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Elaboration and characterization of tubular supports for membranes Microfiltration

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Abstract ▬ This work is focused on the purification and exploitation of used water; using ceramic filters made up from local raw materials widely available with a low price; they are as kaolin and $CaCO_3$. In the technical procedure two ways are followed. The first one is by samples are made in the form of tubes using extrusion method which were afterwards sintered at 1200 °C for 1 h. It has been found that support had interesting characteristic; an average pore size of about 5.8 µm, a porosity ratio around 52.3% and a flexural strength ≈ 78 MPa. Moreover, the pore size distribution is almost homogeneous. The surface and the cross-section morphologies observed through a scanning electron microscope (SEM) are also homogeneous. In the second way these supports were selected as substrates for the membrane layers used in micro filtration (MF). The membrane layers were elaborated from TiO_2, using slip casting technique. The specimens were subsequently sintered at 1100 °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 0.37 µm and a layer thickness ≈ 22.7 µm. The water permeability measured is 760 l/ (h.m^2.bar).

***Keywords**:* Kaolin; Calcite; Supports; Membranes; Microfiltration; Extrusion.

I. Introduction

With the rapid industrialization over the past two decades, the demand for drinking water as a precious resource has increased tremendously in terms of quantity and quality [1]. The scarcity of such a precious resource in the world has led the water reclamation for the conservation and recovery of drinking water .Progress has been made with regards to the use of micro/ultra filtration (MF/UF) membranes as an advanced water treatment process for producing high quality drinking water with small footprint [attracted increasing attention for its successful [2.3]. Porous ceramic membranes have been known for years and used in many industrial processes due to their excellent properties, such as high separation efficiency, excellent thermal stability, high pressure resistance, chemical stability, long term durability and long life with bio inertia [4.5].

In general, ceramic membranes consist of thin ceramic layers laid on porous ceramic supports. A membrane support provides a mechanical strength to the top-layer membrane in order to withstand the stress induced by the difference of pressure applied over the entire membrane which must at the same time have a low resistance to the filtrated flow[1]. However, kaolin is still a preferred raw material for porous ceramics [6]. Various kaolinite clays have been employed to prepare porous mullite based ceramics [7, 8]. The marketed supports are generally manufactured from compounds such as alumina (Al_2O_3), cordierite ($2MgO.2Al_2O_3.5SiO_2$) and mullite (3Al2O3.2SiO2) [9-13] which have a relatively elevated cost [14]. In our membrane research, novel hybrid metallic–ceramic membranes, with a comparable graded multilayer structure as conventional ceramic membranes and supported by a porous metallic material are developed. The functional layers of these membranes are made of ZrO_2 or TiO_2 and have pore sizes which are similar to those of current all-ceramic mesoporous and microporous membranes for e.g. UF, NF [15]. are often used to remove particles, micro-organisms, and colloidal materials from suspensions [8]. Asymmetric membranes

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usually consist of a thin top-layer responsible for separating components, and a porous ceramic support with a single or multiple intermediate layers imparting the required mechanical strength to the composite membrane [6]. Among the identified source of pollution of aquatic environment, the industrial wastewaters which contain heavy metals and also different micro pollutants with low molecular weight cause serious damages [16]. Some anions such as nitrate, phosphate, sulfide, fluoride are others source of pollution, for example phosphate anions are responsible of the eutrophisation of the river and their rejection is strictly controlled to limit their impact in the environment [17]. Fluoride ions are also known to give damage for human health in the North Africa countries where their concentration in the water source is too important. our attention was focused.

In this study the membranes supports are made up from kaolin sintered at 600 °C for 30 min and the addition of variable amounts of CaCO3 15 wt% (K15C) because it helps in forming pores with suitable dimensions. After that, samples are treated with heat 1200 °C for two hours using bottoming method to get supports with a porosity ration (Vp= 52.3%) and a gap diameter average about 5.8 µm having a unilateral interstitial distribution pattern. These supports were selected as substrates for the membrane layers used in MF. The membrane layers were elaborated from titanium oxide, adopting slip casting technique. The specimens were subsequently sintered at 1100 °C. The microstructure and porosity as well as the permeability have been also studied. It has been found that the average pore size (APS) is about 0.37 µm and a layer thickness was around 22.7 µm. The membrane permeability was 760 l/h.m^2.bar.

2. Experimental procedures

2.1. Analysis of the raw materials

Two mineral powders, kaolin and Calcium carbonates (CC),were selected in this study, for the elaboration of ceramics membrane supports. Kaolin and CC were derived from Guelma and Constantine regions (Algeria), respectively.

The chemical composition of the kaolin DD3 used in present work given in weight percentage (wt%)of oxides is: 45.90 wt% SiO_2; 37.49 wt% Al_2O_3; 0.40 wt% Fe_2O_3; 1.52 wt% Mn; 0.41 wt% CaO;0.01 wt% MgO; 0.44 wt% TiO_2;0.41wt%K_2O. The majority of the used powder (81 wt%) consists of SiO_2 and Al_2O_3, it shows that kaolin The halloysite structure The chemical composition of $CaCO_3$ given in wt% of oxides. The purity of CaO obtained from calcined calcite was about 99.7%, using X-Ray Fluorescence (XRF) analysis. It contains, mainly, 0.15 wt% Fe_2O_3, 0.05 wt% Al_2O_3 and 0.03 wt% Na_2O as impurities. As reported by Min et al. [18], this raw material may be classified as a high-purity calcium oxide (CaO $\geq$ 99.0%). Moreover, it has been confirmed by XRD spectrum of calcium carbonate powder that only $CaCO_3$ phase was detected. This spectrum shows also that the calcium carbonates powder is well crystallized (Fig. 1b).

The Particle Size Distribution (PSD) of used raw materials for the support elaboration is illustrated in Fig. 2.

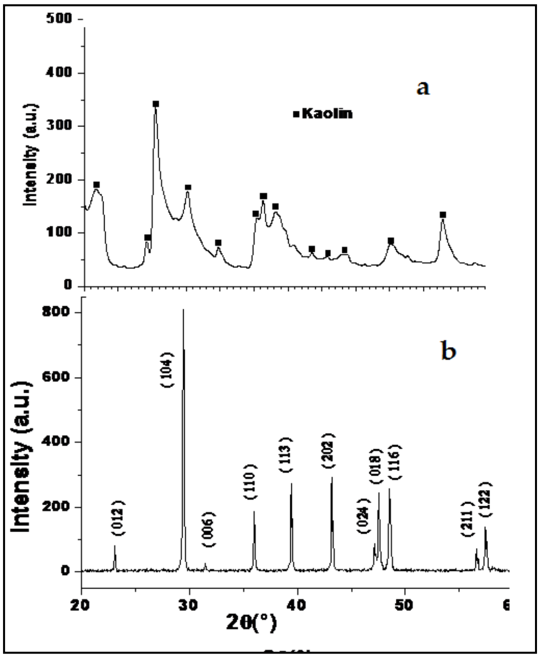

Fig. 1. XRD spectra of raw materials. (a) Kaolin, (b) calcite.

This method gave average particle size in the order of 0.8 µm [18]. The kaolin powder, obtained by calcinations of the finally ground mineral coal at 600 °C, showed average particle size less than 1.21 µm [18].. The average particle size of calcium carbonate were gave average particle size in the order of 4.8µm. SEM images of the powders are reported as shown in Fig. 3. Kaolin powder presents particles with the form of aggregates and have a mixed lamellar or platelet shapes.

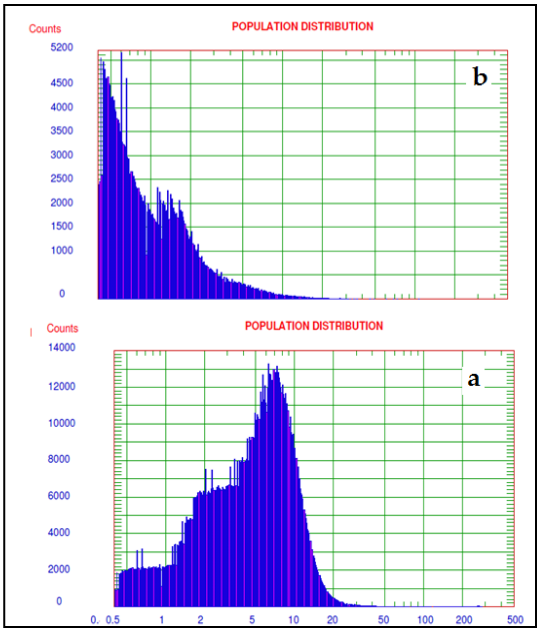

Fig. 2. Particle size distribution for different raw materials. (a) Kaolin, (b) calcite

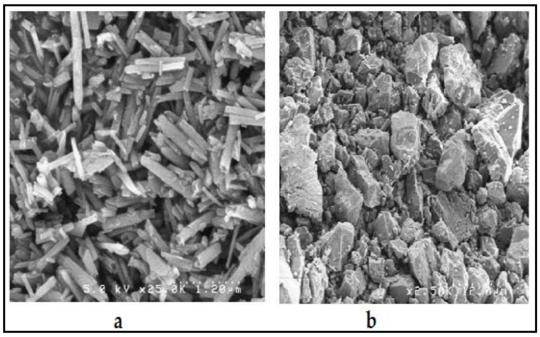

Fig. 3. SEM micrograph of the powder. (a) Kaolin, (b) calcite.

2.2. Supports elaboration

The tubular configuration support was obtained by an extrusion method of a mixture of kaolin (85 wt%), $CaCO_3$ (15 wt%) and organic additives in correct proportions to adjust the paste rheological properties. The used organic additions were 3 wt% of methocel as a plasticizer and 3 wt% of amijel as a binder.

2.3. Characterization techniques

Many techniques have been used to investigate the support prepared from kaolin and CaCO3and its TiO_2 membrane. The structure was determined by X-ray diffraction (XRD) using a Philips X' Pert X-ray diffractometer operating with CuKα radiation (λ=1.54056 Å). The total porosity, average pore size or diameter and pore size distribution have been determined by mercury intrusion porosimetry (Micromeritics, Model Autopore 9220) for samples sintered at different temperatures. The morphology, surface quality and thickness of intermediate and top-layer membranes were examined with scanning electron microscopy (SEM). The particle size distributions of kaolin and calcite powders were measured in a water suspension after ultrasonic dispersion using a laser granulometer (Coulter LS230, Malven Instruments) (France).

The MF layer deposition was carried out using a High Speed Centrifuge (JANETZKI, Model T23) (Germany).

The mechanical strength of sintered specimens was measured by a compression test with a constant displacement rate of about 0.2 mm/min, using a universal mechanical testing machine (Zwick 10 K) (Germany). Nitrogen adsorption measurements were performed at 78 K to determine BET surface area using ASAP 2020 volumetric adsorption analyzer (from Micromeritcs). Prior the adsorption measurements, each sample was degassed at 300 °C for 2 h. The tangentialfiltration experiments were performed using a home-made lab plant at room temperature and the working pressure was obtained using air gas source.

2.4. Membranes elaboration

Median the particle size distribution of TiO_2 0.69 µm was determined by DLBS, which gave an average particle size in the order of (Fig. 4). He slurry for centrifugal casting was prepared by adding TiO_2 powder (12 wt%) into distilled water (DW) (60 wt%) and stirring. Then, the polyvinyl alcohol (PVA) (Rhodoviol 25/140 (Prolabo)) with 28wt%, used as a binder was added to the TiO_2 solution and stirred at a room temperature. To minimize and prevent the deposition by slip casting, the support was first dipped in pure water for 30 min. After wards, the prepared suspension was poured into the support. Then, After drying, the tubes were sintered at 1100 °C for 1 h.

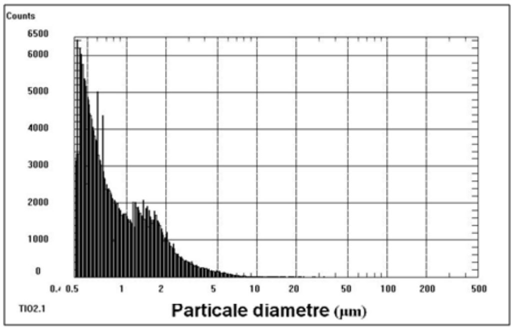

Fig. 4: Particle size distribution of TiO_2 powder.

3. Results and discussion

Porous ceramics supports are generally needed for membrane manufacturing. For the development of high-quality supports, the following properties are of a major importance: PSD, total porosity ratio, surface quality with the absence of large defects or large pores, mechanical properties and chemical stability [19]. The total porosity, APS and PSD have been determined by mercury intrusion porosimetry.

Phase identification is of great importance before any support and membranes fabrication, because the presence of certain phases may limit their application for water filtration only, rather than acid filtrations or gas separations. Fig. 5 shows the XRD spectrum of K15C mixture sintered at 1200 °C for 1 h. The main observed phases are mullite ($3Al_2O_3•2SiO_2$) and anorthite ($CaO•Al_2O_3•2SiO_2$). For example, mullite is a useful refractory for high-temperature ceramics applications, because of its low thermal expansion and high creep resistance. In addition to this, it has a high load bearing capacity, abrasion and corrosion resistance. The formed phases mentioned above are chemically stable in acids. The objective of this section is to prepare porous mullite–anorthite based ceramics but relatively well sintered. Really, Fig. 6b confirm the relatively good sinter-ability of samples sintered at 1200 °C These identified phases are of great importance because of their promising physical and mechanical properties. The presence of these 2 phases may also extend their use, even under severe atmosphere conditions. After XRD and pore characterization, we made mechanical strength measurements which are also of great importance since porous supports should resist the applied pressure during the solution filtration. In addition, a flexural strength of about 78 MPa was obtained for samples sintered at 1200 °C for 1 h.

It should also be remarked that these mechanical properties are generally acceptable especially for MF and/or UF membranes applications. Finally, the best conditions to prepare the support are established at a sintering temperature of about 1200 °C.

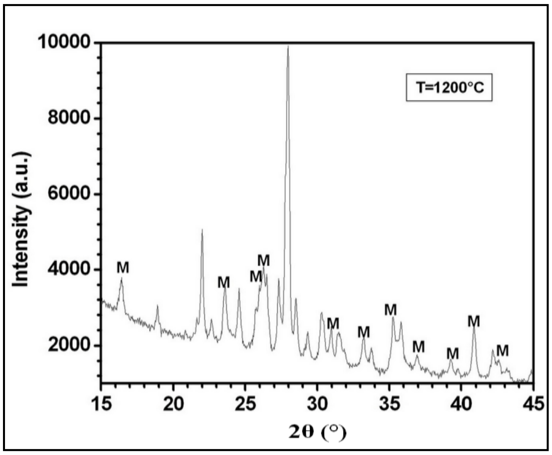

Fig. 5. XRD spectrum of support sample sintered at 1200 °C for 1 h

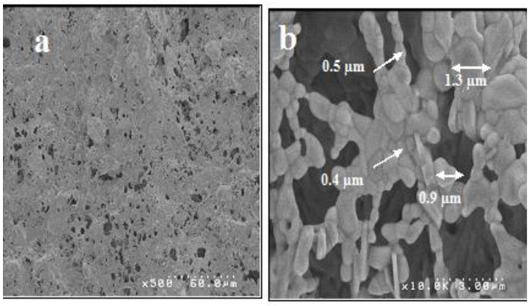

Fig. 6: SEM micrographs of support surface (K15C) samples, using process 2, sintered at 1200 °C (a and b) .

The SEM images reported in Fig. 7 show the surface and the cross-section of a membrane consisting of a TiO_2 MF layer coated by a centrifugal casting method on a macro-porous support. The membrane microstructure shows a good homogeneity which is an important property for potential MF applications. The membrane surface morphology confirms the highly porous structure with a good PSD, which are judged important conditions for the fabrication of good quality membrane layers [20]. The membrane surface looks smooth and does not show any defects such as scale forming or cracks. The thickness of the MF layer may be controlled by the percentage of the mineral powder added into the suspension and the coating time. Under the used coating conditions, a TiO_2 layer has been produced within an average thickness of about 22.7 µm. It can be observed that a top layer deposited from a TiO_2 using the centrifugal casting method, has a uniform thickness and presents a good adhesion with the support.

The PSD of the porous membrane sintered at 1100 °C for 1h are illustrated in Fig.8. The major conclusions that can be drawn from these results are that the APS of TiO_2 layer is around 0.37 µm.

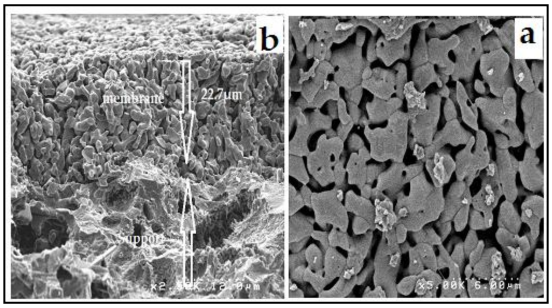

Fig. 7. SEM micrographs of multilayer system. (a) Cross-section; support and membrane, (b) surface of top layer membrane

Finally, the prepared MF membrane sintered at 1100 °C was characterized by its DW permeability, using a home-made pilot plant at a room temperature. The working pressure was obtained using an air gas source.Fig. 8shows that the DW permeability through the membrane measured as a function of time depends on the applied pressure. A stable flux is obtained after a few minutes. Theflux increases with the applied pressure and the average permeability is about 760 l/h m2bar (Fig.9).

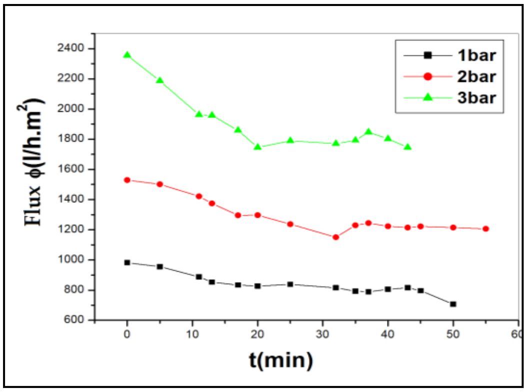

Fig. 8. Pore size distribution of support and top layer membrane.

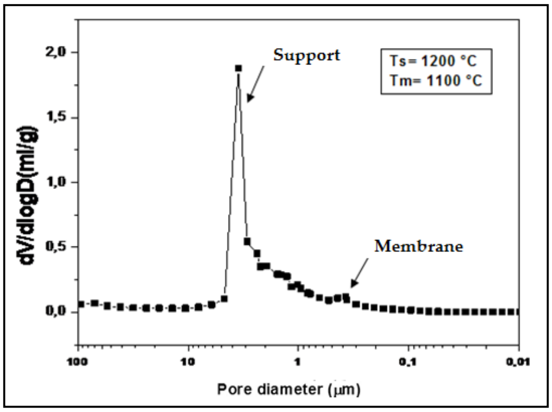

Fig. 9: Water flux versus time, at 3 working pressures, using DW.

4. Conclusions

In this work, we expose ceramic supports (K15C) with a low cost and good characteristic by local raw materials, for the general used water filtration process. All these, without chemical additions which may be unsanitary for humans life. Pure water concerns as pharmaceutical, alimentary and chemical industries because it helps the improvement of products, insure consumers and decreases production's cost and keeps the equipment safety. It was found that the pore structures may be controlled by a sintering temperature, and supports sintered at different temperatures interesting characteristics; of porosities ratio around 52.3%. Moreover, those pores sizes distributions are almost homogeneous (mono-modal type). New ceramic microfiltration membranes made of TiO_2 have been prepared and characterized. The obtained membrane was defect free and has the following characteristic thickness of about 22.7 µm, mean pore diameter of 0.37 µm. Almost the same stabilized permeate flux was obtained (about760 l/h m^2).These experimental results show TiO_2 is an appropriate material for the development of microfiltration membranes which could be applied to the industrial wastewater treatment

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