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Elaboration of zirconia microfiltration membranes tested with methylene blue filtration

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ABSTRACT

Macro-porous ceramic supports, with a zirconia top layer, for microfiltration (MF) membranes, were prepared from local low cost raw materials. For this, the extrusion method was used. The characterization of the raw materials and the study of the effect of the sintering temperature on the morphology, pore size distribution and the mechanical properties of supports were studied. For example, it was found that, the porosity and the average pore size for a tubular ceramic support fired at 1,350°C during 1 h are about 47% and 6.4 μm, respectively. The elaboration of the zirconia top-layer is performed by the slip casting method. This membrane can be used for MF; indeed, it showed a good rejection performance of methylene blue: 70%. It is also suitable for waste water treatment.

Keywords: Porosity; Supports; Microfiltration; Ceramic membranes

1. Introduction

Membranes technique is one of the most attractive separation methods, because of its low cost and its high selectivity. Microfiltration (MF) and ultrafiltration (UF) are often used to remove micro particles, microorganisms and colloidal materials from suspensions; they can be used, for example, for the treatment of waste water. Microfiltration membranes can be prepared with a wide variety of materials and are made using different methods of manufacture. Alternatively, polymer membranes can be used for microfiltration but the ceramic ones have many advantages such as high strength, extreme pH values, high thermal stability, durability and ease of cleaning [1–4]. These properties make ceramic membranes interesting candidates for separation. They are used in various fields such as water and wastewater treatment by virtue of their advantages over conventional water treatment technologies.

For the preparation of ceramics membranes, the most widely used oxide ceramics are zirconia, titania and alumina. The preparation of zirconia membranes is described by several authors [5–9]. Gestel et al. [5] prepared active layers from zirconia. The ZrO_2 membrane is deposited on a support layer of alumina interlayer. Kroll et al. [6] have described the synthesis process of zirconia ceramic micro-tubes for bacteria filtration with pore sizes ≤0.2 μm. Kanchapogu et al. [7] made TiO2 membranes with an average pore size (APS) of 0.8 um. Yang et al. [8] used $ZrO_2/\alpha\text{-}Al_2O_3$ membrane with APS of 0.2 μm for the separation of oil–water emulsion and achieved a rate of 99.8% of oil rejection. Lee et al. [9] Prepared MF layers with pore sizes from 200 to 300 nm from Al_2O_3 slurries on a tubular support of alumina.

In this study, macroporous supports were prepared from quartz sand and calcium carbonate (calcite). Tubular ceramic supports with 6 and 10 mm inner and outer diameters, respectively, were prepared by the extrusion of a ceramic paste. Afterwards, the supports were sintered at 1,350°C

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and 1,400°C. A membrane with a zirconia top layer with a high porosity ratio, deposited by slip casting method, has been also, prepared. An investigation of its performance has been made. The motivation behind this work is because of the importance of this kind of membrane in the filtration process.

2. Materials and methods

2.1. Supports elaboration

Two natural ceramic powders were used for the elaboration of the membrane supports, namely: Calcite ($CaCO_3$) and quartz sand (SiO_2). The chemical composition of these materials, given in weight percentages (wt.%) of oxides, is presented in Table 1. The quantitative analysis of calcium carbonates and quartz sand, reveals that both have a purity of about 99%.

For our tests, a tubular ceramic support was fabricated by the extrusion method of a mixture of quartz sand (80 g), calcium carbonate (20 g) and 4 g of amijel; an organic additive was used as a binder.

2.2. Top layer preparation

A microfiltration (MF) membrane was fabricated from zirconia using powder suspension technique. A deflocculated suspension of zirconia is obtained by the mixing of 12 wt.% ZrO_2 powder, 30 wt.% hydroxyethyl cellulose (4% aqueous solution) and 58 wt.% distilled water.

The deposition of the slip on the support (sintered at 1,350°C), was performed by the slip casting method. The tube was closed at one end and filled with the suspension. The deposition time is about 1 min. Then, after drying at room temperature, the membrane was sintered at 1,100°C for 1 h.

2.3. Methylene blue rejection experiments

Methylene blue rejection performance of the prepared membrane was investigated using an aqueous solution containing 2 g/L of Methylene blue. During microfiltration, the permeate solutions were collected and the Methylene blue concentration was analyzed using a Jenway UV/VIS 7315 spectrophotometer at a wavelength 292 nm. From the feed and permeate concentrations, the percentage of solute rejection is calculated using the equation:

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

where C_f and C_p are the concentrations of the feed and permeation solution, respectively.

3. Results and discussion

Porosity and pore size distributions are important indicators of microstructure and physical characteristics of prepared samples. Measurements have been made using mercury porosimetry (autopore 9500), for supports sintered at different temperatures (for 60 min). The pore size distribution curves specimens sintered at 1,350°C and 1,400°C are illustrated in Fig. 1. Supports sintered at 1,350°C for 1 h are found to have an average pore size around 6.4 µm and a porosity ratio of about 47%; where-as the supports sintered at 1,400°C have an average pore size around 11.8 µm and a porosity ratio of about 47%.

The obtained results show that there is no significant dependence of open porosity on the sintering temperature while the average pore size (APS) increases with it. Apparently, the increase in sintering temperature encourages the coalescence of pores which, in turn, leads to a larger average pore size.

Concerning water permeability, Fig. 2 shows the variation of the flux with time and pressure for ceramic supports sintered at 1,350°C. The flux stabilizes after few minutes; it depends on the applied pressure. While the average water permeability is around 16,550 L/(h·m^2·bar).

Distilled water permeability measurements for the prepared supports sintered at different temperatures, are shown in Fig. 3. It suggests that there is an increase in permeability, when the sintering temperature is increased. As shown in Fig. 3, the water permeability of the support sintered at 1,400°C for 1 h is much higher than that of the supports sintered at 1,350°C. For example, a permeability

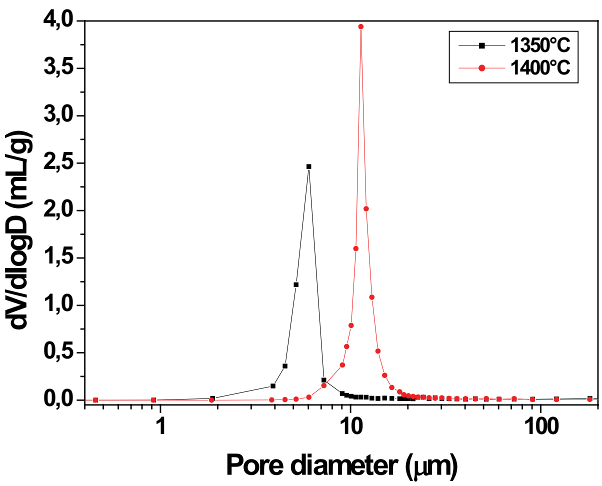

Fig. 1. Pore size distribution for samples sintered at 1,350°C and 1,400°C for 1 h.

Table 1
Chemical compositions of raw materials, expressed as weight percentage, for the different oxides (obtained with the X-ray fluorescence technique)

	SiO_2	CaO	Al_2O_3	K_2O	SO_3	MgO	P_2O_5	Fe_2O_3	Na_2O	TiO_2
Quartz sand	99.0	0.18	0.26	0.06	0.01	0.04	0.01	0.12	0.03	0.03
Calcite	0.15	99.6	0.10	0.01	0.02	–	0.01	–	–	–

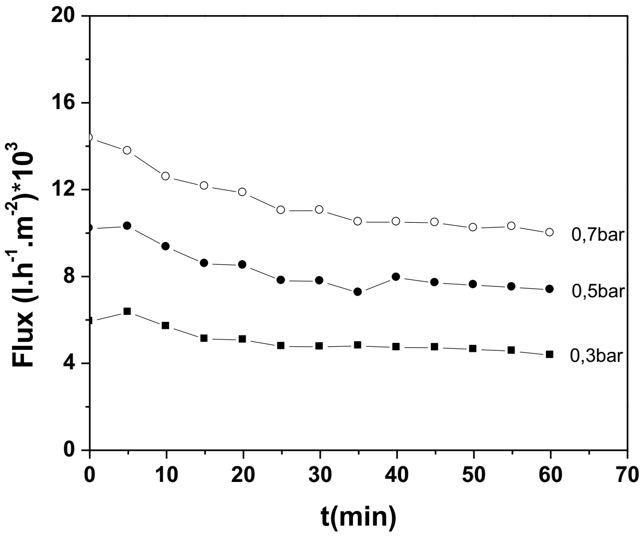

Fig. 2. Water flux vs. time, at three working pressures, for supports sintered at 1,350°C.

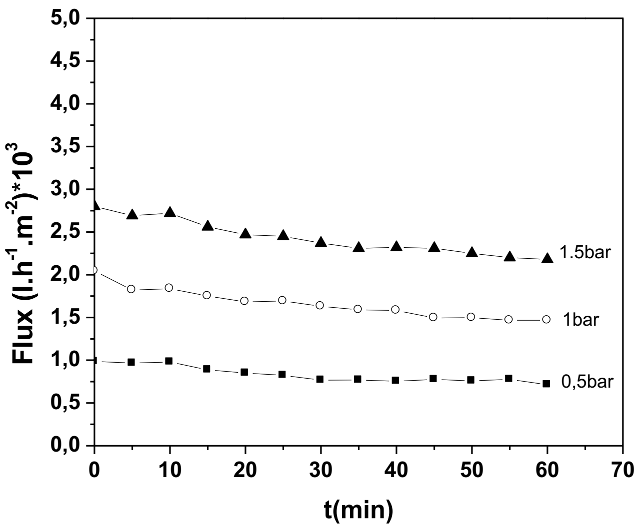

Fig. 4. Water flux for a multilayer system (support 1,350°C + Zirconia top layer 1,100°C) vs. time, at 3 working pressures, using distilled water.

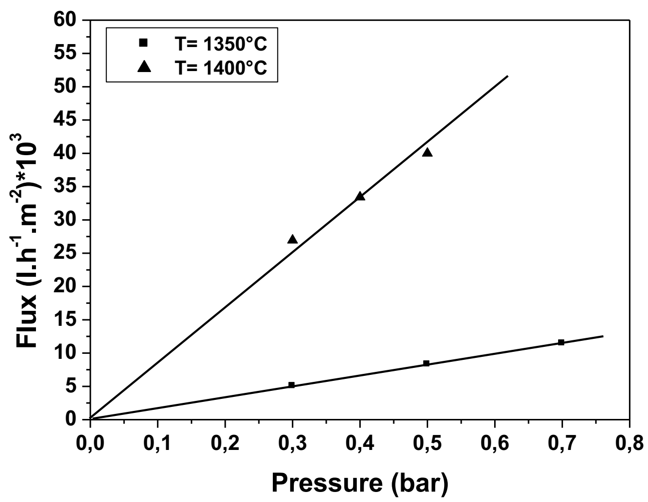

Fig. 3. Distilled water flux variation as a function of different applied pressures for membrane supports sintered at different temperatures for 1 h.

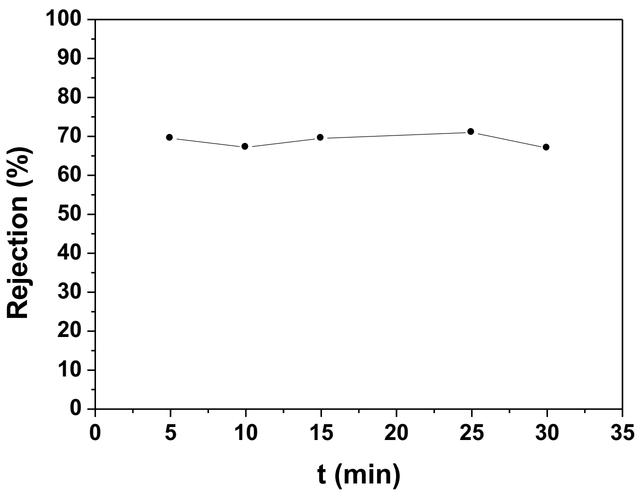

Fig. 5. Rejection rate of Methylene blue solution vs. time of the multilayer system, at operating pressure equal to 0.3 bar.

of about 54,000 L/(h·m^2·bar) was achieved for supports sintered at 1,400°C, with an APS around 11.8 μm and a porosity ratio of ≈47%. Whereas a permeability of about 16,550 L/(h·m^2·bar) was obtained for supports sintered at 1,350°C; the porosity ratio and APS have as values ≈47% and 6.4 μm, respectively. The higher water permeability obtained for supports sintered at 1,400°C, it is the result of two main factors: large APS and high porosity ratio. High permeability is a very important property of membrane supports performance.

The effect of sintering temperature on the flexural strength was also investigated. The results show that the latter is closely related to the average pore size which in turn, is sintering temperature dependant. For example, flexural strength is 20.3 MPa when we have an average pore size around 6.4 μm and a porosity of 47%; whereas it is about 17.9 MPa for supports having an APS around 11.8 μm and a porosity ratio of ≈47%.

Microfiltration membrane is known to be characterized by its water permeability. Fig. 4 suggests that water flux is a function of both time and applied pressure. The average permeability is about 1,600 L/(h·m^2·bar). The water permeability coefficient of the membrane is different from that of the supports. The supports have a higher average pore size and thus exhibit higher water flux.

The rejection rate vs. time, at an operating pressure equal to 0.3 bar, is presented in Fig. 5. Based on these results, we can see the efficiency of the filtration membrane and its ability to reduce Methylene blue concentration in the solution. Indeed, the selectivity rate reaches 70%. This may be caused by dye adsorption on the membrane surface during the experiment runs; this may justify the blue coloration of the membrane after use [10]. The rejection depends, in fact, on the material porosity [11], the conformation of the solution used for the filtration tests and electric interaction between the solutions and the membrane. As methylene blue is cationic soluble in water, there is ionic interactions between the membrane and the solute; this plays a major role in the transport of ions across the membrane in terms of diffusion and migration, thus, affecting the rejection rate [12].

4. Conclusions

In this study, microfiltration ceramic membrane with a zirconia top layer was made by the slip casting technique, whereas supports were prepared by the extrusion method. The best performance for the support is obtained when the firing temperature is about 1,350°C. In this case, the porosity ratio, the average pore size, the compression strength and the permeability are about 47%, 6 μm, 20 MPa and 15,500 L/(h·m²·bar), respectively. Furthermore, as an application, the rejection performance (reduction of methylene blue concentration) results, enable us to conclude that zirconia membranes can be used for tangential microfiltration, particularly for solution purification.

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