 e–05	7.22 e–05	5.77 e–05	6.40 e–05	6.29 e–05
J_{est}, m/s	1.74 e–05	2.00 e–05	2.30 e–05	2.02 e–05	1.96 e–05
R_o	0.971	0.988	0.987	0.966	0.987

coefficient higher than 96%. As previously described, as inorganic material content increases in membrane structure, the pore size of membranes increases as well. Other authors [9,16] have already found that this behavior — a pore size increase does not mean a loss in membrane selectivity — may be related to a higher surface hydrophilicity produced, in this case, by the addition of inorganic material.

4. Conclusions

Organic–inorganic membranes were synthesized from PSf and ZrO_2. The presence of inorganic material particles in the casting solution leads to membranes with a higher mean radius of pores and hydraulic permeability, but less sensitive to compaction. In all the cases, the membranes with ZrO_2 present an isoelectric point, which increases with zirconium oxide content. The presence of inorganic material (ZrO_2) in membranes produces an improvement on the stationary flow, important for the design of process. The oil retention coefficient is in all the cases, higher than 97% for ZrO_2 membranes. The fouling phenomena using an oil emulsion represents 97% of the flux declination for PSf membranes, while for those cast with inorganic particles, it represents 60%. The highest fouling was represented by PSf membrane.

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