Desalination and Water Treatment
www.deswater.com

9 (2009) 142–148

1944-3994/1944-3986 © 2009 Desalination Publications. All rights reserved

Preparation and characterization of microfiltration membranes and their supports using kaolin (DD2) and $CaCO_3$

B. Boudaira[a,*], A. Harabia[a], F. Bouzerara[a], S. Condom[b]

[a] *Constantine Ceramics Laboratory, Mentouri University, Constantine 25000, Algeria*
Tel/fax: 213 (0)31 81 88 81, email: boudaira.boukhemis@gmail.com
[b] *Institut Européen des Membranes, UMR 5635 CNRS ENSCM UMII, 1919 Route de Mende, 34293 Montpellier Cedex 5, France*

Received 15 September 2008; Accepted 5 November 2008

ABSTRACT

In this work, the supports for microfiltration and ultrafiltration were prepared with local kaolin (DD2) and calcite mixtures. The choice of these raw materials is based on their natural abundance (lowprice). These supports were made by extrusion technique in order to obtain tubular supports which were afterwards sintered at 1250°C for 2 h. It has been found that supports had interesting characteristics; an average pore size of about 4 µm, a porosity ratio around 52% and a tensile strength ≈ 23 MPa. Moreover, the pore size distribution is almost homogeneous (mono-modal type). The surface and the cross-section morphologies observed through a scanning electron microscope (SEM) are also homogeneous and do not present any macro defects (cracks, etc.). These supports were selected as substrates for the membrane layers used in microfiltration (MF).

The membrane layers were elaborated from zirconium oxide, using slip casting technique. The specimens were subsequently sintered at 1150°C. The microstructure and porosity as well as the permeability have been also studied. It has been found that the average pore size is about 0.35 µm and a layer thickness ≈ 24 µm. The water permeability measured is 1440 $l/h/m^2/bar$. These membranes may also be used as supports for ultrafiltration (UF).

Keywords: Kaolin; Calcite; Supports; Membranes; Microfiltration; Extrusion; Slip casting

1. Introduction

There is much current interest in the application of membranes in separation procedures because of their application in the treatment of big amounts of wastewaters [1]. The use of ceramic membranes has many advantages such as high thermal and chemical stability, pressure resistance, long lifetime, and good defouling properties [2-3]. Ultrafiltration and microfiltration are often used to remove particles, microorganisms, and colloidal materials from suspensions [4]. Asymmetric membrane usually consists of a thin top-layer responsible for separating components, and a porous ceramic support with single or multiple intermediate layers imparting the required mechanical strength to the membrane composite [5]. In fact, the commercial support made of artificial material is an important part of the high price of the membranes, which is why some authors have focused their researches to develop the preparation of low coast supports made of natural raw materials such as clays [6]. The industrial membrane production uses a limited choice of materials. As a consequence, ceramic membranes have a high price. A significant effort was then provided these last years in membrane technology field in order to find new porous ceramics materials at low price [7, 8]. In order to decrease this cost and to evaluate our natural resources, the supports have been manufactured [9, 10], in this work, from

---

*Corresponding author.

Presented at the Conference on Membranes in Drinking and Industrial Water Production, 20–24 October 2008, Toulouse, France.

kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and the calcium carbonates ($CaCO_3$) local raw materials. The choice of these materials has been dictated by their natural abundance (low price) and their thermal stability [11].

2. Analysis of the raw materials

In this study, the supports were prepared from domestic kaolin (DD2) and calcium carbonates derived from Guelma and Constantine regions (Algeria), respectively.

The chemical composition of kaolin (DD2) given in weight percentages of oxides is given in table 1, where the obtained results reveals that this kaolin (DD2) is mainly composed of silica (SiO_2) and alumina (Al_2O_3).

The particle size distribution of kaolin (DD2) and $CaCO_3$ were determined by the Dynamic Laser Beam Scattering (DLBS) technique (Fig. 1). This method gave an average particle size in the order of 2.2 µm and 4.8 µm, respectively.

Fig. 2 shows XRD spectrum of calcium carbonate powder, where only $CaCO_3$ is present. This spectrum

Table 1
Chemical composition of kaolin (DD2) (wt%), using fluorescence XRD analysis.

I.L	TiO_2	F_2O_3	CaO	K_2O	Na_2O	SiO_2	Al_2O_3	Oxides
18.73	0.22	0.23	0.32	0.95	1.12	45.00	33.43	Weight %

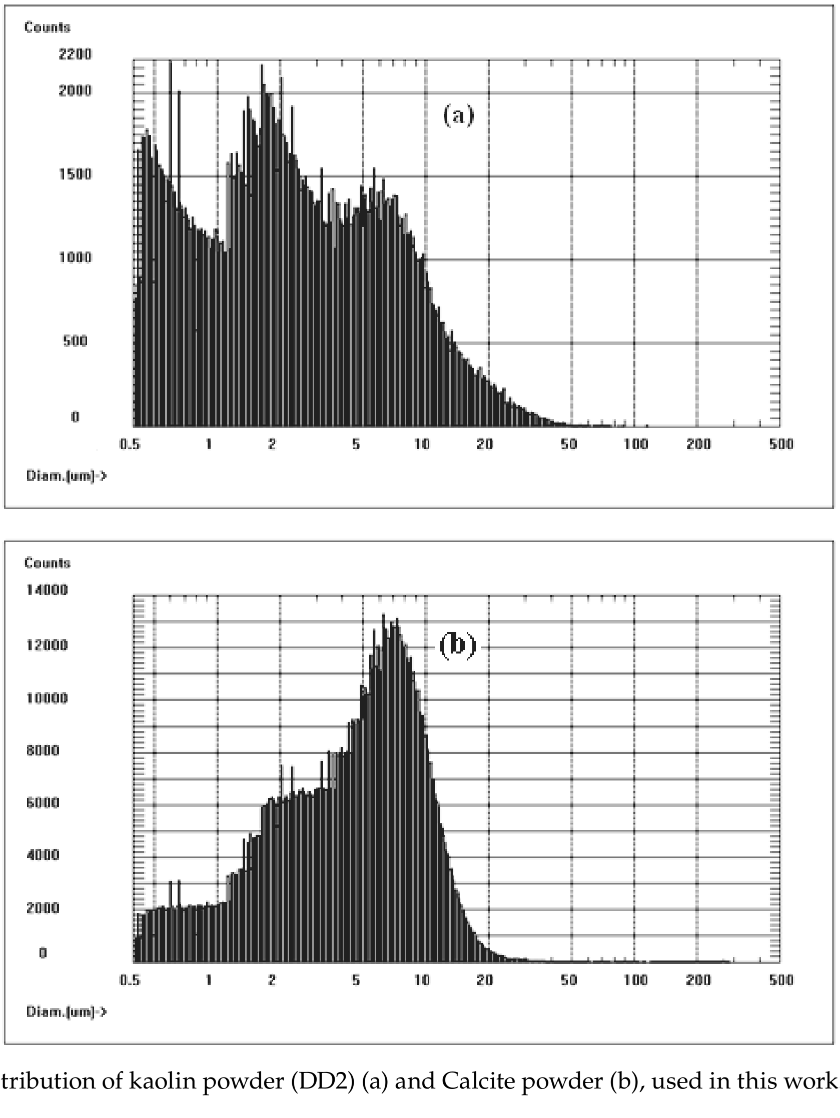

Fig. 1. Particle size distribution of kaolin powder (DD2) (a) and Calcite powder (b), used in this work.

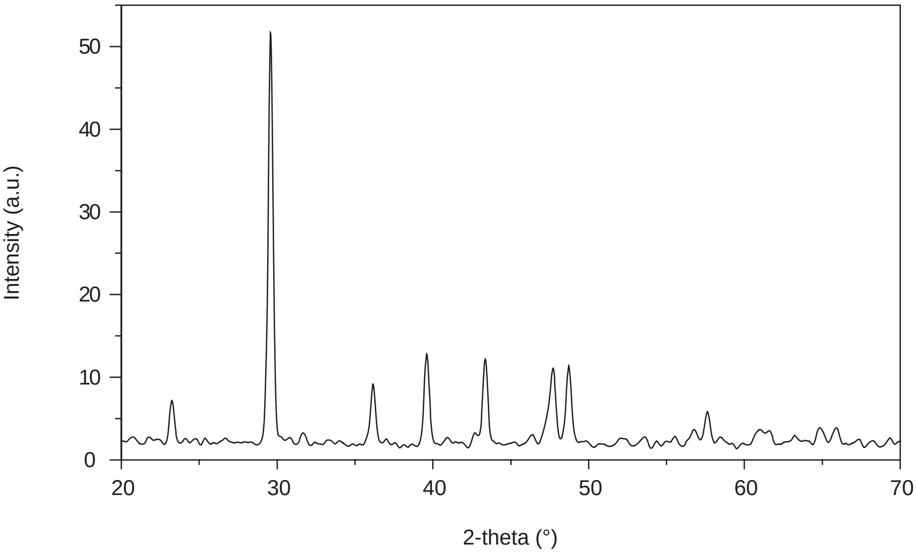

Fig. 2. XRD spectrum of calcium carbonates powder.

shows also that the calcium carbonates powder is well crystallized.

Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) analysisshows the weight loss of kaolin and $CaCO_3$. These two analyses have been carried out under air. The heating rate of the compacts from room temperature to 1200°C was 10°C/min, while the cooling of compacts was carried out in the furnace. TGA curves recorded during compacts heating (Fig. 3a) permit the following remarks. A total weight loss of about 18% of kaolin compacts is measured. In fact, this weight loss consists of two distinct stages. The first one is attributed to the humidity (water added into the starting mixtures) whereas the second stage is related to the departure of water (by vaporization) existing in the kaolin chemical composition itself.These observations are also confirmed by DSC analysis (Fig. 3a), this later exhibits characteristic endothermic peaks at 95, 474 and exothermic peaks at 997°C, where this reaction may be attributed to mullite nucleation [10].

Fig. 3b shows that there is only endothermic peak (mass loss 43.73%) in the range (700–800°C) which is due to thermal decomposition of calcite to form calcium oxide (CaO) and CO_2, this reaction is also confirmed by XRD analysis (Fig. 4).

3. Support elaboration and characterization

The kaolin (DD2) is properly crushed, then calcinated at 540°C for 1 h to be later on sieved at 150 μm. After that, a quantity of 28 wt% of calcium carbonate powder is added.

In order to improve the properties that facilitate the forming, some organic materials, such as 3 wt% methocel, as a plasticizer and 3 wt% amijel, as a binder have been added. This mixture should be continuously mixed up with water so as to get the plastic paste. For a good diffusion of the water in the paste, this latter should be properly covered in a plastic case fore at least 12 h. After that, extrusion technique takes place to make some tubular samples.

For a good drying of these tubular samples, they should be placed at room temperature on rotating aluminum roll.

These dried tubular samples sintered at 1250°C following this program:

$$25°C \xrightarrow{2°C/min} 250°C\ (10\ min) \xrightarrow{5°C/min} 1250°C\ (2h)$$

In order to eliminate organic materials added and avoid the microcrackes in the samples, the rate of sintering chosen is 2°C/min.

The support fired at 1250°C and characterized by mercury porosimetry showed pore diameters centered near 4 μm (Fig. 6) and 52% of porosity. The average pore size is also confirmed by typical micrographs illustrated in Fig. 5.

4. Membrane elaboration and characterization

Due to the chemical and thermal properties of zirconium oxyde, it is widely used for membranes preparation. This powder has a specific surface area which is about 43.5 m^2/g and average particle size of about 0.22 μm. This material has been prepared by Cezus Chimie campany.

For preparing a microfiltration layer with zirconia powder, a deflocculated slip was obtained by mixing

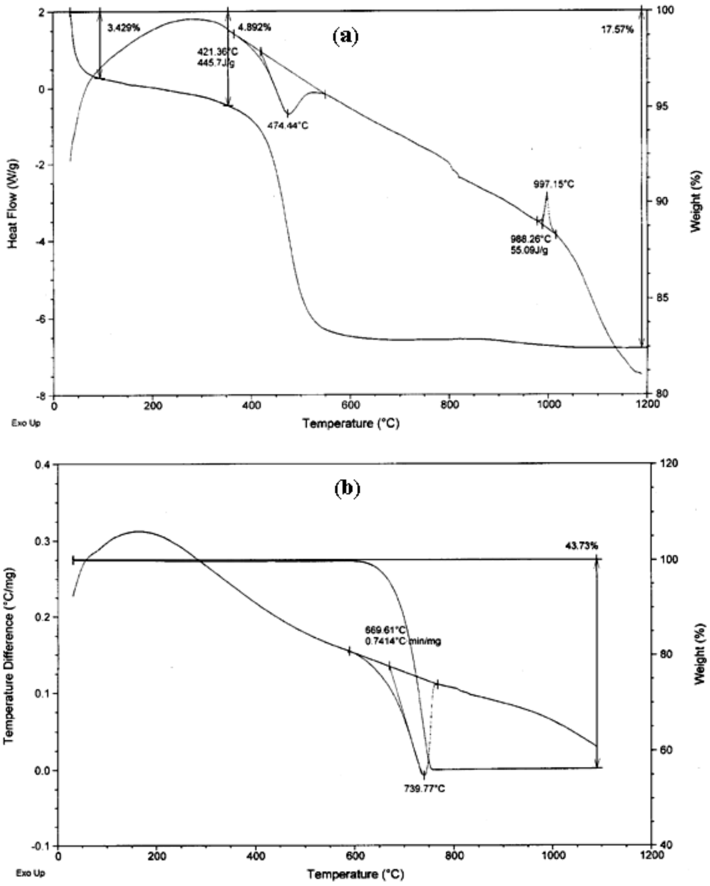

Fig. 3. DSC and TGA curves of natural raw materials: (a) kaolin and (b) Calcite.

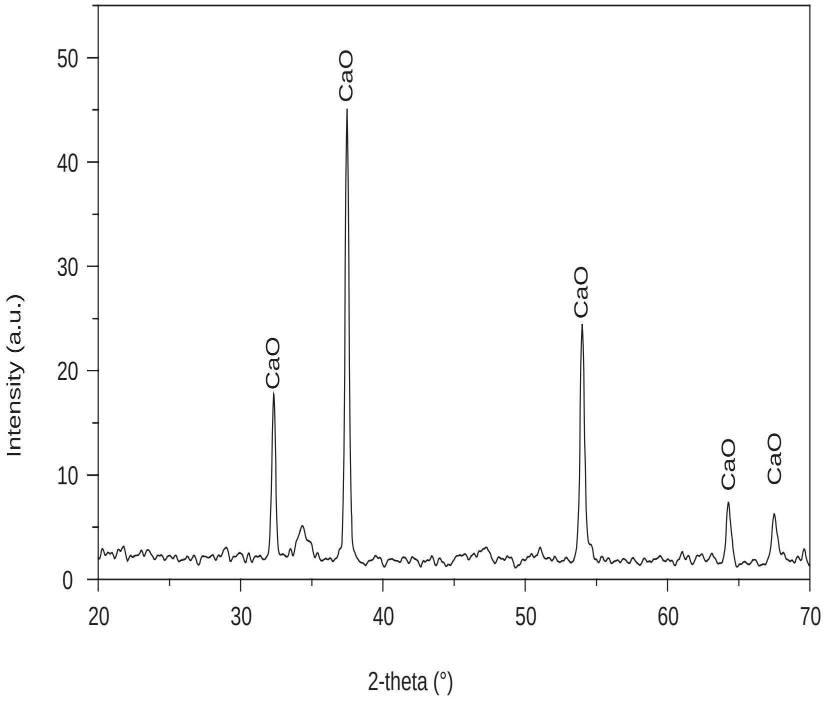

Fig. 4. XRD spectrum of calcium oxide powder, obtained from $CaCO_3$ after calcination at 900°C for 1 h.

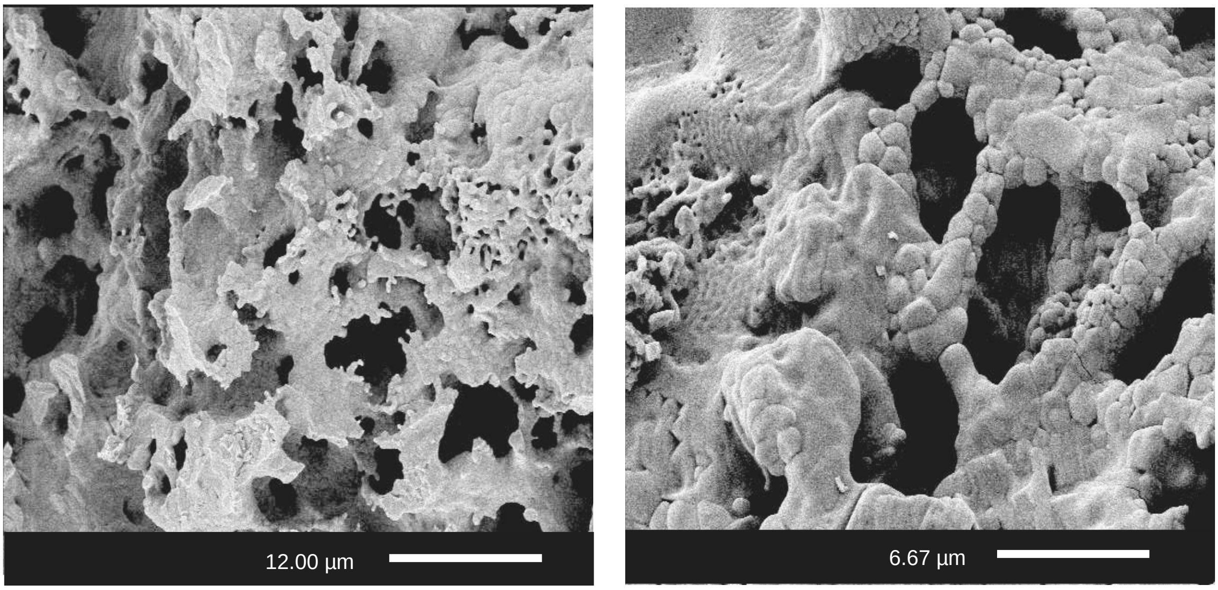

Fig. 5. SEM micrographs of cross-section, left, and the surface, right, of support, sintred at 1250°C for 2 h.

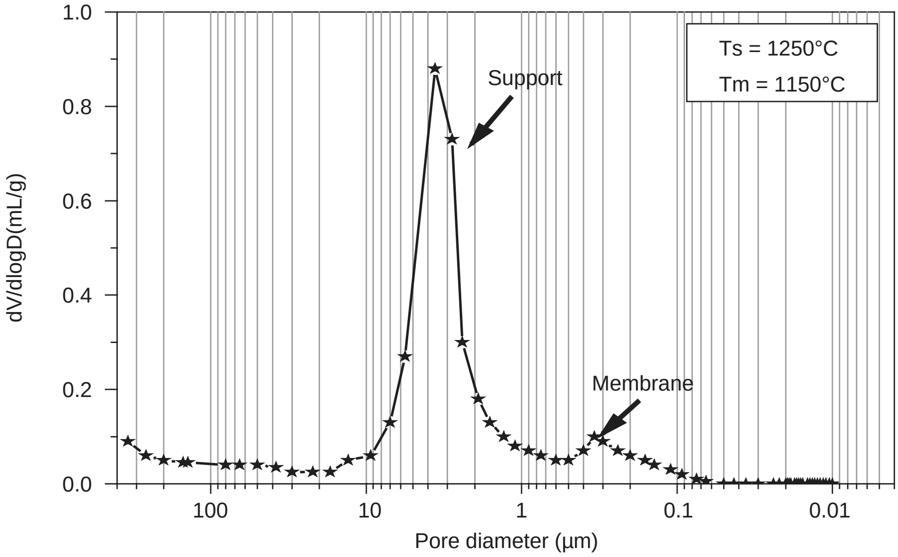

Fig. 6. Pore size distribution of support and membrane.

l0 wt% zirconia powder, 25 wt% PVA (12 wt% aqueous solution) and water (65 wt%). The deposition of the slip on the support was performed by the slip casting method [11]. In this case of the tubular membranes, the tube was closed at one end and filled with the solution. The coating was carried out by capillary suction. The thin layer thickness was determined by the capillary pressure and is depended on the support porosity, on the coating time and on the suspension viscosity [7]. The deposition time was between 5 and 10 min. After drying at room temperature for 24 h, the microfiltration layer was sintered at 1150°C for 2 h. A temperature plate at 250°C for 15 min is necessary in order to eliminate completely the PVA, which is in great quantities in the slip. A relatively slow temperature rate (2°C/min) was needed in order to avoid the formation of cracks on the layer [12]. The distribution of the pore diameters of the membrane was determined by mercury porosimetry. The average pore diameters and the porous volume of the active layer are around 0.35 µm (Fig. 6b) and 52%, respectively. It is known that the particle size distribution (PSD) has an influence on the pore size distribution, as a narrow PSD

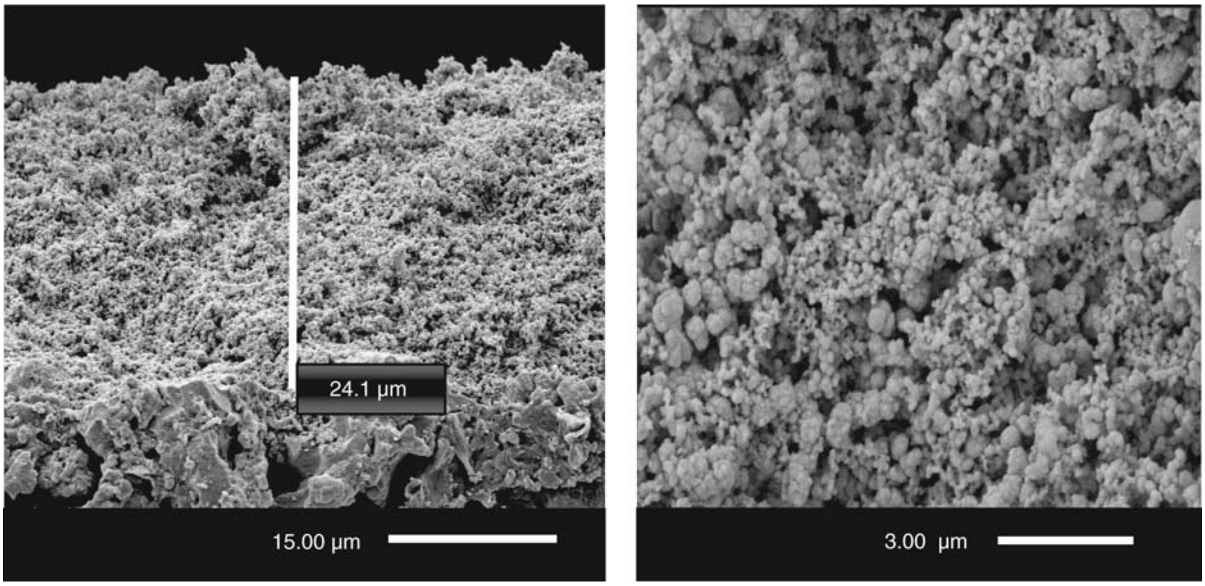

Fig. 7. SEM micrographs of cross-section, left, and the surface, right, of membranes, sintred at 1150°C for 2 h.

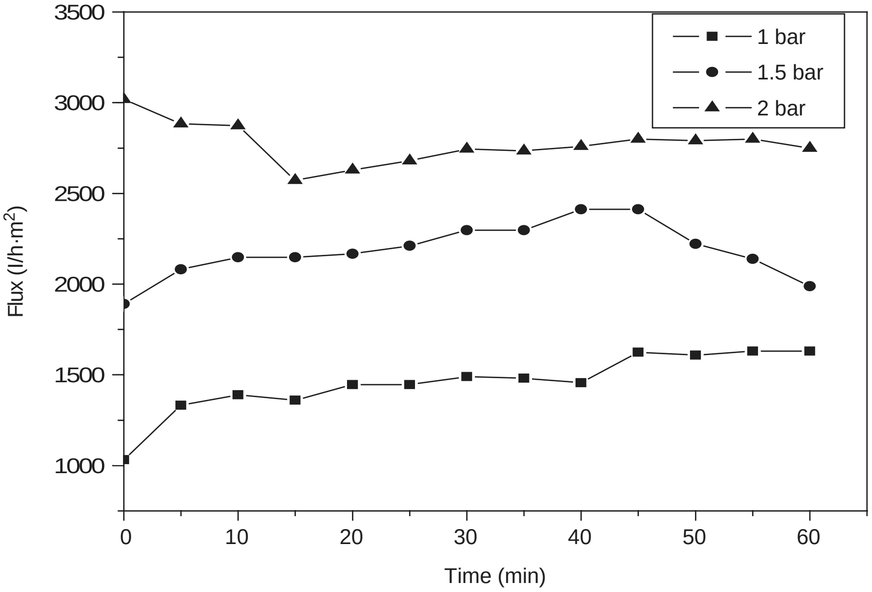

Fig. 8. Water flux as a function of time for three working pressure values.

results in a narrow pore size distribution, while a wide PSD would result in a wider pore size distribution [13]. The pore size indicates that this kind of membranes can be utilized in the microfiltration range [7].

SEM images of the prepared membranes are shown in Fig. 7. This figure gives information on the texture of the elaborated membrane surface [14]. It is noticed that there is no cracks and the pore distribution of the membrane is uniform. The thickness of the microfiltration layer is about 24 µm (Fig. 7), it can be controlled by the percentage of the mineral powder added in the suspension and the period of the deposited time.

Tangential filtration tests were carried out at room temperature. The membrane is immersed in distilled water for 24 h. The water flux through the membrane was measured as a function of time at diffrent transmembrane pressure values, where the flux are stables after period of 15–40 min of filtration depending on the working pressure (Fig. 8).

The permeability was determined from the diffrent flux values for each working pressure. The obtained curve is a straight line with a slope equal to around 1440 l/h/m^2.bar. It is amongst the best permeability values when copered to those reported by other authors [11].

5. Conclusion

The attractiveness in the present work is the development of membrane supports manufactured from local kaolin (DD2) and Calcium carbonat mixtures, available in our country. The ceramic support was formed by extrusion of a ceramic paste from kaolin and calcium carbonats mixtures. The microfiltration layer, deposited on the supports, was obtained by the slip casting technique using suspensions of zirconia powder. This membrane can be used for microfiltration and also used as supports for ultrafiltration.

References

[1] J.M. Benito, A.Conesa, F. Rubio, M.A. Rodriguez, *J. Eur. Ceram. Soc.*, 25 (2005) 1895–1903.

[2] S. H. Lee, K. C. Chung, M. C. Shin, J. I.Dong, H. S. Lee, and K. H. Auh, *Mater. Lott.*, 52 (2002) 266–271.

[3] X. Ding, Y. Fan, N. Xu, *J. Membr. Sci.*, 270 (2006) 179–186.

[4] C. Gaucher, P. Jaouen, J. Comiti and P. Legentilhomme, *J. Membr. Sci.*, 210 (2002) 245–258.

[5] H. Mori, S. Mase, N. Yoshimura, T. Hotta, K. Ayama, J. I. Tsubaki, *J. Membr. Sci.*, 147 (1998) 23–33.

[6] N. Saffaj, S. A. Younssi, M. Persin, M. Persin, M. Cretin, A. Albi, A. Larbot, *Ceram. Int.*, 31 (2005) 205–210.

[7] S. Masmoudi, R. Ben Amar, A. Larbot, H. El Feki, A. Ben Salah, L. Cot, *J. Membr. Sci.*, 247 (2005) 1–9.

[8] S. Rakib, M. Sghiar, M. Rafik, D. Cot, A. Larbot and L. Cot, *Ann. Chim. Sci. Mat.,* 25 (2000) 567–576.

[9] N. Elmoudden, A. Elghazouali, S. Rakib, M. Sghyar, M. Rafiq, A. Larbot et al., *Ann. Chim. Sci. Mat.,* 26 (2001) (2), 5–11.

[10] F. Bouzerara, A. Harabi, S. Achour, and A. Larbot, *J. Eur. Cer. Soc.,* 26 (2005) 1663–1671.

[11] S. Khemakhem, R. Ben Amar, R. Ben Hassen, A. Larbot, M. Medhioub, A. Ben Salah, Cot, L., Desalination, 167 (2004) 19–22.

[12] S. Masmoudia, A. Larbotb, H. El Fekia, Ben R. Amar, Desalination, 190 (2006) 89–103.

[13] H. Bissett, J. Zah, H.M. Krieg, *Powder Technol.,* 181 (2008) 57–66.

[14] S. Khemakhema, A. Larbotb, R. B. Amara, *Desalination,* 200 (2006) 307–309.