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Elaboration of a new flat membrane support from Moroccan clay

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ABSTRACT

The present paper is devoted to synthesis of porous ceramic support from local Moroccan clay (region of Agadir). This material has been dictated by their natural abundance (low price) and their beneficial properties. In this work, we were also interested in the development and the characterization of new mineral support for microfiltration and ultrafiltration membrane. The support, with flat configuration, was prepared from natural clay: the powder was crushed, sieved to 125 μm and mixed with organic additives and water. The obtained paste was then extruded to elaborate a porous structure. The firing temperature of the support is 800°C. After firing, the elaborated support showed an average pore diameter of **11** μm and a porosity of **41**%. The average support permeability determined using pure distilled water is 1,805 L/h m² bar. This porous ceramic tube was used as support to prepare microfiltration membrane which were tested for the filtration.

Keywords: Membrane; Ceramic support; Clay; Characterisation; Microfiltration

1. Introduction

The membrane processes have proved their interest in the industry, such as the use of microfiltration or ultrafiltration membrane processes in the dairy industry [1], due to the development technological and industrial; agricultural and domestic wastes, discharged to several receivers such as rivers, lakes and seas. Ceramic membranes with high performance parameters such as permeation flow and better thermal, chemical and mechanical resistance, controllable micro-structure and little pollution to our environment. Recently, they have been attracting much attention in the scientific community [2]. Unfortunately, commercial ceramic membranes prepared from alumina, titania, zirconia, and silica are too expensive for economic application in environmental technology which requires high permeation fluxes and low costs to treat great volumes of dust-contained hot gas and industrial wastewater. As a result, Actually, most of the scientific workers focused their attention on the preparation of new inorganic membranes for

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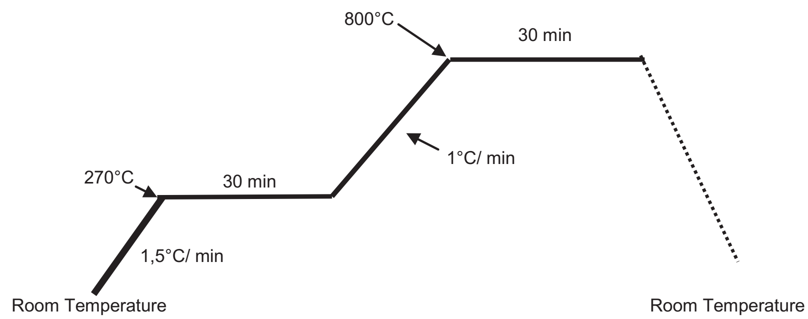

Fig. 1. Thermal treatment of sintering the flat support.

microfiltration using natural non-expensive (both raw materials and preparation process) [3–5].

The development of ceramic membranes based on natural materials and some powder wastes such as fly ash was investigated by several authors. Clays are in abundance and need lower firing temperature in comparison with metal oxide materials (alumina, zirconia, titania, and silica) [6]. Various tubular supports, for microfiltration and ultrafiltration membranes, have been elaborated using different materials such as cordierite, kaolin used by Saffaj et al. [7] and Loukili et al. [8] other Moroccan clays [9,10]. The prepared support presents a porosity of 40–43% and an average pore size in the range of 7–11 μm [11–17]. Our purpose in this work is to develop new supports made from clay, which was a natural material very abundant in the south of Morocco. Elaborated flat disks are intended to be used later as supports for microfiltration and ultrafiltration layers to manufacture ceramic membranes [18], which can be applied in the industrial wastewater treatment.

2. Experimental

2.1. Preparation of support materials

The plastic paste was prepared from natural Moroccan clay powder homogeneously at 125 μm, this powder will be mixed with organic additives and water. Plasticizer and binder are required to prepare a paste with rheological properties allowing the shaping by extrusion. The mixture of clay and organic additives obtained as follows:

(a) Mixing of clay 81.7% w/w, amidon 10% w/w (Amidon de maïs RG03408, Cerestar), Methocel 4% w/w (The Dow Chemical Company), Amijel 4% w/w (Cplus 12,072, Cerestar) and PEG 1,500 0.3% w/w (Prolabo).
(b) The mixture was aged (250 tr/min) during 30 min in order to obtain a good homogeneity.
(c) Adding the water (32% w/w of powders) and Zusoplast 0.24% w/w (Zschimmer and Schwartz).
(d) Pugging for 30 min.
(e) Ageing of the paste: the paste is kept in a closed box for 2 days under high humidity to avoid premature drying and to ensure complete diffusion of the water and organic additives.
(f) Shaping by extrusion and calendered into a thin film which was segmented to form flat disk supports with a diameter of 4.9 cm.
(g) Drying at temperature 40°C during 24 h of the flat support after extrusion.
(h) Thermal treatment: The extruded pieces were sintered at 800°C in furnace (Fig. 1). Process of the ceramic preparation is described in Fig. 2.

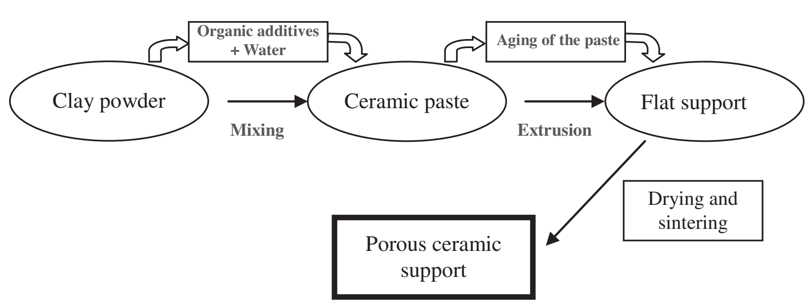

Fig. 2. Diagram for elaboration of porous support by extrusion method.

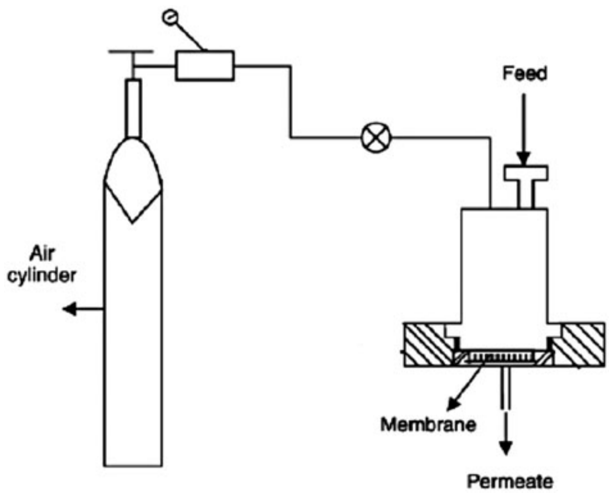

Fig. 3. Laboratory pilot.

2.2. Filtration test

Frontal filtration tests were performed on a laboratory scale filtration pilot (Fig. 3). The support with a filtration area of 15.2 cm^2 and a thickness of 2 mm is placed in the membrane housing and the water is filled in the system from the top (Feed cell). All filtration experiments are conducted at a temperature of 25 ± 2°C. The pure water permeability of support was first studied. This test was conducted to provide guidance to know the permeability of the membrane.

The setup as shown in Fig. 3 used for this experiment consists a Teflon tubular cell with a flat circular Teflon base plate which contains the membrane housing. The deionized water is filled in the tubular section from the top (Feed cell). The membrane is placed in a Teflon casing and sealed with epoxy resin and then place in the membrane housing provided on the base plate. The cell is pressurized with compressed air. The permeability is calculated by tracing the flux vs. the pressure.

3. Results and discussion

3.1. Characterization of clay powder

Energy Dispersive X-ray analysis shows the chemical composition of clay powder,which indexed that silica and alumina are the major constituent of this sample (Table 1).

The thermogravimetric analysis (TGA) and differential (DTA) is shown in Fig. 4. The TGA indicated an important two weight loss between 28 and 322°C and second between 322 and 867°C. This first loss is due to the removal of adsorbed surface water and second of water structure.

Table 1
Chemical analysis of the clay

Element	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	CaO	K_2O	MnO
Weight (%)	43	35	15	3.5	1.5	1.2	0.03

3.2. Elaboration of porous flat supports

The elaboration of a ceramic macroporous support implies the following sequence of operations: (1) preparation of a plastic ceramic paste, (2) shaping by extrusion, and (3) consolidation by thermal treatment. The principal advantage of the organic additives is that they are eliminated by combustion during the thermal treatment. Sintering is a method for making objects from powder, by heating the material in a sintering furnace below its melting point (solid state sintering) until its particles adhere to each other. Fig. 5 shows that the diameter of the elaborated flat support decreases from 4.9 to 4.7 cm after sintering at 800°C; this is due to the shrinkage phenomena after sintering.

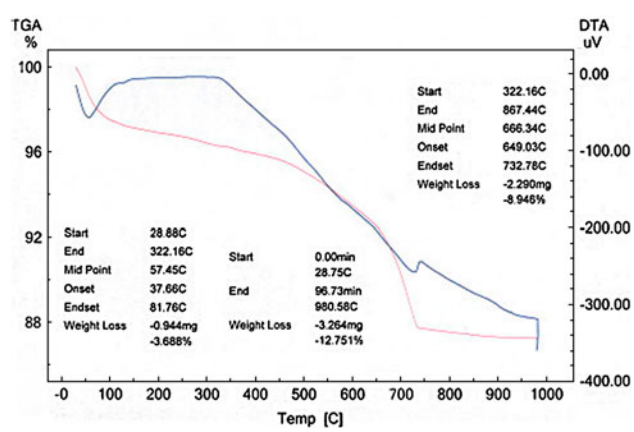

Fig. 4. TGA-DTA of clay.

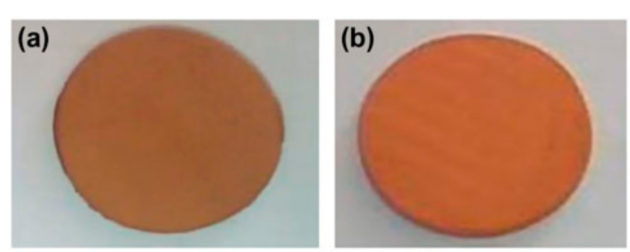

Fig. 5. Flat support views. (a) After drying at 40°C; (b) after sintering at 800°C.

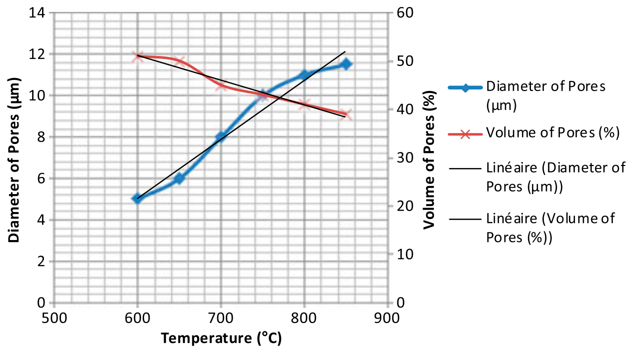

Fig. 6. Pore diameter and pores volume vs. firing temperature of the support.

3.2.1. Characterization of the supports

The sintering temperature is an important parameter which controls the pore diameter of the support and its mechanical resistant. The thermal expansion depends also on the firing treatment. Therefore, the best properties of the final support are achieved by adjusting the conditions for sintering. Fig. 6. shows the porosity and Pores volume is function of temperature.

Finally the mechanical resistance test was performed on the elaborated support, with a filtration area of 15.2 cm^2 and a thickness of 2 mm, was also determined. The measured mechanical strength is about 15 MPa (Fig. 7). Then to control the chemical resistance, the support sintered at 800°C was conditioned by immersion at room temperature and 50°C in soda solution and acid chloride at 0.1 M, for a minimum of 24 h. The results present a good chemical resistance in acidic medium than in basic medium.

3.2.2. Determination of support water permeability

Support was at first characterized by their water permeability. The support is conditioned by

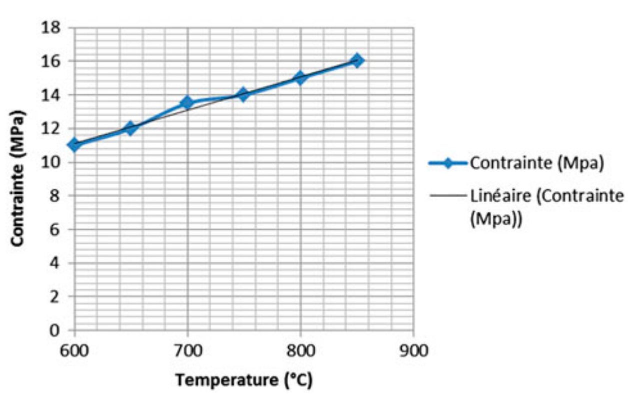

Fig. 7. Mechanical strength vs. firing temperature of the support.

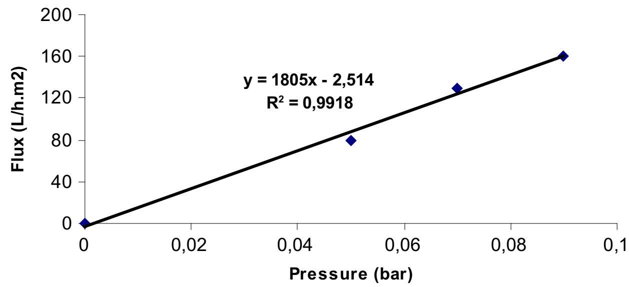

Fig. 8. Water flux vs. working pressure.

immersion in ultrapure water for a minimum of 24 h before filtration tests. The height of a stand was used to control the pressure in the system, The fluxs are measured at different pressures (0.05, 0.07 and 0.09 bar) that each pressure presents a flux about it we determined permeability. Experiments show also that the water flux through the support depends on the applied pressure. The average support permeability determined using pure distilled water is 1,805 L/h m^2 bar (Fig. 8).

3.3. Preparation and characterization of the ZrO_2 microfiltration membrane

Due to the high permeability of the clay support, it is necessary to reduce the pore diameter by an intermediate layer with smaller pore sizes which will be prepared by sol–gel process. The role of the intermediate layer will also prevent the infiltration of the support by the sol. The zirconia intermediate layer was prepared using suspended powders. Details of the method were described by (Broussous et al., 2001; Saffaj et al., 2004). The microfiltration layer was obtain by a deflocculated suspension which is prepared by mixing 10 wt.% of zirconia powder (Cezus chimie 8 m^{2}g^{-1} specific area), 30 wt.% of PVA (12 wt.% aqueous solution) and 60 wt.% DOLAPIX CE 64 as dispersing agent (0.2 wt.% aqueous solution). Dispersion of the particles was achieved by applying ultrasonic agitation for 10 min.

The tap casting process was then applied to coat the porous support. After the deposition of the film on the substrate, the latter will be dried at room temperature, and is carried out and then is fired at 1,100°C (sintering) that will ensure the consolidation of the layer. These last two steps are very important in the development of homogeneous ceramic layers. Finally, a layer of ZrO_2 microfiltration with average pore diameters of 0.23 µm was obtained. (Fig. 9)

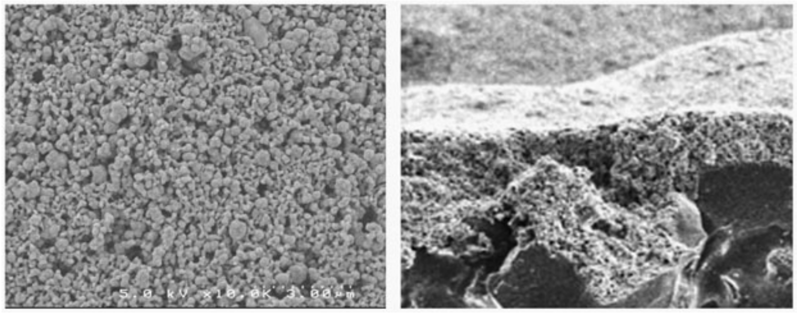

Fig. 9. SEM micrographs of the zirconia microfiltration layer.

4. Conclusion

In this work, we prepared a new ceramic support for microfiltration membrane based on Moroccan clay. The membrane support was prepared by the extrusion of the ceramic past made with clay powder and sintered at 800°C.

The filtration test confirmed the ability of the preparation membrane support that the average support permeability determined using pure distilled water is 1,805 L/h m^2 bar.

Finally, the obtained results supported by the low cost support show that the clay based material is appropriate for the development of supports microfiltration membranes, which could find application for economic treatment of industrial wastewater. These supports were used to deposit layers of ZrO_2 microfiltration.

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