# DEVELOPMENT OF CERAMIC MICROFILTRATION SUPPORT FROM MOROCCAN SAHARA CLAY

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**Abstract:** The new ceramic microfiltration support prepared from Moroccan clay (Laayoune region, South of Morocco) is reported in this paper. To optimize the support elaboration conditions, the powder clay is mixed with organic additives and water. The formed paste is shaped by using an extrusion processing and then sintered at 950 °C. The ceramic supports present a porosity and mechanical strength of 44 % and 12MPa respectively. The layer filtration deposition has been carried out by the slip casting method, in order to test its operation in textile effluents treatment.

**Keywords:** membrane, clay, effluent, Sahara

## 1. INTRODUCTION

Due to their widely application in industrial field, the membrane processes had a great interest in recent years. Filtration whatever, microfiltration or ultrafiltration, is generally referred to by its everlasting service also its disposal capacity of suspended solids and microorganisms [1-3].

The ceramic membranes present several advantages than organic counterpart such as better mechanical strength and thermal and chemical resistances and under aggressive chemicals conditions [4, 5].

Unfortunately, the cost of ceramic membranes is too expensive to assure a large application. To overcome this drawback, the new ceramic microfiltration and ultrafiltration membranes, that were produced based on abundant natural materials such as clay, showed significant advantages from an economic point of view [6].

The aim of this work is to elaborate a new membrane support using natural clay from south of Morocco (Laayoune, Sahara). The steps of elaboration of flat ceramic membrane will be described.

The structural characteristics and chemical stability of the membrane was investigated for various sintering temperatures.

Prosity and structural density were also evaluated to optimize the sintering temperature to get the high porous low –cost ceramic membrane. The support was test by filtration of textile effluents.

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## 2. MATERIALS AND METHODS

After removing the stones and heavy particles from the clay, the powder was then dispersed in 2 L of deionised water for the sedimentation process. The top part was sieved through a 160 µm sieve to remove the larger non-clay fractions and to obtain the fine clay fraction.

The sample were dried at 100 °C and stored in a desiccators. The particle sizing Accusizer model 770 (particle sizing system Santa Barbara) was used to determine the particle size distribution.

The composition of the natural clay was obtained by X-Ray Fluorescence « Panallytical Axios ». The XRD analysis of the treated clay were carried with a X'Pert Pro MPD Panalytical (Cu K ray, Ni Filter).

The sample was heated from room temperature to 950 °C at a rate of 5 °C/min under static atmospheric conditions; $\alpha$-$Al_2O_3$ was used as reference. The prosity of the support was determined by mercury porosimetry (Micrometrics Autopore II 9215).

## 3. RESULTS AND DISCUSSION

### 3.1. Chemical analysis

The chemical composition of these materials is shown in Table 1. The chemicals analysis reveals that the clay powder is formed of a great amount of silica with alumina and iron and magnesium oxide in lower proportion, however the potassium represent as minority element.

Table 1. Chemical analysis of the clay.

| Oxydes | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $K_2O$ | CaO | Lo.I |
|--------|---------|-----------|-----------|------|--------|------|------|
| Weight (%) | 47.17 | 10.88 | 4.98 | 2.80 | 1.39 | 14.62 | 19.4 |

The particle size distribution is represented in Table 2. The particle diameter has ranges from 1 to 36 µm and more than 70 % of the particles present a diameter less than 5 µm.

Table 2. Particle size distribution of the clay.

| Diameter (µm) | Particle size distribution (%) |
|---------------|-------------------------------|
| [10,36] | 10 |
| [5,10] | 20 |
| <5 | 70 |

### 3.2. XRD analysis

The Figure 1 shows the diffraction patterns of the raw and calcined material at different temperatures. The diffraction of the raw clay revealed a strong presence of silica presented by quartz, and mainly gypsum. On the other hand, kaolinite is the phyllitic phase presented in the sample [7, 8].

The disappearance of all the kaolinite reflections resulted by a heat treatment at 600 °C. This phenomena has already been observed by several authors [9-12], it is the result of dehydroxylation of kaolinite in metakaolin which has a poorly organized structure.

This also results of the absence of diffraction lines, indicating that the reaction is not accompanied by any neo-crystallization.

The heat treatment at 1000 °C led to the appearance of new lines, correlated with the formation of hematite and Mullite due of the transformation of metakaolinite.
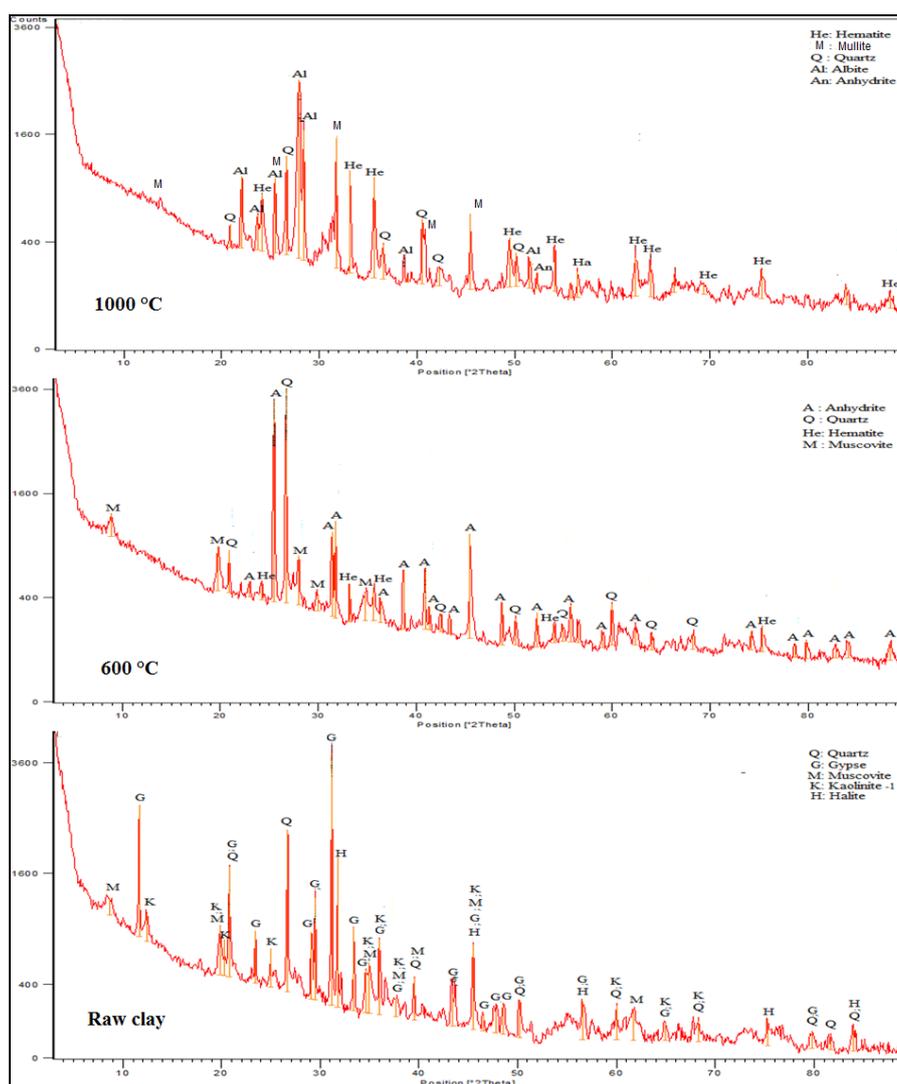
Fig. 1. Diffractograms of the clay at different temperatures.

### 3.3. Elaboration of supports based on Moroccan Sahara clay

The purpose of this study is to realize new membrane's supports, based on natural clay from, Laayoune region (South of Morocco). We have chosen to develop the new support membrane with improved separation properties, high mechanical and thermal stability using inexpressive and naturally abundant materials is of utmost importance for sustainable development and environmental applications.

Before preparing the ceramic paste, the natural clay was crushed and sieved in woven wire sieves of 160 microns. This powder will be blended with organic additives, completely mixed dry to reach an uniform distribution of all components. This mixture in the presence of water enables us to achieve an agglomeration of grains of the desired paste properties (Figure 2).

Table 3. Percentage of each compound in relation to the total mass of powder.

| Product | Function | Quantity (% mass) |
|---|---|---|
| Clay | Ceramic Powder | 99.44 |
| Amidon | Binder | 0.55 |
| Glycerin | Plasticizer | 0.55 M |
| Water | Solvent | 24.86 M |
| Zusoplast 126/3 | Lubricant | 0.26M |
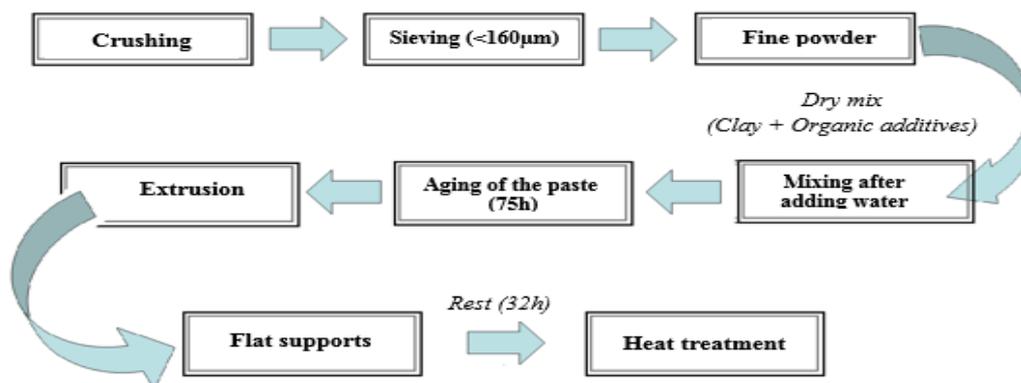
Fig. 2. Schematic of process of membrane support preparation.

After mixing the components composing the ceramic paste (Table 3), the obtained paste was stocked for at least 75 hours in a closed box under high humidity (aging time) to achieve greater consistency and to avoid the formation of air bubbles. The paste was then extruded and calendared into a thin film which was segmented to form a flat disk supports with a diameter of 3.6 cm. The extruded pieces were dried at ambient temperature for 24 hours and placed in an oven at 50 °C for 24 hours.

To optimize the temperature of sintering to obtain a good porosity and acceptable mechanical strength allow us to work at high pressure, we program a firing in a programmable furnace at different temperature (Figure 3). Consequently, the best properties of the final support are achieved by adjusting the conditions for the sintering.

The heat treatment allowed the definitive consolidation of the moulded discs after removing the organic additions. This treatment is a very important step in the elaboration process, is accompanied with the transformation of initial minerals. For this, should be perfectly suited to the product (composition, geometry).
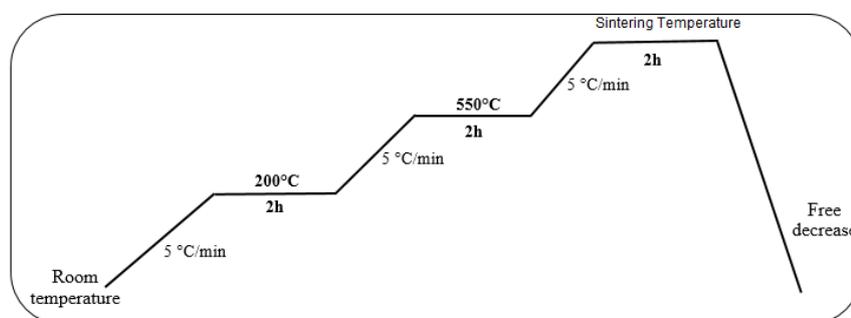


Fig. 3. Scheme of the thermal treatment program used.

The Figure 4 shows the porosity versus the sintering temperature. The porosity of the supports was studied at temperature range between 900 – 1100 °C. The highest resulting values of porosity were found when the sintering temperature is 950 °C, followed by a sharp decrease when temperature reaches 1100 °C.

The mechanical strength versus the sintering temperature is represented in Figure 5. When the firing temperature increases, the mechanical strength increase and reach 13 MPa at 1050 °C. Above this temperature the mechanical strength continue to increase.

Finally, the best conditions to prepare the support are established for a firing temperature of 950 °C. At this condition, the poosity is 44 % and the mechanical strenghth is 12 MPa (Figure 6).
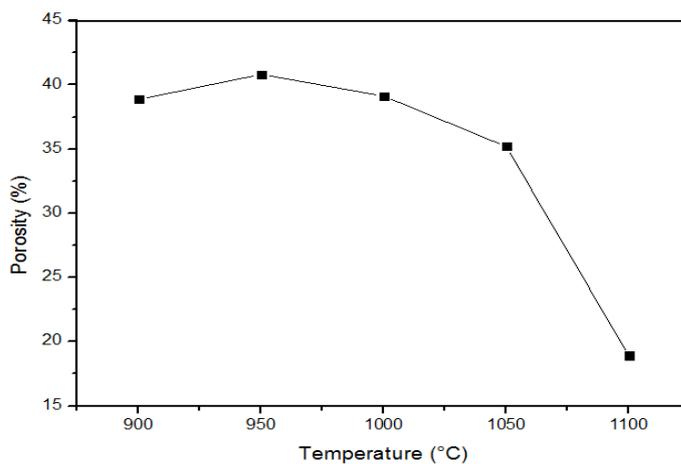
Fig. 4. Porosity versus sintering temperature.
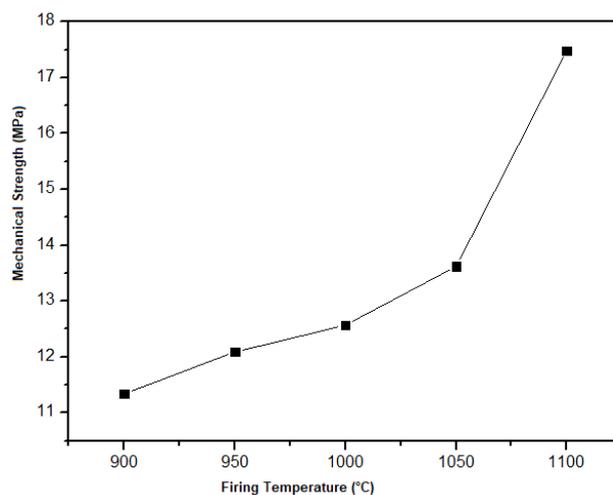


Fig. 5. Mechanical strength versus sintering temperature.
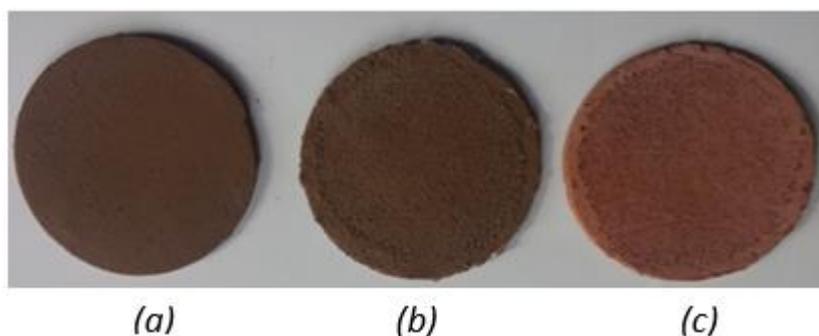


Fig. 6. Images of the flat support: (a) wet; (b) after drying at 40°C; (c) after sintering at 950°C.

Corrosion resistance tests were performed on the membrane supports, sintered at 950°C. Samples were immersed for 8 days in baths of hydrochloric acid solution (pH = 1.01) and NaOH (pH = 13.5) out at 25 °C. After the time limit of immersion, the samples were washed with water and dried.

The results of corrosion resistance show that support resisted better in basic medium than in an acidic medium. The weight loss not exceed 2.3 % for 8 days of immersion in a basic. However, in an acidic the weight loss increased to 5.5 %.

### 3.4 Tests of filtrations
*3.4.1 Determination of permeability*
The experimental set us of frontal filtration is represented in Figure 7, with membrane support sintered at T = 950°C, where they had a 2 mm thickness and a filtration area of 15.1 cm². Before the filtration tests, the membrane had been conditioned by immersion in pure distilled water for 24h. All the filtration experiment was conducted at ambient temperature.

The permeability of distilled water, and the textile effluent clarification were made on the membrane support.
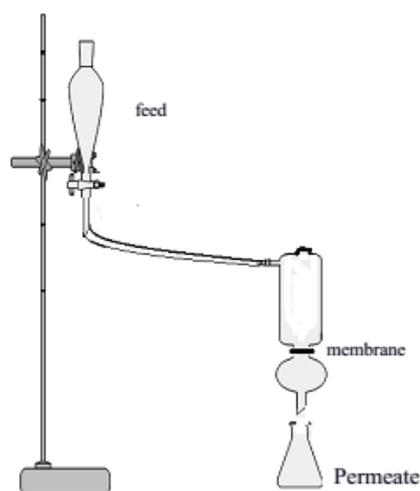


Fig. 7. Scheme of the pilot filtration.

The permeability of distilled water is a key parameter to characterize the membrane supports. For this, we determine the fluxes at different transmembrane pressure (0.12, 0.1, 0.08, 0.06 and 0.04 bar).

The water flux through of the membrane depends on the applied pressure. From the curves given the flux versus time represented in Figure 8, the stabilization of the water flux through the membranes takes minimum values at pressures inferior 0.1 bar. The highest resulting value of water flux was found 340 L/h m² at 0.12 bar in 20 min.
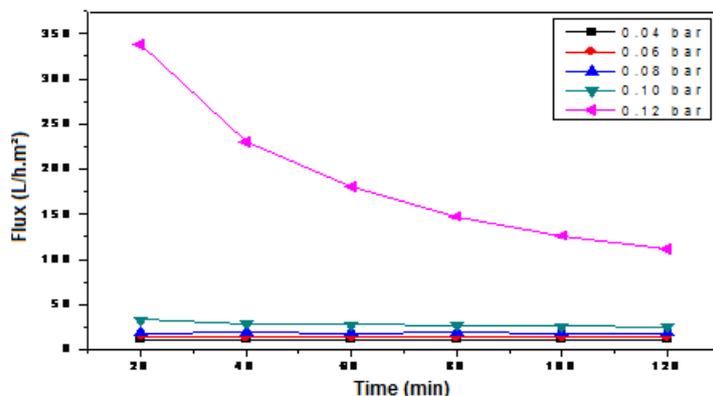


Fig. 8. Water flux versus time of filtration.

The average permeability was determined from the values of flux measured after stabilization of pressure at 0.12 bar. The course of the permeability (Figure 9) shows a maximum value of 281 L/h m² bar, followed by a decrease as a function of time.
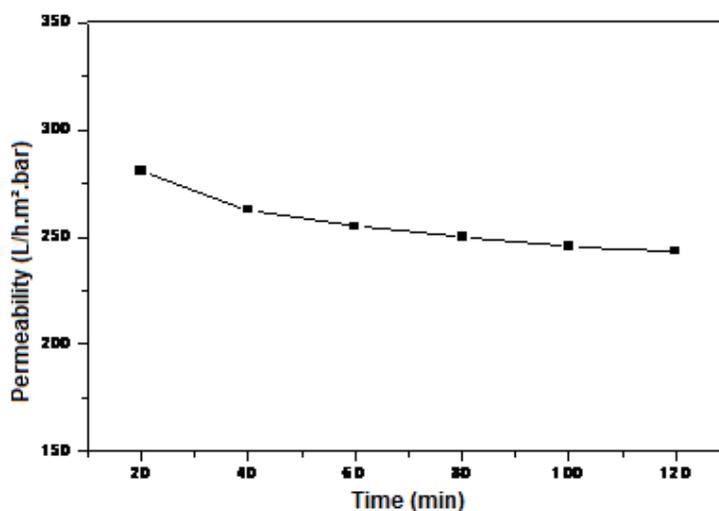
Fig. 9. Water permeability versus time of filtration.

*3.4.2 Textile effluents filtration tests*

The filtration test performance of textile effluents on membranes based on natural clay Moroccan Sahara, were qualified by measuring the turbidity, the conductivity and the pH in these effluents before and after filtration. The results obtained are summarized in the following Table 4.

The filtration on the supports allows a clarification of the studied effluents. The conductivity reduces from 1553 to 1120 µS/cm and the turbidity reduces dramatically.

Table 4. Characteristics of textile wastewaters and permeate of membrane support.

| pH | | Conductivity (µS/cm) | | Turbidity (NTU) | |
|---|---|---|---|---|---|
| Rejection | Permeate | Rejection | Permeate | Rejection | Permeate |
| 7.27 | 8.33 | 1553 | 1120 | 181 | 5.30 |

**3. 5. Development of a flat microfiltration membrane, based on Saharan's clay**

The aim of this part is the development of a microfiltration membrane utilizing the previously prepared supports. The membrane is produced by the slip casting technique where the driving force is a capillary suction. The layer thickness depends on the properties of the used material, such as porosity, capillary pressure, the volume fraction of the solid in the slip [13-15].

The slip intermediate layer was prepared using 10 % weight of the natural clay powder (fraction smaller than 40 microns), a 30 % PVA weight (12 % of aqueous solution weight ) and 60 % of DOLAPIX EC 64 weight, as dispersing agent (aqueous solution of 0.2 % by weight). The dispersion of particles was assured by 30 min ultrasonic agitation.

To coat the ceramic substrate, is then applied to the casting process valve. After the film deposition on the substrate, it is dried at room temperature and then baked at 950 °C, to achieve the filter layer's consolidation. To finally obtained a microfiltration layer with average diameters of 0.45 µm.

The various production steps of flat microfiltration membrane are summarized in the Figure 10.

The slip (Figure 11) composition is considered to be optimal, when the coating allows the production of thick layers sufficient to assure a complete and homogeneous covering of the wall of the ceramic disks; and this, to improve the disposal of polluting species.
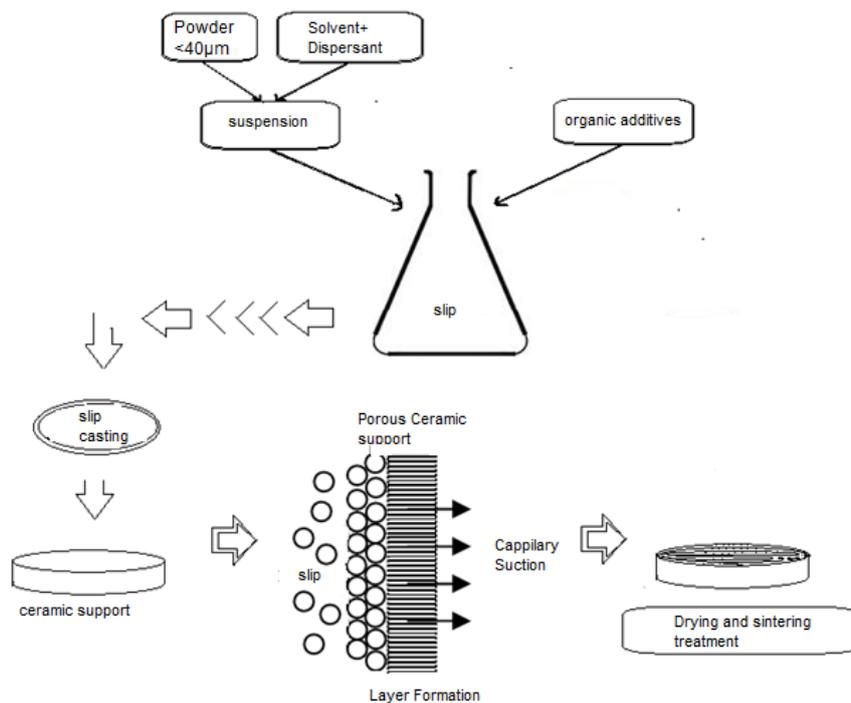
Fig. 10. Steps in the realization of a membrane by the technique of casting of slip.



Fig. 11. Deposit of the slip.

## 4. CONCLUSIONS

We successfully prepared membrane support from natural material with a low cost compared in the other commercial supports. The membrane support was prepared by extruding ceramic paste derived from natural Sahara Moroccan clay and sintered at 950 °C. The properties of the support are satisfying in terms of porosity and mechanical and structural

The performed filtration tests confirmed that the support prepared, based on Saharan clay, is suitable in the development of a microfiltration membrane. This membrane could find an economical application in the wastewater treatment.

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