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Preparation and characterization of composite membranes ceramic/PSf and ceramic/PA 66

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ABSTRACT

In this paper, ceramic/polymer composite membranes have been prepared to evaluate the efficiency of polymer deposition on the ceramic support from to separation process of Ultrafiltration. Polymers used were polyamide 66 (PA 66) and polysulfone (PSf). The composite membranes were obtained immersing the supports into polymeric solutions to top layer formation. The presence of polymeric layer was observed on the surface of composite membranes by means of the Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Egg albumin (EA) solution was used to determine the rejection of the composite membranes. The ceramic support showed a higher flux value as expected, since its function is to favor flux passage. The composite membrane ceramic/PA 66 showed a higher flux than that of composite membrane ceramic/PSf. The EA rejection measured by reading the absorbance was 14, 42, and 62% to the support, composite membranes ceramic/PSf and ceramic/PA 66, respectively.

Keywords: Composite membrane; Membrane characterization; Ceramic/polymer membrane

1. Introduction

Ceramic materials have been arousing big interest in their application in membrane separation processes. The amphoteric character of many metallic oxides may result in electropositive surfaces, neutral or electronegative, where, depending on the characteristics, it favors the membrane–support interface. Consequently, selectivity of the separation process can be controlled by adjusting the characteristics of the membrane surface [1,2]. Ceramic–polymer composite membranes have been studied in order to improve a good mechanical resistance [3–7].

The composite membranes present a ceramic matrix (support) and a polymer top layer, where the polymer acts as a filling (penetration) and covering surface material [8]. The function of the polymeric film is to promote high selectivity while the inorganic porous support favors high flux [9]. These membranes are attractive because they have properties from both materials generating positive results in the separation processes. Some important properties of ceramic membranes are high chemical and thermal resistance, cleaning, and longer life [10]. Another important fac-

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tor in the preparation of ceramic–polymer composite membranes is the combination of preparation parameters both of the porous support and the polymeric top layer. Sintering conditions of inorganic material, polymeric solution concentration, contact time between the ceramic support and casting solution are important factors that can influence membrane efficiency. As a result of this combination, there is increase in the selectivity and hydraulic resistance of the composite membranes [11]. Recent works showed a good performance of organic/inorganic composite membranes in separation process such as ultrafiltration and pervaporation systems [12,13].

Based on this context, two different polymers like, polyamide 66 (PA 66) and polysulfone (PSf) were used to prepare the composite membranes. The aim of this paper is to characterize ceramic–polymer composite membranes as to morphology and permeability.

2. Experimental

2.1. Materials

α-Alumina powder (Alcoa Alumínio S.A.) (90%) was used as membrane support. Commercial PA 66 from Alfa Chem. Co. and PSf from Aldrich were received in pellet form. The pure formic acid (Merck, 98%) was used as the solvent for PA 66, and DMAc (N,N´-dimethylacetamide) (Merck 99%), was used as the solvent for PSf.

2.2. Preparation of composite membranes ceramic/polymer

The supports for the membranes were obtained by pressing (VEB-Werkstoffprüfmaschinen 283-35) the ceramic powder compacted under 80 MPa. The α-alumina supports in form of discs had 2.5 mm thickness and 50 mm diameter. The supports were submitted to a thermal treatment in a electric muffle, starting at room temperature to maximum temperature of 1,300 ˚C at a rate of 10 ˚C min^{-1} and cooled down to 30 ˚C at the rate of 10 ˚C min^{-1}.

After synthesis of ceramic supports, the composite membranes were prepared by putting the α-alumina supports in a stove at 100 ˚C for 12 h, and then cooling them in a room temperature for 16 h.

The polymers used to impregnate the surface of the α-alumina supports were PSf and PA 66. The supports were immersed for 2 h separately in solutions PSf 5 wt% in DMA and PA 66 5 wt% in formic acid. The polymer-impregnated supports were vacuum-dried at 30 ˚C for 6 h for the evaporation solvent and consequent film formation on the surface support. The membranes remained in a stove at 100 ˚C for 12 h to be later characterized as to morphology and hydraulic permeability.

2.3. Fourier transform infrared spectroscopy - FTIR

In order to confirm polymer deposition on the surface of the ceramic support, FTIR with reflectance accessory (ATR) was used. The top layer membranes were characterized using Nicolet spectrophotometer Impact 400. The FTIR spectra were recorded in the wave number range from 400 to 4,000 cm^{-1}.

2.4. Scanning electron microscopy (SEM)

The samples were initially fractured and gold-coated. The top layer and cross-sections morphology of the membranes was obtained by SEM Shimadzu SSX 550 operated at 10 kV.

2.5. Pure water flux

The pure water flux was measure for one hour at 1 bar. Pure water flux was measured with parallel flow type cell (area 16 cm^2) and J_w values were calculated using Eq. (1).

$$J_w = \frac{V}{A \cdot \Delta t} \tag{1}$$

where V is quantity of the permeate (L), A is membrane area (m^2), and Δt is permeation time (h).

2.6. Determination of protein rejection

Egg albumin (EA) (45 kDa) solution prepared at a concentration of 100 ppm was used to determine the rejection of the composite membranes. Protein rejection was measured by reading the absorbance on the 280 nm wavelength using a Genesys Ultraviolet Spectrophotometer, 10UV, Termo Spectronic (UV-Visible). The retention (%RP) was calculated by Eq. (2).

$$\%\text{RP} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

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

3. Results and discussion

3.1. FTIR analysis

According to the characterization obtained by FTIR, Fig. 1(a) and (b), the main molecular vibrations

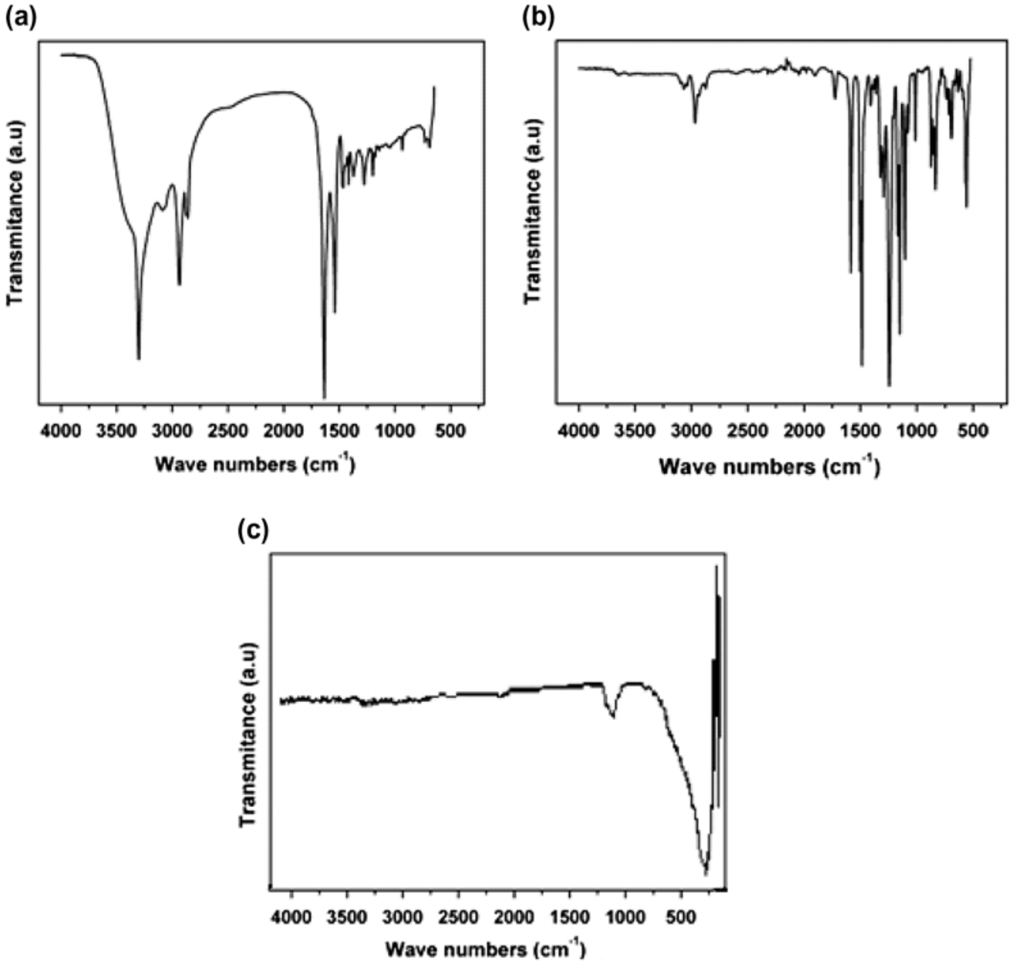

Fig. 1. FTIR-ATR spectra of membranes (a) M-PA (ceramic–polyamide composite membrane), (b) M-PSf (ceramic–polysulfone composite membrane), and (c) ceramic support.

Table 1
Absorbances (FTIR) on the surface of M-PA and M-PSf membranes

Polyamide 66		Polysulfone	
Wave numbers (cm^{-1})	Attribution	Wave numbers (cm^{-1})	Attribution
3,302	$\nu_{\text{N–H}}$	2,967 and 2,872	$\nu_{\text{C–H (CH3)}}$
2,936 and 2,861	$\nu_{\text{C–H(CH2)}}$	1,504	$\nu_{\text{C=C}}$
1,635	$\nu_{\text{C=O (secondary amide)}}$	1,327	$\nu_{\text{S=O}}$
1,416	$\nu_{\text{C–N}}$	1,245	$\nu_{\text{C–O}}$

ν = stretching.

are shown in Table 1. The vibrations of molecular bonds of each polymer demonstrated that the polymer is present on the surface of the ceramic support and did not suffer change in its chemical structure.

The support was also submitted to FTIR by ATR system analysis, Fig. 1(c), but did not show absorption bands in region of polymers, which indicate that the spectra observed on the surface of composite membranes are PA 66 and PSf, respectively, Fig. 1(a) and (b).

3.2. Membrane morphology

Micrograph analyses (SEM) of ceramic/polymer composite membranes are shown in Fig. 2. Comparing

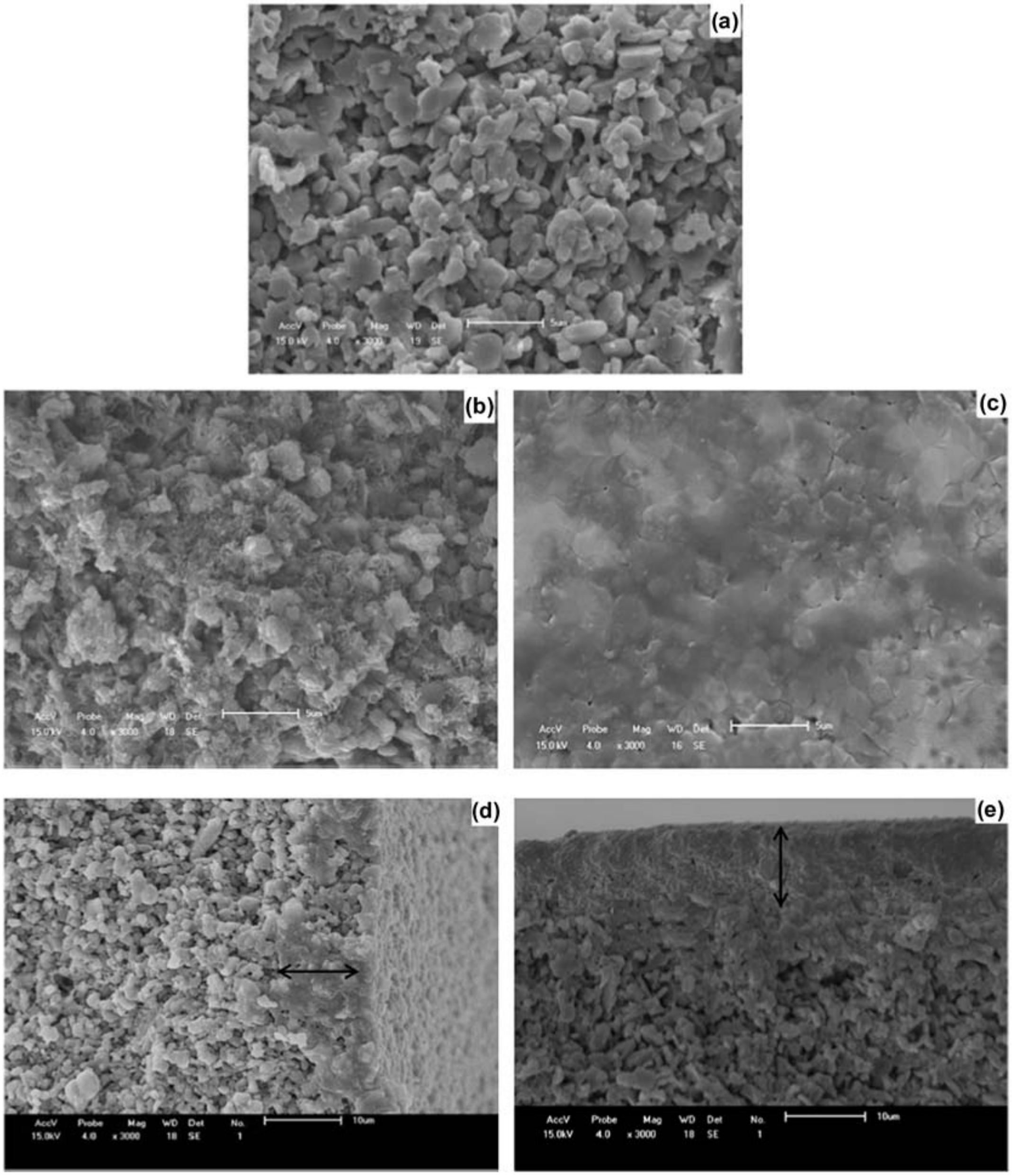

Fig. 2. SEM images of surface and cross sections composite membranes ceramic-polymer (3000×): (a) support (top layer), (b) M-PA (top layer), (c) M-PSf (top layer), and (d) M-PA (cross-section), (e) M-PSf (cross-section).

the surface images of the composite membranes was observed that the organic separation layers were successfully coated onto the supports. It was possible to verify good covering and pore filling of the ceramic support with the penetration of the polymeric solution into it. However, the PSf covering on the support appears to be denser when compared to that of PA 66. In general, it is clear that the empty spaces of the ceramic support observed in Fig. 2(a) were filled with the deposition of polymers, Fig. 2(b) and (c). Deposition and layer formation of both polymers onto the ceramic support were also confirmed by the permeated flux results discussed as follows. Fig. 2(d) and (e) shows the cross sections of the ceramic composite membranes PA 66 and PSf, respectively.

3.3. Pure water flux

The structural stability of the composite membranes depends on good adhesion between the sepa-

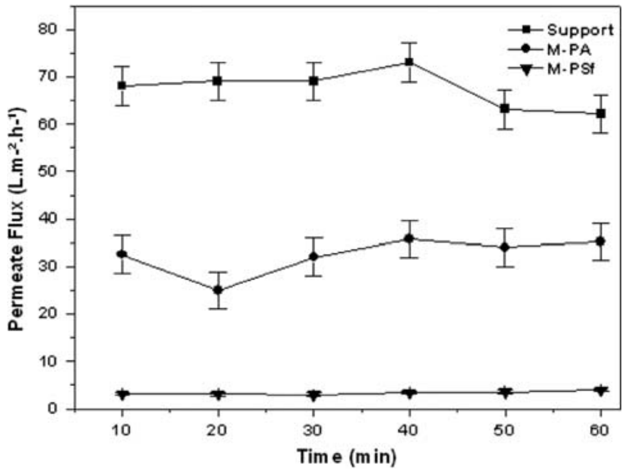

Fig. 3. Pure water flux for support and composite membranes (ceramic, M-PA 66, and M-PSf).

ration layer and the ceramic support [14]. Based on the permeability results presented in this paper, the composite membrane showed stable behavior during the tests. After 50 min, the flows were stable. As expected, flux values presented by the support were higher to those flux values presented by membranes covered by the polymer, a result which was also observed in the paper by Liu and Li [6].

The polymeric layer seems to have strongly influenced the flux values increasing resistance to water flux. The M-PA membrane showed a higher flux than that of the M-PSf membrane. The pure water flux (Fig. 3) measured at 1 bar at the end of 60 min were 62, 35, and 4 $L \cdot m^{-2} h^{-1}$ for the ceramic support, M-PA, and M-PSf membranes, respectively. Thus, this result can be explained by the characteristics of the polymeric layer formed on the surface of the ceramic support.

3.4. Rejection measurement

The membranes were submitted to permeation of protein solution (EA, 45 kDa) for one hour and a mean flux and rejection were obtained (Fig. 4). The membranes showed the same performance shown in permeation of pure water, but the protein flux is slightly low, due to the presence of solute in the water [15].

The molecular weight cut-off (MWCO) of a membrane will depend, mainly, on the preparation conditions of this membrane. Many studies show the characterization of membranes prepared with the same polymer, but depending on the use of additives or preparation method, the membranes presented different MWCO [16,17]. In this work, the EA rejection presented by the support was 14%, while the membranes M-PA and M-PSf showed rejection of 42 and 62%. Comparing the composite membranes prepared with PA 66 and PSf, it is clearly shown that membranes showed different behaviors. The membrane permeability and rejection data suggest that the dense layer of PSf on the support surface directly influenced the low flux and higher rejection of the M-PSf membrane [18].

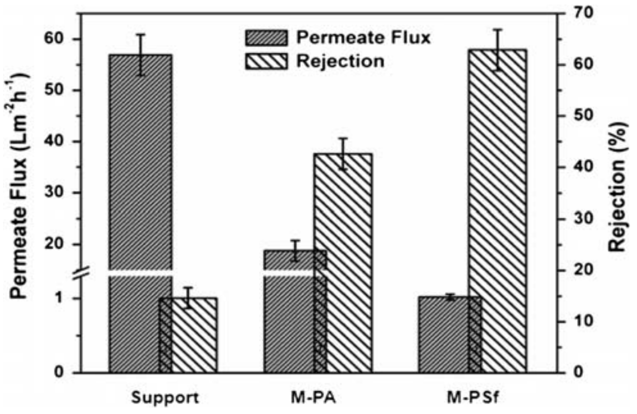

Fig. 4. Mean values of permeate flux and EA rejection for ceramic support and composite membranes (M-PA 66 and M-PSf).

The composite membranes M-PA and M-PSf may be recommended for protein separation with molecular weight greater than 45 kDa. However, a detail investigation (i.e. polymer concentration, method of surface layer deposition) is required to find out optimum condition or the better rejection performance.

4. Conclusions

Ceramic/polymer composite membranes were obtained through direct immersion of α-alumina ceramic support in different polymeric solutions of polyamide and PSf. The prepared membranes presented differences both in their morphological and permeability characteristics, thus proving that the polymeric layer deposited on the support surface strongly influences the final characteristics of the membrane, with increase in the rejection (%) and decrease permeation flux principally the M-PSf.

Acknowledgments

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