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Elaboration and characterization of ceramic membrane supports from raw materials used in microfiltration

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ABSTRACT

There is a much current interest in the application of membranes in separation procedures because of their application in the treatment of big amounts of wastewaters. The use of ceramic membranes has many advantages such as a high thermal and a chemical stability, a pressure resistance, a long lifetime, and good defouling properties. Microfiltration (MF) and ultrafiltration are often used to remove particles, micro-organisms, and colloidal materials from suspensions. In this work, the supports for MF were prepared with local clays and calcite mixtures. The choice of these raw materials is based on their natural abundance (low price) and interesting microstructures. These supports were made by an extrusion technique in order to obtain tubular supports, which were afterward sintered at 1,250˚C for 1 h. It has been found that the elaborated supports had interesting characteristics; an average pore size of about 4 μm and a porosity ratio around 50%. Moreover, the pore size distribution is almost homogenous (mono-modal type). The surface and the cross-section morphologies observed through a scanning electron microscope are also homogenous and do not present any macro defects (cracks, etc.). Moreover, these supports were tested with distilled water. A cross-flow microfiltration was performed. The result showed a good retention of supports turbidity.

Keywords: Kaolin; Calcite; Supports; Membranes; Microfiltration; Permeate flux

1. Introduction

Calcite ($CaCO_3$), dolomite ($CaCO_3{\cdot}MgCO_3$), natural derived hydroxyapatite: HA: $Ca_{10}(PO_4)_6(OH)_2$, kaolin, feldspar, and quartz are mainly amongst the abundantly available raw materials in Algeria. Many studies have already been published for valorizing these native raw materials. These topics concern advanced ceramics [1–3], ceramic membranes [4–10], and bioceramics [11–17]. For instance, calcite and dolomite coupled with highly pure SiO_2 were also used for fabrication of highly resistant wollastonite ($CaSiO_3$) [13] and diopside ($CaMgSi_2O_6$) [14] based bioceramis, respectively.

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In this way, an attempt has been done in order to use clay and calcite local raw materials for ceramic membrane supports production.

The specific properties of ceramic membranes, which have attracted the attention of academic and applications scientists are: long-term stability at high temperatures [4,7,18], resistance to harsh environments, resistance of high pressure drops, inertness to microbiological degradations, and easy cleanability and catalytic activation. However, a membrane support provides a mechanical strength to a top layer to withstand the stress induced by the pressure difference applied over the entire membrane, and must simultaneously have a low resistance to the filtrate flow [19]. The marketed supports are manufactured generally from compounds such as Al_2O_3, $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, SiO_2, and $3Al_2O_3{\cdot}SiO_2$, which have a relatively elevated cost. In order to decrease this cost and to valorise the natural resources [6,20], the supports have been manufactured from local raw materials. Moreover, because the ceramic filters are generally constituted of a thick support (2,000 μm) and mono or multi thin membranes (from 10 to 40 μm for each one), this paper is mainly focussed on the ceramic support rather than their deposited membranes. Therefore, replacing the more expensive starting materials, mentioned above, by other cheaper raw materials used in supports (which constitute about 99% of the filter mass) is significantly important. The prepared supports were used for the treatment and the wastewater discoloration.

2. Experimental procedures

2.1. Raw materials

Two mineral powders were selected for the elaboration of these microfiltration ceramic membrane supports:

Clay: The chemical composition of the clay used in the present work, given in weight percentages (wt.%) of oxides, is: 50.56 wt.% SiO_2; 34.15 wt.% Al_2O_3; 01.15 wt.% Fe_2O_3; 00.02 wt.% CaO; 00.31 wt.% MgO; 00.28 wt.% TiO_2; 7.18 wt.% K_2O; and a 6.35 wt.% of solids lost by calcination. It can be said that the clay powder is essentially formed of large amounts of silica and alumina. Fig. 1 presents the XRD pattern of the clay; it shows that kaolinite (K), quartz (Q), and muscovite (M) are the main crystalline minerals existing in this clay.

Calcium carbonates: The quantitative analysis of these calcium carbonates ($CaCO_3$) showed that the purity of this raw material is about 99.6%. The particle size distribution of $CaCO_3$ was determined by the

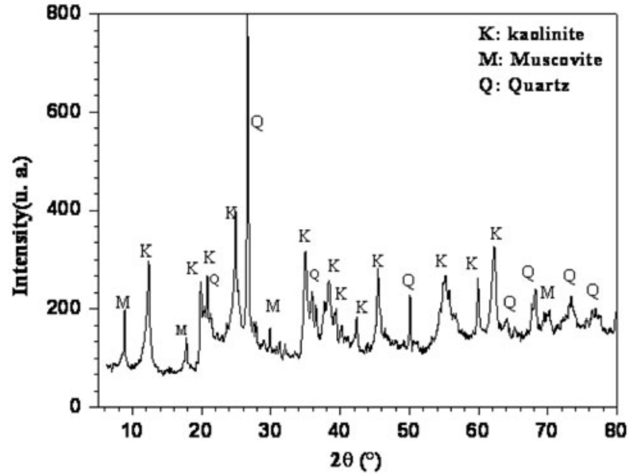

Fig. 1. XRD spectrum of used clay powders.

dynamic laser beam scattering technique. This method gave an average particle size in the order of 4.8 μm.

2.2. Supports preparation using an extrusion method

Extrusion is a process technology for the production of ceramic tubes. In extrusion: a stiff paste is compacted and shaped by forcing it through a nozzle. In general, the manufacturing process of tubular ceramic supports using extrusion method includes the following steps:

- Steps of mixing various materials, including raw materials, organic additives, and other extrusion-aid materials to form a paste.
- Passing the paste through an extruder to form a cylindrical, tubular supports.
- Placing the tubular supports on rotating rollers to cause the support to rotate and to dry.
- Firing the tubular ceramic support. The firing will remove all organic binders and chemicals utilized in the ceramic manufacturing process, such as the CO_2, amijel, and methocel. It will also remove any residual water not removed.

In this work, the tubular configuration support was obtained by an extrusion method of a mixture of clay, calcium carbonate, and organic additives in correct proportions to adjust the rheological properties of the paste. The organic additions used are: 3 wt.% of methocel, as a plasticizer and 3 wt.% of amijel, as a binder. After drying at room temperature, supports were sintered at different temperatures (1,150–1,250 °C) for 1 h. Fig. 2 shows a photo graph of tubes extruded

Fig. 2. A photograph of the prepared supports.

and sintered at 1,250˚C, within 10 and 6 mm outer and inner diameters, respectively.

The total porosity, average pore size (APS) and pore size distribution have been determined by mercury intrusion porosimetry for supports sintered at different temperatures.

2.3. Filtration pilot

Cross-flow microfiltration tests were performed on a laboratory pilot at room temperature. Fig. 3 shows the schematic of the filtration system. The pilot system consisted of a tank, a feed pump, a flow meter, and a membrane module. The working pressure was applied using an air gas. Pressure values were monitored by sensors and recorded. The determination of the water membrane permeability was performed with distilled water.

3. Results and discussion

3.1. Phase identification

XRD data for the sample sintered at 1,150˚C are shown in Fig. 4. The main crystalline phases identified were ghelinite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$).

3.2. Supports characterization

The porosity measurement and the APS have been carried out on supports sintered at different temperatures. The obtained results are summarized in Table 1. Consider this table, which presents the pore size and the porosity. It is clear that the pore size and the porosity are temperature dependent. As would be expected, the porosity decreases when the sintering temperature is increased. For example, supports, sintered at 1,150˚C, had a porosity ratio about 52% and an APS around 1.3 μm, whereas these values where 49% and 3.5 μm, respectively, for supports sintered at 1,250˚C.

Tangential filtration tests were performed using a homemade pilot plant at a room temperature. The water flux through the supports was measured as a function of time at different trans membrane pressure values. Fig. 5 shows that the water flux through the support membrane depends on the applied pressure. A stable flux is obtained after few minutes and the average permeability is about 2,244 and 12,500 l/h m^2. bar for supports sintered at 1,150˚C (S1) and 1,250˚C (S2), respectively.

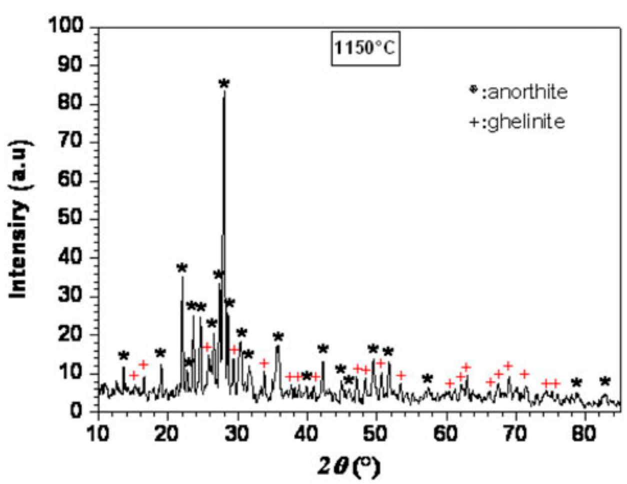

Fig. 3. XRD spectrum of prepared supports sintered at 1,150˚C, for 1 h.

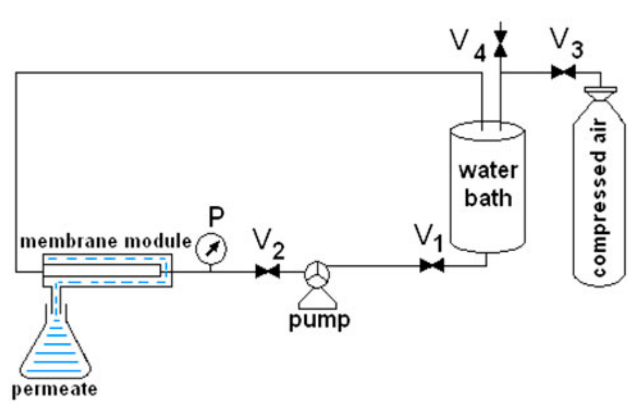

Fig. 4. A schematic process used for the filtration system.

Table 1
Some characteristics of the prepared supports

Samples	Pore size (μm)	Porosity ratio (%)
S1 (1,150˚C)	1.3	52
S2 (1,250˚C)	3.5	49

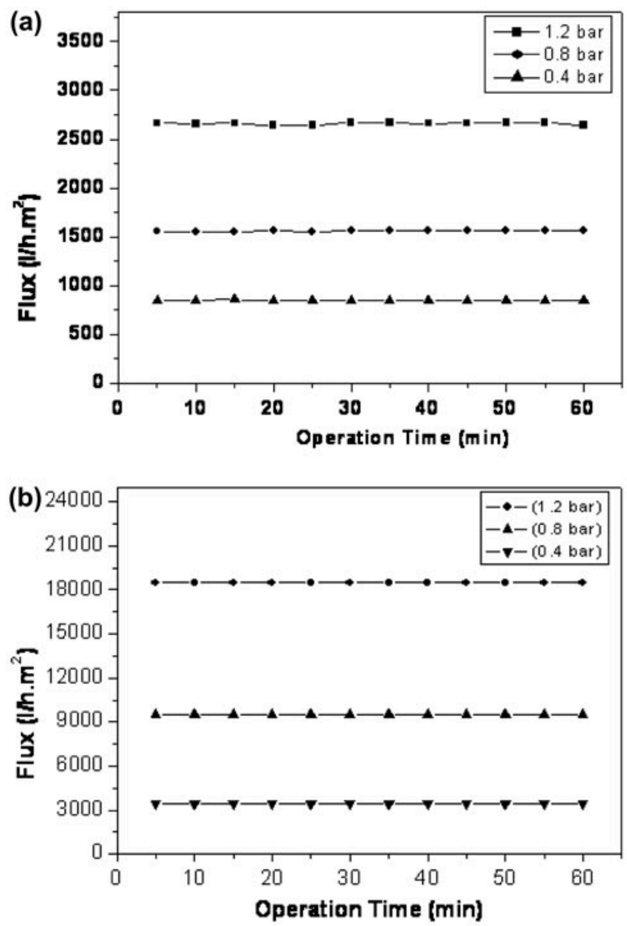

Fig. 5. Permeate flux versus time, at 3 working pressure values, using distilled water for S1 and S2 sintered at 1,150 and 1,250˚C for 1 h, respectively.

The water permeability coefficient of the S2 is significantly different from that of the S1. Both supports S1 and S2 have identical thicknesses, closer porosity (%) but different APS (Table 1), and thus exhibited different water flux data as shown in Fig. 5. The tube (S2) sintered at 1,250˚C, has a higher APS and thus exhibited higher water flux. This may indicate that pore size may be considered as a more important factor than porosity to determine the flux.

The mechanical resistance test was performed using the compressive strength. The effect of sintering temperature on the mechanical properties of the membrane supports was also investigated. The resulting ceramics tube sintered at 1,150˚C have a compressive strength of ≈25 MPa and a Young's modulus of 4 GPa for 52% total porosity. The Young's modulus of the present porous ceramics is relatively lower than that of dense ceramics. This is thought to be due to the presence of pores. It should also be remarked that these mechanical properties are generally acceptable especially for Microfiltration (MF) and/or ultrafiltration (UF) membranes applications.

Table 2
The effluent turbidity before and after filtration, by using the elaborated supports

	Turbidity (NTU)
Raw effluent	259
Permeate (Using S1)	37
Permeate (Using S2)	99

The effect of filtration on the water quality was clear. Almost all suspended solids and some of the colloids were retained and thus the retentions of suspended solids, turbidity, and color were good.The characteristics of the effluent before and after filtration are illustrated in Table 2. The obtained results are very interesting. In fact, a very important decrease in turbidity (about 80% for supports sintered at 1,150˚C) can be observed.

Fig. 6 shows a noticeable elimination of suspended matter illustrated by the change in the effluent color as well as the turbidity elimination.

Finally, it should also be remarked here that using ceramics (oxides) in this work and others [21] instead metallic products [22,23] is well justified, particularly for wastewater purification.

Fig. 6. A photograph of wastewater before and after the support MF treatment.

4. Conclusions

In this work, ceramic membrane supports were prepared by extrusion method. They can be used as supports for MF membranes of and/or UF applications. Furthermore, the effect of APS of supports on permeability was investigated. Moreover, these supports are characterized by a reduced manufacture cost since the used raw materials are very abundant (in Algeria) and their mechanical properties seem to be acceptable, especially for MF and/or UF membranes applications.

Acknowledgments

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