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Elaboration of tubular titania microfiltration membranes for wastewater treatment

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ABSTRACT

Microfiltration (MF) membrane processes have become an established technology in the treatment of wastewater. In this paper, the making of a tubular composite membrane is described; macroporous tubular ceramic supports have been made using the extrusion technique; the MF top layer has been prepared from a titania powder suspension using the slip casting technique. Porosity, average pore size (APS), and pore size distribution of the membranes have been obtained from mercury porosimetry measurements. The morphology, surface quality, and thickness of the top-layer membrane were examined with scanning electron microscopy. The used MF membrane layer has a thickness of 35 μm or so and an APS value of about 0.8 μm. The performance of the MF ceramic membrane was assessed through the evaluation of both water permeability and rejection.

Keywords: Membranes; Average pore size; Porosity; Supports; Wastewater

1. Introduction

Studies on the elaboration of membranes for wastewater treatment have undergone rapid growth during the last years. Because of their application in the treatment of wastewaters, there is much interest nowadays in the application of membranes in such separation procedures [1–6]. Consequently, removing oil from wastewater is an important aspect of pollution control in many fields of industry. The use of ceramic membranes has many advantages such as high thermal and chemical stability, pressure resistance, long lifetime, and good defouling properties [7,8]. Microfiltration (MF) and ultrafiltration (UF) are often used to remove particles, microorganisms, and colloidal materials from suspensions [9]. An asymmetric membrane usually consists of a thin top-layer responsible for separating components and porous ceramic support with single or multiple intermediate layers imparting the required mechanical strength to the membrane composite. In fact, the support made of artificial material makes an important part of the high price of the membranes; this is why some authors have focused their research on the development of low-cost supports made of natural raw materials such as clays. In order to decrease this cost and to exploit our natural resources, the supports have been prepared, in this study, from quartz sand (SiO_2) and calcium carbonates ($CaCO_3$) which are local raw materials. Moreover, the fabrication of tubular ceramics membranes, using slip casting method, is described.

2. Experimental procedures

2.1. Elaboration of supports

The procedure for the preparation of membrane supports is similar to that described in a previous paper [10]. The tubular support was prepared from Algerian natural quartz sand (QS) (SiO_2 = 98% purity) and calcium carbonate (CC) ($CaCO_3$ = 99% purity). In this work, the support

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has a tubular configuration. It is obtained by the extrusion method of a mixture of quartz sand (77 wt.%), calcium carbonate (19 wt.%), and organic additive in appropriate to adjust the rheological properties of the paste. The organic additive used as a bender was: 4 wt.% of methyl cellulose. After drying, at room temperature for 24 h, the supports were sintered at a temperature of 1,425°C for 1 h.

2.2. Preparation of titania MF membrane layer

The powder suspension technique was used to prepare the titania layer. A deflocculated suspension of titania is obtained by the mixing of 10 wt.% TiO_2 powder, 30 wt.% aqueous solution of hydroxyethyl cellulose and 60 wt.% distilled water (DW). Afterward, it was deposited on the support layer by using the slip casting method. Then, after drying at room temperature, the membrane was sintered at 1,050°C for 1 h.

2.3. Oil rejection experiments

The membranes oil rejection performance was investigated using an aqueous solution containing 500 mg L^{-1} of oil. The solution was prepared using a mechanical mixer for 24 h. During MF, the permeate solutions were collected in a graduated cylinder and the oil concentration was analyzed using a Jenway UV/VIS 7315 spectrophotometer at a wavelength 297 nm. From the feed and permeate concentrations, the percentage of solute rejection was calculated using the equation:

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

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

3. Results and discussion

Porosity, average pore size (APS), and pore size distribution (PSD) of the samples were determined using mercury porosimetry (Autopore 9500, Micromeretics). The obtained supports sintered at 1,425°C for 1 h, have a porosity ratio of about 46%, and an APS around 12 µm. These supports have been selected as substrates for MF membranes.

One of the most important properties of membrane support is its permeability. This parameter is typically used to provide an indication of the capacity of support to process the permeate; a high permeability means a high throughput [11]. Supports of ceramic membranes require a highly open porosity and adequate APS to reduce flow resistance [12]. Fig. 1 shows the variation of water flux with time and pressures for supports sintered at 1,425°C. A stable flux is obtained after a few minutes. However, it depends on the applied pressure. The average water permeability is around 27 m^3 (h m^2 bar)$^{-1}$.

MF membrane layer made of titania was coated by slip casting on the ceramics support. Fig. 2a shows the SEM images of the top layer surface. Fig. 2b is the cross-section view of the support and the titania layer. It shows that the membrane has an asymmetric structure and the thickness of the layer is about 35 µm. This membrane microstructure shows good homogeneity which is an important property for potential MF applications.

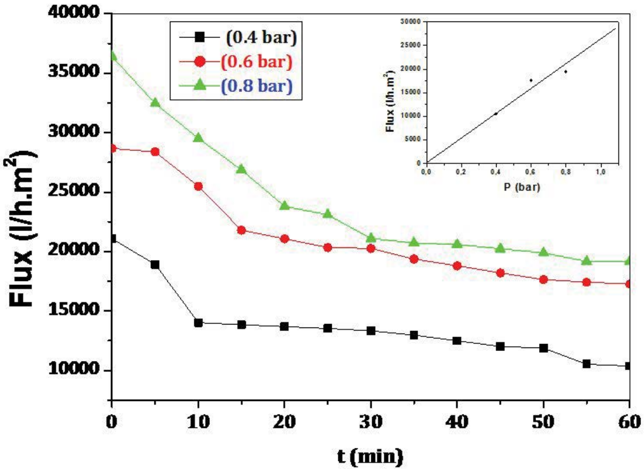

Fig. 1. Distilled water flux vs. time at three working pressures for ceramic support.

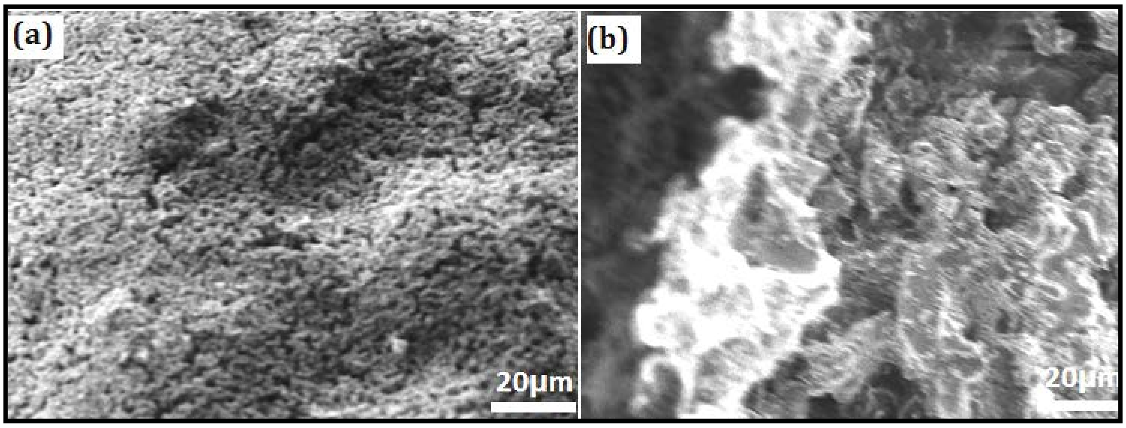

Fig. 2. SEM micrographs of a bi-layer system (a) surface of top layer and (b) cross-section; support and top layer.

Fig. 3 shows the PSD curve for the titania membrane coated on macroporous support and sintered at 1,050°C for 1 h. The PSD is narrow; it ranges from 0.5 to 1.6 µm and has an APS of about 0.8 µm. This APS value indicates that this kind of membranes can be utilized in the MF applications.

Permeability measurements were taken on a tangential filtration homemade pilot plant. Distilled water (DW) has been used to characterize the permeability at room temperature. As can be seen from Fig. 4, a fast decrease in the flow value during the first minutes of the test then stabilizes beyond ≈20 min. This is the case for the three pressures studied. We note also the existence of compatibility between the applied pressure and the flow, the increases the value of the flow, which is due to the high thrust of water through the pores of the membrane. For example, at a pressure equal to 0.3 bar, the estimated flow value is 360 L h^{-1} m^{-2}; then at 0.6 bar; up to a pressure of 1 bar the flow goes up from 630 to 1,140 L h^{-1} m^{-2}. The average permeability is around 1,150 L h^{-1} m^{-2} bar^{-1}.

This kind of membranes could be used to treat industrial wastewater effluents. As an illustration, a rejection study has been carried out testing our membrane; considering the case of a solution containing 2 g of motor oil in 4 L of water. The size of oil droplets in the emulsion was measured using an optical microscope connected to a digital camera. Fig. 5 shows a photograph of the prepared oil-in-water emulsion. It shows that almost 90% of the droplets have a diameter below 5 µm. Analysis of the microscopy image shows that the droplet sizes of this emulsion system are in the range of 1–4 µm. It can also be noticed that larger oil droplets can reach sizes above 10 µm.

Fig. 6 shows the evolution in time of the flow rate for the oil solution, for different values of pressure. We record on the curve the increasing flow values with the pressure applied. We note also that the flow decreases at the beginning of the test then stabilizes at certain values depending on the pressure. These values are small compared to the case of distilled water; when using distilled water the flux is two times higher than that of wastewater. Its value is about 1,140 L h^{-1} m^{-2} bar^{-1}, whereas we have about 600 L/h^{-1} m^{-2} bar^{-1} for wastewater. An explanation may be proposed: possibly the membrane pores capture some small oil droplets within its structure leading to the decline in the permeate flux.

The rejection rate vs. time, at different operating pressures, is shown in Fig. 7. Based on these results, we can see the efficiency of the filtration membrane and its ability to reduce oil concentration in the solutions. Indeed, the selectivity rate reaches 85% for a pressure of 0.6 bar. We also note that the latter increases with time and decreases as the applied pressure increases. The increase in the rate of selectivity over time may be due to the accumulation of oil droplets at the membrane surface and the formation of another layer above the membrane [1]. This is mainly attributed to the blockage of pores by oil droplets [13]. However, higher operating pressures are not recommended for this micro-filtration system. It is fairly evident that we have a decrease in oil rejection when the pressure is increased. The increased pressure forces oil drops through the membrane pores; it is the reason for the decreased rejection percentage. Finally, it should also be concluded here

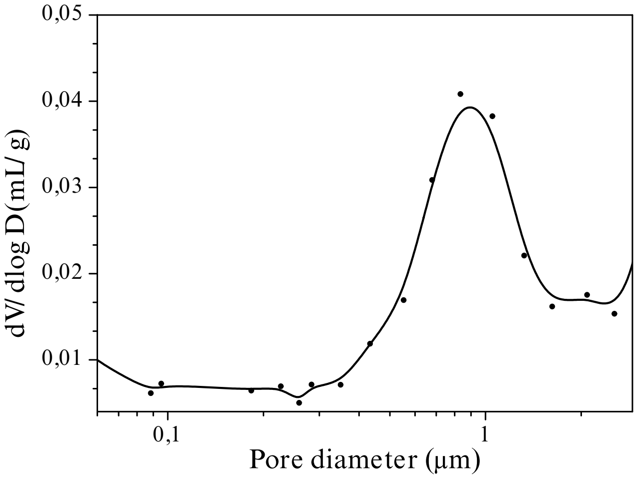

Fig. 3. Pore size distribution of titania membrane sintered at 1,050°C.

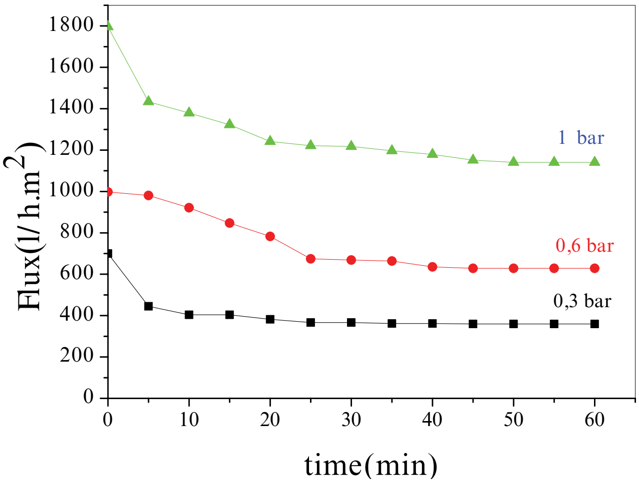

Fig. 4. Distilled water flux vs. time, at three working pressures.

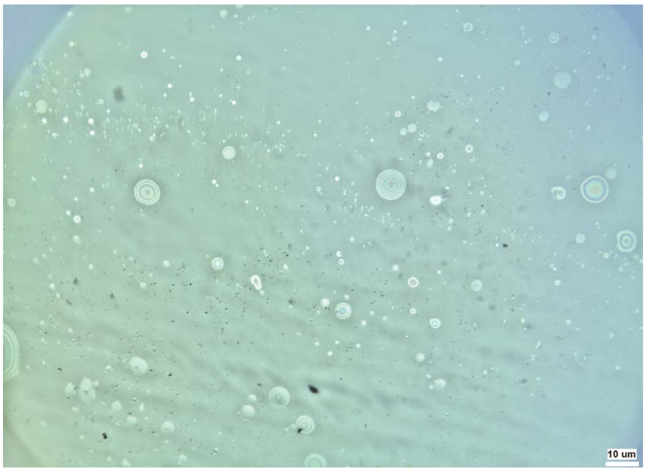

Fig. 5. Optical microscopy on the size of oil droplet.

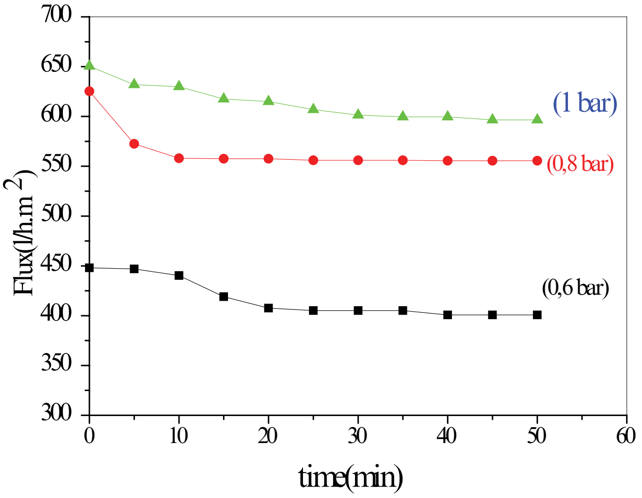

Fig. 6. Oil solution flux vs. time at three working pressures.

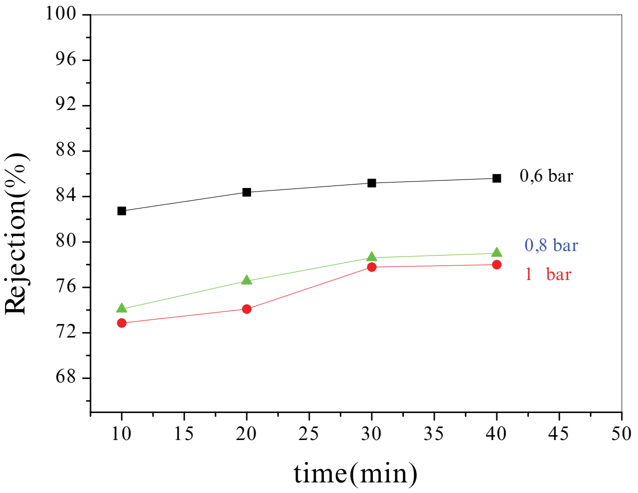

Fig. 7. Rejection rate vs. time at three working pressures.

that using ceramics membranes is well justified, particularly for wastewater purification, as confirmed by this study.

4. Conclusions

Composite ceramic membranes in a tubular configuration have been prepared and studied. They consist of an alternative support layer and a top layer. These ceramic supports have been obtained by extrusion using quartz sand (QS) and calcium carbonates (CC) as starting materials. Moreover, MF ceramic membranes were prepared from titania powders using a slip casting method. The result is an MF layer having an APS of about 0.8 µm, a narrow PSD, noticeable efficient by in the elimination of suspended matter, and good water permeability. It can be concluded, that in the microfiltration wastewater treatments, titania ceramics membranes, are suitable for oil/water separation.

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