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# Preparation and characterization of membrane supports for microfiltration and ultrafiltration using kaolin (DD2) and $CaCO_3$

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## ABSTRACT

The ceramic products are extremely interesting in the field of the membrane supports because of their mechanical resistance, chemical inertia, long working life, and thermal stability. This work is mainly focussed on ceramic supports rather than its deposited membranes because it constitutes about 99% of the filter mass. Therefore, replacing the more expensive starting materials ($Al_2O_3$) by other low cost raw materials (kaolin and calcite) for supports fabrication is significantly important. Consequently, the supports for microfiltration (MF), ultrafiltration, and nanofiltration were prepared with local kaolin (DD2) and calcite mixtures. The choice of these raw materials is based on their natural abundance (low price). These supports were made by extrusion technique order to obtain tubular supports which were afterward sintered at 1,150˚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 50.5%, and a three-point flexural strength ≈28 MPa. Moreover, the pore size distribution was almost mono-modal type. The surface and the cross-section morphologies observed through a scanning electron microscope were also homogeneous and do not present any possible macro defects (cracks, etc.) These supports were selected to be substrates for the membrane layers used in MF.

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

## 1. Introduction

In recent years, a great deal of research has been devoted to development of new types of inorganic membranes [1]. A membrane support provides mechanical strength to a membrane 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 [2]. Membrane processes are more and more used in industrial processes such as water treatment and surface industries with a wide variety of modules

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designs [3]. The development of membrane processes to treat wastewater is generally limited because the price of the membranes is too high, which is particularly true for the inorganic membranes [4]. A significant effort was then provided these last years in membrane technology field in order to find out new porous ceramics materials at low price [5] because the marketed supports are generally manufactured from compounds such as alumina ($Al_2O_3$), cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), and mullite ($3Al_2O_3{\cdot}2SiO_2$) [6–10].

In order to decrease this cost and to evaluate our natural resources, many works have already been carried out [11–25]. Since 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 work is then mainly focussed on the ceramic support elaboration 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. So, what do low cost raw materials mean? The alumina price is at least about 100 times greater than that of kaolin. Another important advantage is the substantial gain in energy obtained by decreasing the sintering temperature from about 1,600˚C to about 1,250˚C [17], when alumina supports were replaced by the proposed supports. Besides this, about 50% of the prepared supports are pores, which may also be considered as a gain in mass. The relatively lower theoretical density of the prepared supports (2.8 g/cm$^3$), when compared to that of alumina (3.98 g/cm$^3$), is also another interesting advantage. More recently, it has been demonstrated that besides these advantages, the fabricated membrane supports have also comparable mechanical strength than that of alumina [17]. Indeed, a flexural strength of 87 ± 2 MPa was obtained for 100 wt.% $Al_2O_3$ samples sintered at 1,620˚C for 2 h [26], whilst nearly the same flexural strength value (87 ± 6 MPa) was also measured for compacts sintered only at 1,250˚C for 1 h, using the proposed process. Therefore, this study is mainly devoted to the development of ceramic supports [1] using Algerian natural materials (kaolin (DD2) and calcium carbonate ($CaCO_3$)) [27] less expensive and which are abundantly available in our country (Algeria). It should also be mentioned here that using ceramics (oxides) instead metallic products [28,29] is well justified, particularly for water filtration or purification.

## 2. Characterization techniques

The total porosity and pore size distribution were measured by mercury porosimetry (Micromeritics, Model Autopore 9500). This technique is based on the penetration of mercury into a membrane's pore under pressure. The intrusion volume is recorded as a function of the applied pressure and then the pore size is determined.

The mechanical strength of sintered specimens was measured by the three-point bending method (universal LLOYD Instruments, LRX apparatus) using a span of 30 mm and a cross-head speed of 10 mm min$^{-1}$. All experiments were carried out on a series of at least five bars to report an average strength for each series, following the International Standard (IS) specifications.

Phase compositions of prepared samples were identified by X-ray diffraction (XRD) (Bruker, D8 Advance) (Karlsruhe, Germany) with a CuK$\alpha$ radiation ($\lambda = 0.154$ nm) and an Ni filter, working voltage 40 kV, and working current 30 mA.

The microstructure of sample surfaces was observed using a SEM (Hitachi, JSM-6301 F) (Tokyo, Japan) working at 7 kV as an accelerating voltage. Before SEM observation, all samples were gold coated.

Structural evolutions of kaolin and calcite powders were evaluated by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC), using a SETARAM TG-DTA 92 apparatus.

These two analyses have been carried out under air. The heating rate of the compacts from room temperature to 1,200˚C was 10˚C/min, while the cooling of compacts was carried out in the furnace.

## 3. Characterization of the natural materials powders

The starting raw materials were domestic kaolin (DD2) and calcite ($CaCO_3$) derived from Guelma and Constantine regions (Algeria), respectively. The particle size distribution of these materials was determined by the dynamic laser beam scattering technique (Fig. 1). This method gave an average particle size in the order of 2.2 and 4.8 μm, respectively [27]. The kaolin and calcite powders were characterized by different methods: SEM, X-ray fluorescence, XRD, DSC, and TGA.

The SEM shows that the natural kaolin (DD2) powder in stick form had almost the same mean particle size and a homogeneous distribution (Fig. 2(a)). On the other hand, the calcite does not have a particular form, but its distribution remains homogeneous [30] (Fig. 2(b)).

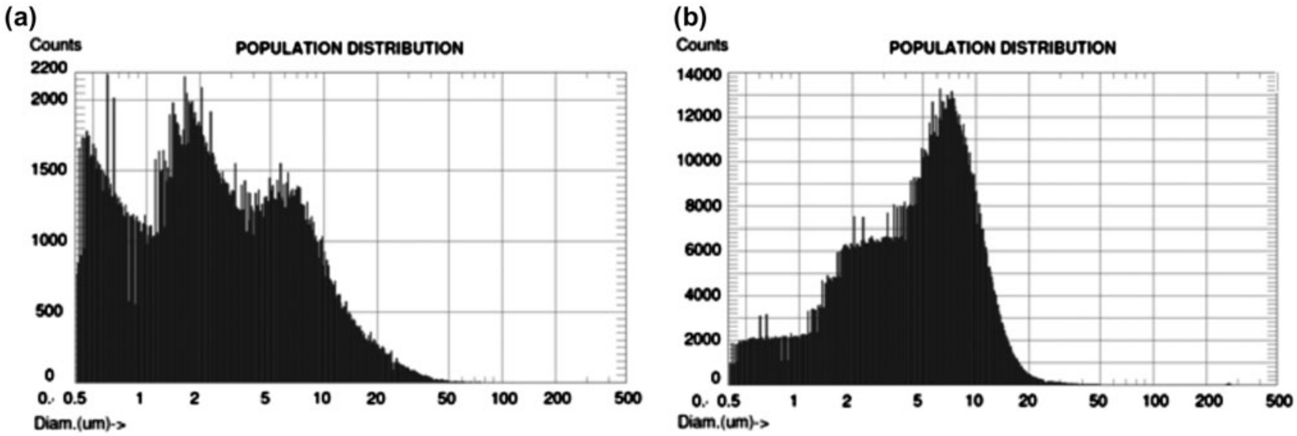

Fig. 1. Particle size distribution of powders used in this work. (a) kaolin powder (DD2) and (b) calcium carbonate powder ($CaCO_3$).

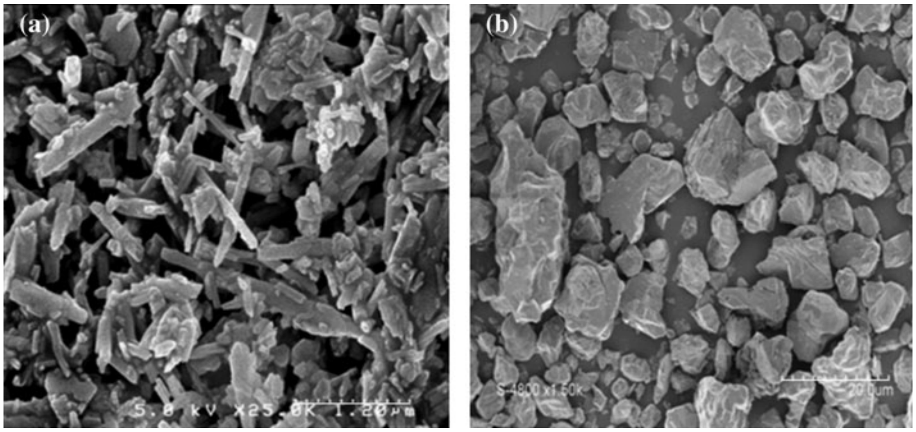

Fig. 2. (a) SEM images of natural kaolin (DD2) and (b) calcium carbonate.

Table 1
Chemical composition of kaolin (wt.%), using fluorescence XRD analysis [15]

| Oxides | Weight (%) |
|---|---|
| $Al_2O_3$ | 33.43 |
| $SiO_2$ | 45.00 |
| $Na_2O$ | 1.12 |
| $K_2O$ | 0.95 |
| CaO | 0.32 |
| $Fe_2O_3$ | 0.23 |
| $TiO_2$ | 0.22 |
| I.L | 18.73 |

### 3.1. Chemical analysis

The chemical composition of kaolin (DD2) given in weight percentages of oxides is given in Table 1. The obtained results reveal that this kaolin (DD2) is mainly composed of silica ($SiO_2$) and alumina ($Al_2O_3$) [31]. The quantitative analysis of these calcium carbonates showed that the purity of this raw material is about 99.6% [32].

### 3.2. XRD analysis

The XRD pattern of the kaolin (Fig. 3) shows that kaolinite (K), illite (I), calcite (C), and quartz (Q) are the main minerals present in the clay.

Fig. 4 shows XRD spectrum of calcium carbonate powder, where only $CaCO_3$ is present. This spectrum shows also that the calcium carbonates powder is well crystallized [31].

### 3.3. Thermal analysis

The DSC and TGA were realized by a thermobalance instrument-type (2960 SDT V3.0F) which gives

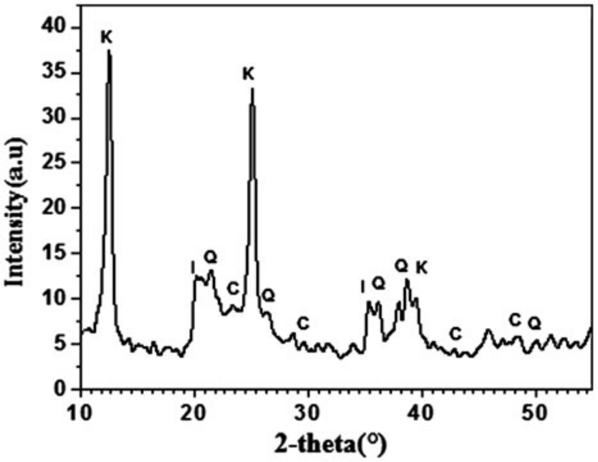

Fig. 3. XRD spectrum of natural kaolin (DD2), C: carbonate; I: illite; K: kaolinite; Q: quartz.

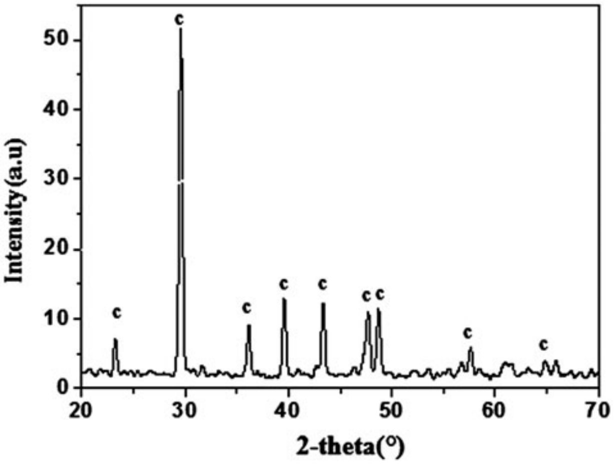

Fig. 4. XRD spectrum of a calcium carbonate powder.

simultaneous curves of DSC and TGA. The DSC curve of natural kaolin and calcium carbonate mixtures (Fig. 5) exhibits characteristic endothermic peaks at 51.18, 488.98 and 727.15°C. 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 [2]. However, the third peak is due to the thermal decomposition of calcite to form calcium oxide (CaO) and $CO_2$ [31] whereas the later peak may be attributed to mullite nucleation [2]. These observations are also confirmed by TGA analysis (Fig. 5) which permits the following remarks. A total weight loss of about 10% of kaolin (peaks 51.18 and 488.98°C) and 11.5% of calcite (peaked at 727.15°C).

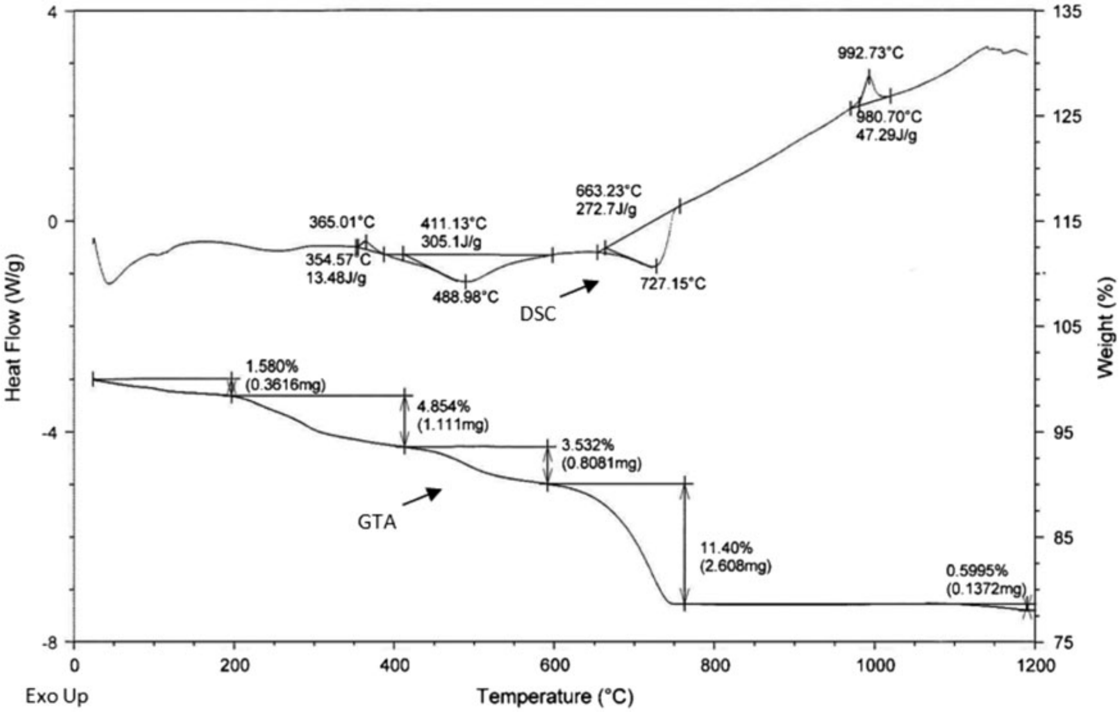

Fig. 5. DTA and TGA curves of natural kaolin and calcium carbonate mixtures.

## 4. Supports elaboration

### 4.1. Preparation of the paste

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 and 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 for at least 12 h [31].

### 4.2. Paste extrusion

The extrusion technique takes place to make some tubular samples.

### 4.3. Drying and sintering

For a good drying of these tubular samples, they should be placed at room temperature on rotating aluminum roll [31]. These dried tubular samples sintered at 1,150˚C (Fig. 6) following the program shown in Fig. 7. In order to eliminate organic materials added and avoid the micro-cracks in the samples, 2˚C/min was chosen as a heating rate.

Fig. 6. Image of tubular membranes supports prepared from two different kaolin types, 1: DD2 kaolin type, 2: another kaolin type.

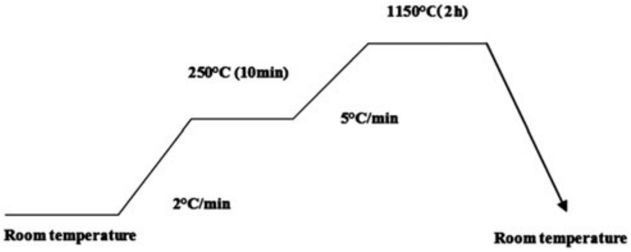

Fig. 7. Scheme of the thermal treatment.

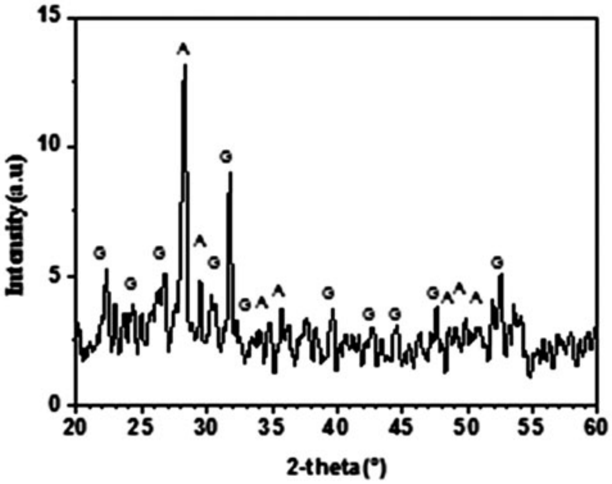

Fig. 8. XRD spectra of samples sintered at 1,150˚C for 2 h, A: Anorthite, G: Gehlenite.

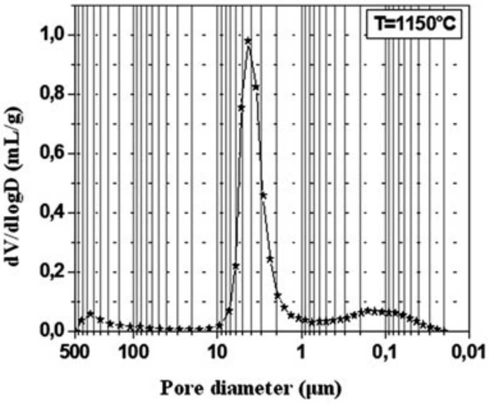

Fig. 9. Pore size distribution in samples, sintered at 1,150˚C for 2 h.

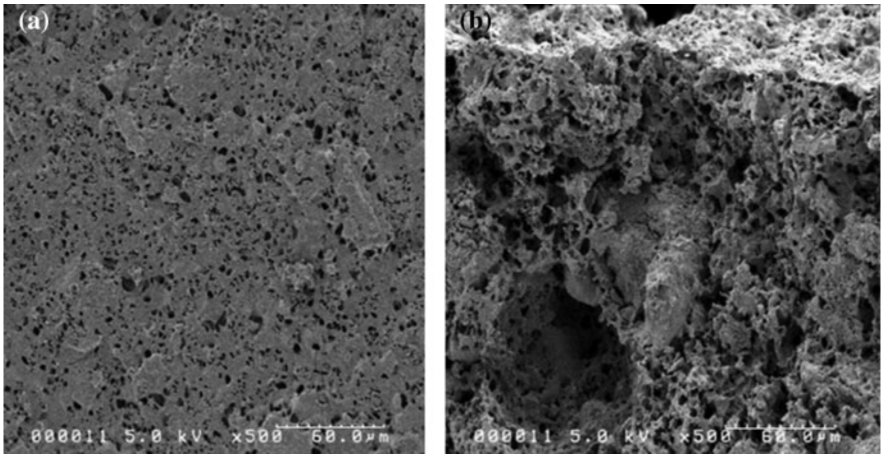

Fig. 10. (a) SEM images of surface and (b) cross-section of supports, sintered at 1,150˚C for 2 h.

## 5. Supports characterization

### 5.1. Phase identification

XRD was used to identify the formed phases in samples, heated at 1,150˚C. The main phase detected in samples fired at different temperatures was anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), which is a predominant phase with a small amount of Gehlenite ($Ca_2Al_2SiO_7$) phase where the diffraction peaks decrease with increasing the sintering temperature, as shown in Fig. 8. In addition to this, they have a high load-bearing capacity, an abrasion, and a corrosion resistance. The formed phases mentioned above are chemically more stable, in acids, than alumina-based ceramics [17,33,34].

### 5.2. Pore characterization

The support fired at 1,150˚C and characterized by mercury porosimetry showed pore diameters centered near 4 μm (Fig. 9) and 50.5% of porosity. The average pore size (APS) is also confirmed by typical micrographs illustrated in Fig. 10.

### 5.3. Flexural strength

The best three-point flexural strength value was about 28 MPa. This strength may be controlled by many factors. So, a general correlation seems to exist between densification, microstructural changes (APS, pore distribution and total porosity), and flexural strength in sintered compact as follows:

Densification and grain size are the dominant factors controlling strength; since most of the total pores were intergranular, the substantial increase in strengths of samples corresponded to a parallel increase in density which means a decrease in porosity ratios.

Pore size and distribution influenced by sintering temperature is a factor controlling strength. Therefore, pores coalescence becomes a predominant factor.

## 6. Conclusions

In this study, supports for microfiltration (MF) and ultrafiltration (UF) have been prepared from local raw materials (kaolin (DD2) and calcium carbonate mixtures) by the use of extrusion method where tubular configuration was obtained. It has been found that supports sintered at 1,150˚C had interesting characteristics; an APS about of 4 μm, a porosity ratio above 50.5%, flexural strength ≈28 MPa, and a pore size distribution is mono-modal type. These supports can be used for MF, UF, and nanofiltration.

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