Preparation of new ceramic supports macro-porous for microfiltration and ultrafiltration membranes based Moroccan clay

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Abstract: *The aim of this work is to develop Moroccan clay of the Meknes-Tafilalet region operated as basic raw material for the production of tubular supports mono-channel macro-porous for a microfiltration and ultrafiltration membranes. During the development, several parameters are controlled such as: the chemical and mineralogical composition of the initial powder, the particle size, final sintering temperature and final sintering time. Thus, we have defined a method of preparing of the clay pasta by varying the quantity of added organic matter, the volume of water, the time of mixing and kneading, and the aging time. The supports are obtained by extruding of a plastic paste prepared with a good optimize percentage of the organic matter. These have allowed us to improve the characteristics of the final product such as; the porosity and the mechanical resistance. The supports are dried in the open air, and then treated in an electric furnace at different final sintering temperatures according to a definite thermal program. The results show that the obtained ceramic supports after heat treatment at 1000 °C for three hours are characterized by a high porosity (P = 36 %), very good chemical resistance (1,11 % for the attack acid HNO_3/1N and 0,28 % for the attack basic NaOH/1N), best mechanical performance (R = 190 daN) and good permeability to water (F = 3329 $L/h.m^2$ for 1 bar).*
Keywords: *Clay, supports, sintering, porosity, mechanical and chemical resistance.*

I.   Introduction

The supports are prepared by shaping of a ceramic powder followed with consolidation by sintering. The Shaping is possible if the paste formed from the powder, has a rheological properties of those neighboring of the clay [1, 2]. The shaping method depends on the geometry of the final product and the tubular configuration is well suited for tangential filtration.

The different steps for preparing ceramic materials is the choice of the nature and particle size of the ceramic powder, the choice of organics additions, the optimal volume of water, the time of mixing and kneading, the aging time paste, shaping by extrusion, and the time of drying and sintering [3, 4]. The base material used for the preparation of these materials is Moroccan clay of the Meknes-Tafilalet region. Due to mechanical, thermal and chemical performance of the rock and its abundance in nature, it turned out that it may be the basic raw material for producing ceramic single-channel for micro and ultrafiltration membranes.

Several studies have been conducted in this field, with use of local clay and the organics additions very expensive [5, 6, 7, 8], and in order to produce porous supports and chemically efficient, thermally and mechanically with a lower cost of production, we have employed the wood powder as an organic addition in the elaboration of these supports. In this work, we report the fabrication of tubular macro-porous ceramic support from Moroccan clay by extrusion followed by sintering. The characteristics of the support were discussed as a function of sintering temperature.

II.   Materials And Methods

1. Elaboration of ceramic mono-channel supports:

The figure 1 shows the different steps for the preparation of the ceramic mono-channel supports with a clay rock for a microfiltration and ultrafiltration membranes.
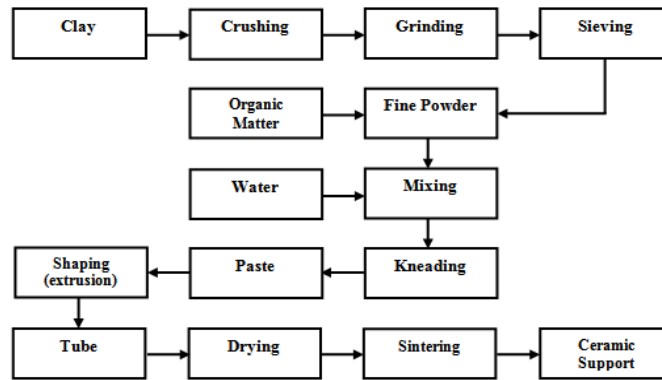
Figure 1: Steps for the preparation of the macro-porous ceramic supports

1.1. Preparation of the ceramic paste:

The optimal formulation of the ceramic precursor paste was carried out in an empirical way [1, 2]. The plastic paste was prepared from the clay powder mixed with the organic additives and water. Plasticizer and binder are required to prepare paste with rheological properties allowing the shaping by extrusion, drying and baking.

After study the different sizes, our choice was fixed on the use of the powders with the particle sizes less than 400 μm. The maximum use of the organic matter is 15 % by weight of the wood powder, seen its availability in large quantities and less costly (solid waste from the wood industry) in order to obtain the best final characteristics of the porosity and the mechanical resistance. Table 1 present the parameters of the formulation of the used clay.

Table 1: Parameters of the formulation of the used clay

Formulation	F15
Time of mixing (min)	15
Time of kneading (min)	20
Volume of water (ml/Kg)	330
Aging time (h)	>72

1.2. Shaping of the tubes and thermal treatment:

The paste is extruded by an extruder by mono-channel tubes. The length of the extruded tubes varied from 50 cm to 1 m. The elaborated wet tubes are cut to different lengths and left in the open air for drying 3 days at maximum, all depending on the climate and the content of water introduced into mixing, After drying, the supports are treated by a thermal treatment in a programmable furnace at different final temperatures in order to finale consolidation for the shaping tubes. Figure 2 shows the thermal program.
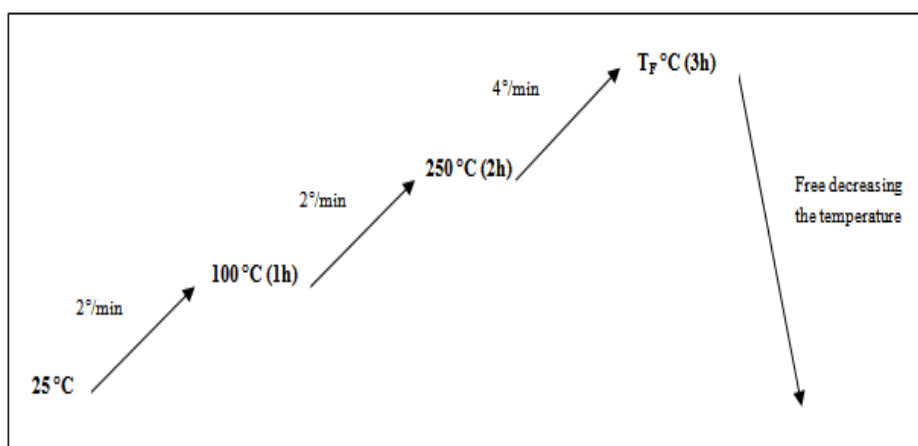

Figure 2: Thermal Program for clay tubes

All of the tubes are prepared sintered at 800, 900 and 1000 °C and the final sintering time is 3 hours (Figure 3).
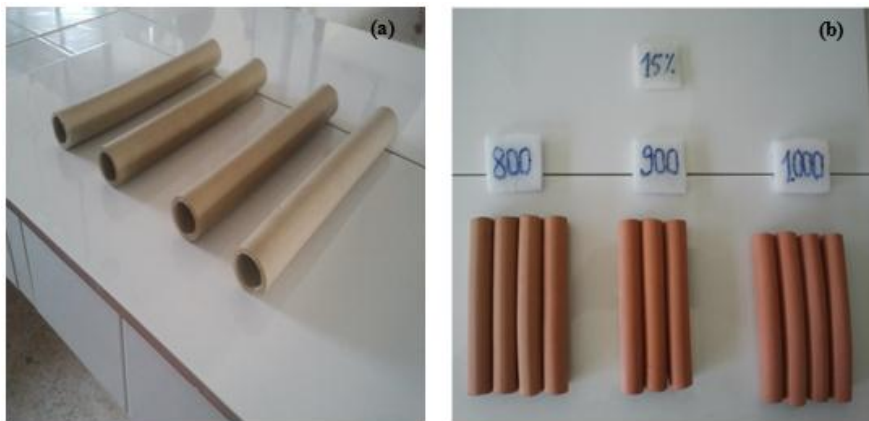
Figure 3: Tubular ceramic supports (S15), (a) before sintering and (b) after sintering (800, 900 and 1000) °C/3h

2. Permeability tests:

The tests of permeability were carried out using on a laboratory pilot plant. Figure 4 gives the diagram of the laboratory pilot.
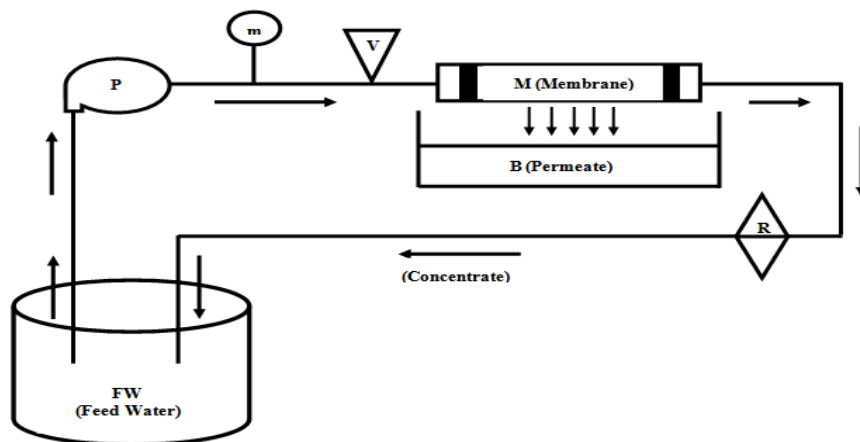

Figure 4: Pilot of the tangential filtration at the laboratory scale

Electric pump with adjustable flow rate (P), manometer (m), safety valve (V), membrane module (M), regulator of pressure (R), permeate water (B), feed water (FW).

III.   Results And Discussion

1. Characterization of Moroccan clay:

1.1. Quantitative chemical analysis:

The chemical compositions for the clay to the raw state are performed by X-ray Fluorescence [9, 10], the results is given in table 2.

Table 2: Chemical composition of clay

Formula of oxides	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	MnO	Na_2O	K_2O
Mass percentage	57,61	16,97	13,20	5,10	2,60	0,11	0,67	2,60

It reveals that the clay powder is essentially formed of large amount of oxides silica and alumina in lower proportion with 75 % by total mass, that allows concluding the mechanical efficiency of clay, and we noted the presence of a very large percentage of iron oxide about 5,10 % responsible for the red coloring of ceramic supports after thermal treatment [1].

2. Characterization of supports:
2.1. Thermal Program:
The sintering temperature is an important parameter which controls the cracteristics of final products such as: porosity, mechanical and chemical resistance. For this, the field of sintering temperature is varied between 800 and 1000 °C. The adapted thermal program was shosen for several reasons including [1, 2, 3]:

- At 100 °C, we have a bearing the 1h to ensure slowly the evaporation of the moisture of the water molecules.
- At 250 °C, we have a level for 2 hours to degrade the organic matter (wood powder) and to leave the pores to the inner of the elaborated parts. Finally, we have the bearings of final sintering temperatures (800, 900 and 1000 °C) during 3h.
- Knowing that the rapid degradation of the added organic matter can causes the defects in the ceramic structure. For this reason, we chose to apply a slow rise in temperature up to 250 °C (cooking speed is 2 °/ min).

2.2. Porosity test by water:
The principle of this test is to measure the percentage of total pore volume relative to the total mass of the dry sample by using the water for 24 hours at 25 °C, according to the following equation [11]:

$$P = (M_W / M_D) \; x \; 100$$

With:

P: total porosity (%);
M_W : mass of water which absorbed the equivalent pore volume (g);
M_D : mass of dry sample (g).

Figure 5 gives the graphical representation of the total porosity versus the final sintering temperatures for 15 % of the supports of the organic additions (S15).
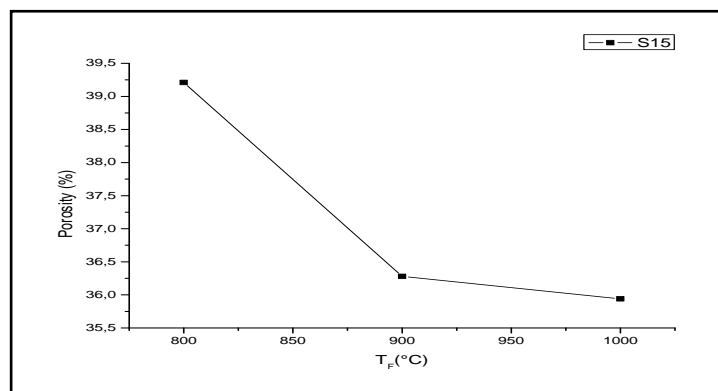

Figure 5: Total porosity versus the final sintering temperature for supports S15

The total porosity decreases with increasing temperature of the final sintering (of 39,21% to 35,94%), and also the value of porosity is very important to the lowest temperature (800 °C) with a mechanical resistance very low, because the welding clay grains is not performed at this temperature good way [1].

2.3. Chemical resistance:
The test of chemical resistance was carried out on samples ceramic supports (S15), treated at different final sintering temperatures in acid medium (HNO_3) and basic (NaOH) at various concentrations at 25 °C for 24 hours [1, 2]. The results of the chemical attack are presented in tables 3 and 4.

Table 3: Mass loss of the samples as a percentage of supports S15 after the acid attack at different concentrations of HNO_3 for different final sintering temperatures

T_F (°C)/3h Concentration	800	900	1000
	$\Delta m/m$ (%)		
1 N	1,62	1,15	1,11
0,3 N	0,89	0,75	0,69

Table 4: Mass loss of the samples as a percentage of supports S15 after the basic attack at different concentrations of NaOH for different final sintering temperatures

T_F (°C)/3h Concentration	800	900	1000
	Δm/m (%)		
1 N	0,42	0,29	0,28
0,3 N	0,17	0,12	0,10

The analysis of the results of the chemical resistance shows that the mass loss varied between 0,69 and 1,62 % for the acid attack, and varied between 0,10 and 0,42 % for the basic attack, for the tubular supports (S15) treated at different final sintering temperatures, the results show that the elaborated supports are characterized by a good chemical resistance to corrosion.

2.4. Mechanical resistance of the compression:

The test of compression consists to subjecting a test specimen having a rectangular section, placed between the platens of a press, with two opposing axial forces [12, 13]. Figure 6 shows the evolution of the values of mechanical resistance of the compression for samples (F15) treated with different final sintering temperatures.
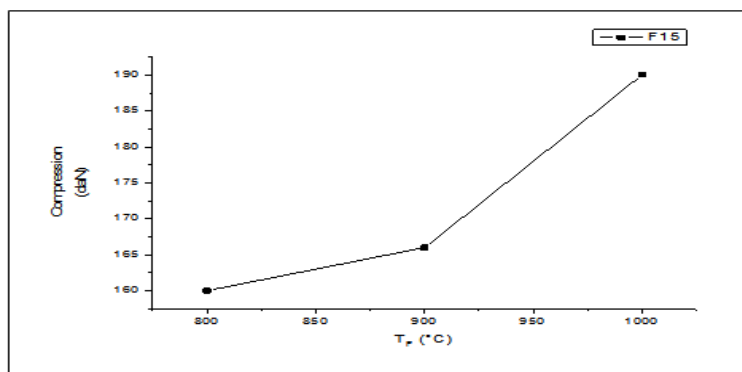

Figure 6: Mechanical resistance of the compression versus the final sintering temperature for specimens of formulation (F15)

The results show that the mechanical resistance increases with increasing the final sintering temperature (of 160 daN to 190 daN). The maximum value of the mechanical compression resistance is observed at 1000 °C, which shows that the sintering is best towards the high treatment temperatures. Therefore the ceramic supports sintered at this temperature during 3 hours are more effective mechanically compared to the other sintered supports at 800 to 900 °C.

2.5. Permeability tests:

Figures 7 and 8 give the variations of the flow versus time (F = f (t)) and versus circulation pressure (F = f (P).
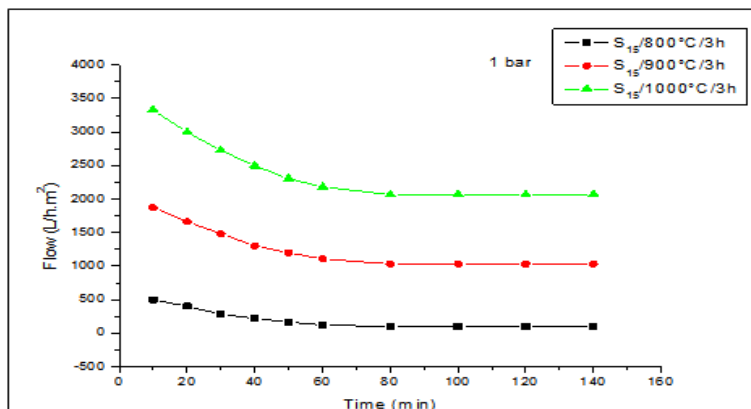

Figure 7: Variation of flow versus time for supports S15 treated at different final sintering temperatures (pressure = 1 bar)
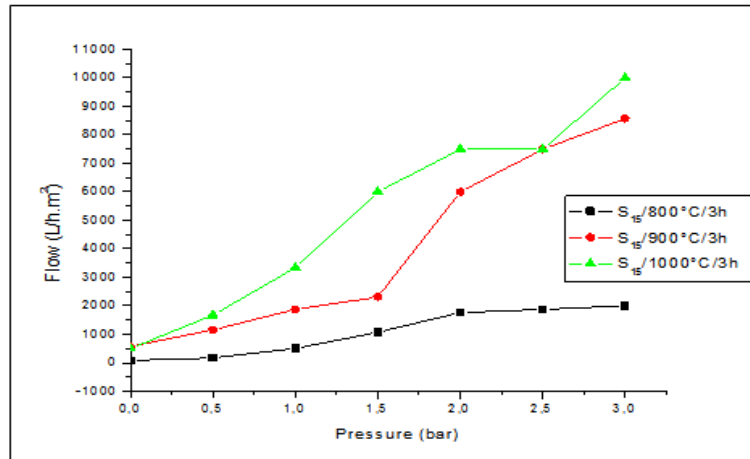
Figure 8: Variation of the flow versus pressure for supports S15 treated at different final sintering temperature

The results show that in the start of filtration, the values of the flow are higher for the all ceramic supports treated at 800, 900 and 1000 °C. Also, the flow decreases versus time (after 80 minutes of filtration for supports (S15): $Flow_{S15/800/1bar}$ = 99 L/h.m^2; $Flow_{S15/900/1bar}$ = 1033 L/h.m^2 and $Flow_{S15/1000/1bar}$ = 2066 L/h.m^2), this can be explain to the phenomenon of concentration polarization [14], by the formation of the very thin water layer at the interface to the water-surface internal of the ceramic support, the concentration of this layer liquid is higher than that the feed solution, and also remain stationary and decreases the pore size for the supports.

The results show that the permeate flow increases versus pressure for them supports treated at 900 and 1000 °C, the value of flow varied from the $Flow_{S15/900}$ = 1152 L/h.m^2 for 0,5bar to $Fow_{S15/900}$ = 8562 L/h.m^2 for 3bar and $Flow_{S15/1000}$ = 1664 L/h.m^2 for 0,5bar to $Flow_{S15/1000}$ = 9989 L/h.m^2 for 3bar.

IV.   Conclusion
In this work a new support of microfiltration and ultrafiltration membranes was prepared from natural powders derived from Moroccan clay. This kind of ceramic support presents the following characterizations:
- A good improvement of sintering of the supports according to different temperatures.
- The values of the porosity of the treated supports at 900 and 1000 °C are very similar but with different mechanical resistance.
- The chemical attack is very important when the solutions are very acidic and almost zero in the case of the basic solutions for the supports 15 % to the organic matter.
- The specimen of formulating (F15) treated at 1000 °C during 3h is characterized by a good mechanical resistance of the compression.
- The ceramics supports S15 treated at 1000 °C/3h present the very higher permeate flow.
- The sintered supports S15 at 1000 °C during 3 hours are characterized by a good state of sintering, best porosity, excellent chemical and mechanical performances and good permeability.

These results show that the ceramic supports the 15 % of the organic matter sintered at 1000 °C/3h can be used for the deposition of the layers for the microfiltration and ultrafiltration membranes.

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