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Production of Supports and Filtration Membranes from Algerian Kaolin and Limestone

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\section*{Abstract}

In this work supports and microfiltration (MF) membranes were manufactured from raw kaolin and lime extracted from limestone. The effects of the relatively lower sintering temperature, ranging from 800° to 1100°C, on the porosity, average pore size, pore-size distribution and strength of supports have been investigated. It has been found that the average pore size in tubular membrane supports, measured by mercury porosimetry, was about 7 µm while the pore volume was 48% for supports sintered at 1000°C with a flexural strength of about 30 MPa. The samples sintered at 1000°C were selected as supports for production of MF membranes. Active membrane layers were elaborated from anorthite powder (CaO.Al\textsubscript{2}O\textsubscript{3}.2SiO\textsubscript{2}), using the slip-casting technique.

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\section*{1. Introduction}

There is much current interest in the application of membranes in separation procedures because of their potential for the treatment of large quantities of wastewater [1]. The use of ceramic membranes has many advantages such as high thermal and chemical stability, pressure resistance, long lifetime, good resistance to fouling, and the ease of cleaning [2, 3]. Ultrafiltration (UF) and microfiltration (MF) operations are often used to remove particles, microorganisms, and colloidal materials from suspensions [4].

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Asymmetric membranes usually consist 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 composite membrane [5].

At present, the production of industrial membranes provides a limited choice of materials. As a consequence, the price of ceramic membranes is high, and a significant effort has been expended in recent years in the membrane technology field in order to develop new porous ceramic materials using inexpensive clays and kaolin. These materials are in abundance and require sintering temperature lower than those for metal oxide materials [6, 7].

In order to decrease membrane cost and to evaluate our natural resources, we have manufactured supports from local raw materials, kaolin (Al₂O₃.2SiO₂.2H₂O) and lime extracted from limestone (CaCO₃) [8-10]. The choice of these materials has been dictated by their natural abundance (and consequent low price) and their thermal stability [9, 11-12]. This paper describes the results of these efforts.

2. Analysis of the raw materials

In this study, the supports and membranes were prepared from domestic kaolin (DD3) and calcium oxide extracted from calcium carbonates obtained respectively from the Guelma and Constantine regions of Algeria. XRF analysis showed that kaolin contains mainly SiO₂ (43.69 wt%) and Al₂O₃ (37.27 wt%) with CaO (0.38 wt%), Fe₂O₃ (0.64 wt%), MgO (0.06 wt%) and MnO (0.41 wt%). Similar analysis of the calcite revealed that the kaolin (DD3) is composed mainly of silica (SiO₂) and alumina (Al₂O₃). The particle size distributions of the kaolin (DD3) and CaCO₃ were determined by the Dynamic Laser Beam Scattering (DLBS) technique, with the results shown in Fig. 1.

![Fig.1. Particle size distribution of powders used in this work. (a) kaolin powder (DD3); (b) Calcite powder](image)

3. Support elaboration and characterization

For preparation of membrane supports the kaolin (DD3) is properly crushed, then calcined at 520°C for 1 hour to be later sieved at 200 µm. After that, an amount of about 20 wt% of lime powder is added. In order to improve the properties that facilitate the synthesis, some organic materials have been added, such as 4 wt% methocel as a plasticizer and 4 wt% amijel as a binder. This mixture must be continuously mixed with water so as to obtain a plastic paste. For good dispersion of the water in the paste, this mixture should be covered in a plastic case for at least 12 h. After that, an extrusion technique is used to form some tubular samples. For good drying of these tubular samples, they are placed at room temperature on rotating aluminium rolls. In these studies the dried tubular samples were sintered at various temperatures ranging between 800 and 1100°C following this program:

\[
2\degree\text{C/min} \quad 25\degree\text{C} \rightarrow 5\degree\text{C/min} \quad 250\degree \text{C} (2\text{ h}) \rightarrow 800 - 1100\degree \text{C} (3\text{ h})
\]

In order to eliminate the added organic materials and to avoid formation of microcracks during sintering of the samples, the initial rate of heating was chosen to be 2°C/min. The effect of the relatively lower sintering temperatures, ranging from 800° to 1100°C, on the porosity and average pore size is shown in Fig. 2.
The data clearly reveal that the effect of temperature on average pore size is characterized by a sharp increase in pore size with increasing sintering temperature while the porosity is stabilised between 40 and 50% for all prepared samples.

Fig. 2. Effect of sintering temperature on average pore size (left) and pore volume (right) of supports.

The supports fired at 1000°C and tested by mercury porosimetry showed pore diameters centered near 7 µm (Fig. 3) and 48% of porosity. The average pore size is also confirmed by typical micrographs such as that illustrated in Fig. 4. These supports have been selected as substrates for MF.

Fig. 3. Pore size distribution of supports sintered at 1000°C for 3 h.

Fig. 4. SEM micrographs of supports sintered at 1000°C for 3 h.

4. Membrane elaboration and characterization

For preparing a microfiltration layer based on anorthite powder (CaO. Al₂O₃. 2SiO₂) [13], a deflocculated slip was obtained by mixing 10 wt% anorthite powder, 30 wt% PVA (12 wt% aqueous solution) and water (70 wt%). The deposition of the slip on the support was performed by the slip casting method [6, 9]. This layer, after being dried at room temperature, was sintered at 850°C for 2 h.

The distribution of the pore diameters of the composite membrane was determined by mercury porosimetry. The average pore diameters and the porous volume of the active layer are around 0.5 µm and 50%, respectively, as seen in Fig. 5.

It is known that the particle size distribution (PSD) has an influence on the pore size distribution, as a narrow PSD results in a narrow pore size distribution, whereas a wide PSD would result in a wider pore size distribution [4].
The pore size obtained here indicates that this kind of membrane may be used in the microfiltration range [5].

![Pore size distribution of support and membrane.](image)

SEM images of the prepared membranes are shown in Fig. 6. This figure gives information on the texture of the elaborated membrane surface. It is seen that there are no cracks and that the pore distribution of the membrane is uniform. The thickness of the microfiltration layer is about 33 µm (Fig. 6); it can be controlled by the percentage of the mineral powder added in the slip suspension and the duration of the deposition time.

![SEM micrographs of membranes sintered at 850°C for 2 h. (left) cross-section; (right) surface](image)

**5. Conclusions**

The attractiveness in the present work is the development of supports and MF membranes manufactured from local kaolin (DD3) and calcium oxide mixtures that are available in our country. The ceramic support was formed by extrusion of a ceramic paste of kaolin and calcium carbonate mixtures. The MF layer, deposited on the supports, was obtained by the slip-casting technique using suspensions of anorthite (CaO.Al₂O₃.2SiO₂) powder. This membrane may be used for MF and also used as a support for UF and Nano-Filtration (NF) membranes.
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