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Preparation and characterization of flat membrane support based on Sahara Moroccan clay: application to the filtration of textile effluents

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ABSTRACT

The present paper is devoted to synthesis of porous ceramic support from local Sahara Moroccan clay. This material is characterized by its natural abundance and its beneficial properties. The support with flat configuration was prepared from natural clay. The powder was crushed and sieved to 125 μm. The extrusion was performed by applying the uniaxial pressing. SEM, XRD, and DTG characterizations techniques were used. The elaborated flat support sintered at 950°C showed apparent porosity and water absorption of 40.81% and 25.25%, respectively. The water permeability of elaborated support is about 121 L/(h m^2 bar) after 2 h of filtration. The support performance was evaluated by filtration of textile effluents with a good retention of suspended particles present in textile effluents.

Keywords: Textile effluents; Ceramic support; Flat disk; Microfiltration; Moroccan Sahara clay

1. Introduction

Industries such as textiles industry release often colored matter in water bodies without treatment. On the other hand, most of the dyes used in the textile industries are stable to ultraviolet light and are not biodegradable. They are also impervious to aerobic digestion, making these dyes a long-term water pollutant. In addition to the conventional treatment methods that generate sludge to be removed thereafter, other remediation techniques are developed for the treatment of industrial waste containing heavy metals and toxic compounds. Current techniques for depollution of effluents include membrane processes that present increasingly competitive energy and techno-economic performances and whose development is constantly progressing.

Most of the membranes currently marketed are organic membranes and are commonly used. However, the mineral membranes have promising potentialities in particular due to their greater mechanical, thermal and chemical resistance than those of organic membranes. These characteristics correspond to the current needs of the industry for applications under aggressive conditions, whether at the level of the solvent used, the temperature or the pH of the solution to be treated.

Ceramic membranes based technologies for wastewater treatment have emerged in recent years as important separation and purification methods in various process industries to

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prevent the pollution of water resources caused by different sources. Inorganic membranes (oxide based) such as Al_2O_3, ZrO_2, and TiO_2 have attracted more attention due to their high mechanical, chemical, and thermal resistance properties [1]. That can potentially be applied in water treatment. However, these oxide-based membranes are expensive, As a result, actually, most of the scientific workers focused their attention on preparation of new low-cost support membranes using natural materials (both raw materials and preparation process) [2].

From a technical advantage, the development of ceramic membranes based on natural materials and some waste powders such as fly-ash was investigated by several authors. Clays are in abundance and need low firing temperature in comparison with metal oxide materials (alumina, zirconia, titania and silica) [3–7]. Various tubular supports, for microfiltration and ultrafiltration membranes, have been elaborated using different materials such as cordierite, kaolin used by Saffaj et al. [8] and Loukili et al. [9] other Moroccan clays [10–12]. The prepared support presents a good porosity of 40%–43% and an average pore size in the range of 7–11 μm [13–17]. Majouli et al. [18] labored new tubular ceramic membrane from local Moroccan perlite for application to treatment of industrial wastewaters. Bouazizi et al. [19] developed a new ceramic membrane from Moroccan bentonite for the microfiltration of industrial wastewater. In another work, Achiou et al. [20] described the development of a new flat ceramic membrane on ceramic support made from bentonite and micronized phosphate for microfiltration and ultrafiltration. Achiou et al. [20] fabricated and characterized flat and tubular ceramic microfiltration membranes made from natural Moroccan pozzolan.

The main objective of the study presented in this work is the development of new low-cost microfiltration ceramic flat support based on natural clay made from Sahara Moroccan and their application to the filtration of textile effluents.

2. Experimental setup

2.1. Sample clay

The raw materials used to prepare flat ceramic microfiltration membranes were collected from Moroccan Sahara (Oued Saquia Hamra) located at the entrance of Laayoune. This clay material was sampled at a depth of 1.5 m and at the end of level of this pool.

After collecting the clay material, stones and other heavy particles were removed from the samples by sieving. The clay material was crushed and about 500 g of the powder was dispersed in 2 L of deionized water. After sedimentation of the clay particles, the top part or supernatant was sieved through a 125-μm sieve to remove the larger non-clay fractions and to obtain the fine clay fraction. The samples were dried at 105°C and stored in desiccators.

2.2. Elaboration of flat membrane porous support

The process of developing ceramic supports is detailed in Fig. 1. The clay powder was crushed and sieved to obtain a homogeneous fine fraction less than 45 μm, the sample was spread in a stainless steel mold, pressed less than 12 tons using a hydraulic press (uniaxial pressing). The elaborated flat disks 2 mm thick and a diameter of 4 cm were heat treated in programmable oven (type Nabertherm P320 Controller mark). The thermic treating program ended at a temperature ranging from 900°C to 1,100°C, with plateaus at 250°C for the elimination of absorption water and 750°C for order composition of calcium carbonate (Fig. 2).

2.3. Instruments

Several characterization techniques were used to determine the characteristics of utilized clay and elaborated microfiltration support. The particle sizing AccuSizer model 770 (particle sizing system Santa Barbara) was used to determine the particle size distribution. X-ray fluorescence analyses were performed on a dispersion wavelength spectrometer, model SRS 200. While, the XRD analysis of the raw treated clay (Fig. 3) was carried out with a Siemens D5000 diffractometer (Cu Ka ray, Ni Filter). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed with simultaneous DTA–TGA 2960 instrument.

The infra-red spectrum (Fig. 4) was determined by using a Scimitar Series FTS 2000 Digilab spectrophotometer in the range of middle infra-red of 400–4,000 cm^{-1} (Fig. 5). The prepared support membranes were also characterized by

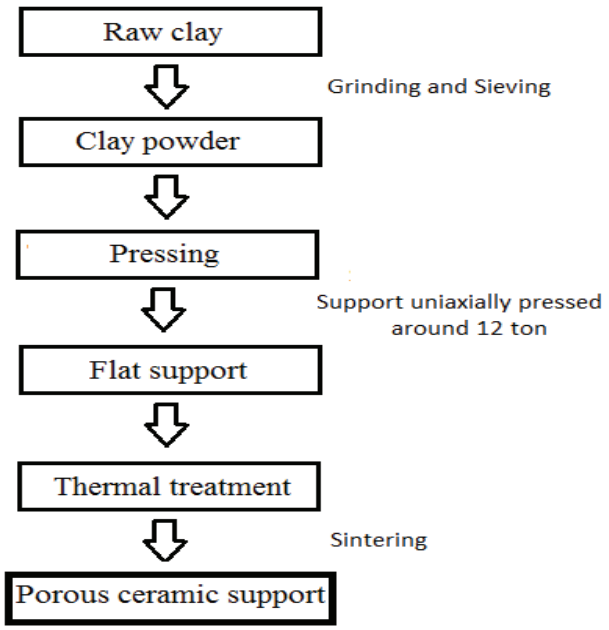

Fig. 1. Process of elaboration of flat ceramic support.

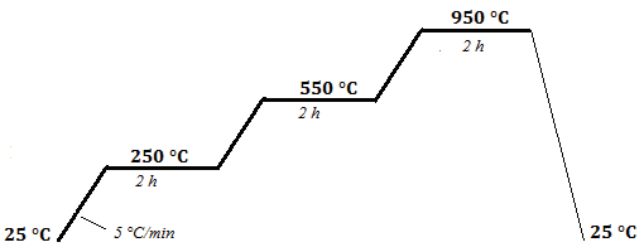

Fig. 2. Thermal program.

scanning electron microscopy (Hitachi S-4500). The pore size of the membrane was estimated by image processing of SEM pictures using ImageJ software (v.1.44e). The apparent porosity and water adsorption were measured in accordance with ASTM C373-88 method 674-88.

The mechanical strength was measured in a bending load of three-point method according to ASTM. The chemical resistance of the optimized support was evaluated by weight loss after bathing the samples in concentrated HNO_3 solution (pH = 1.5) and NaOH solution (pH = 13).

2.4. Filtration tests

Frontal filtration test was performed on a laboratory scale filtration pilot (Fig. 3). The support with a filtration area of about 5.3 cm^2 placed in the membrane housing and the water is filled in the system from the top (feed cell). All filtration experiments are conducted at room temperature (22°C ± 1°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 of a Teflon cell with a flat circular Teflon base plate which contains the membrane housing. The membrane is placed in a Teflon casing and sealed with epoxy resin and then placed in the membrane housing provided on the base plate. The permeability is calculated by tracing the flux vs. the pressure.

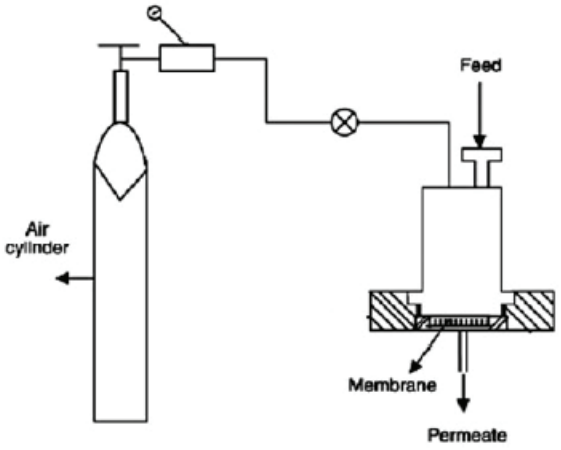

Fig. 3. Laboratory pilot.

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, alumina, and calcium oxide are the major constituents of this

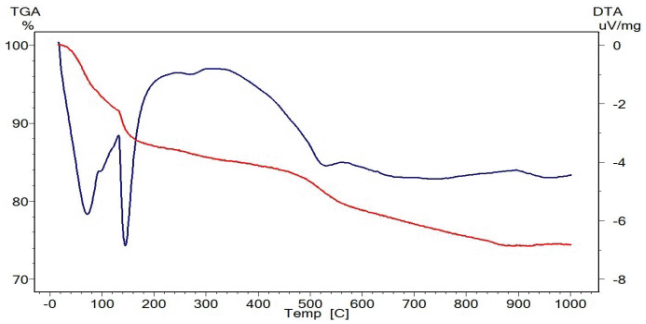

Fig. 5. TGA–DTA of clay.

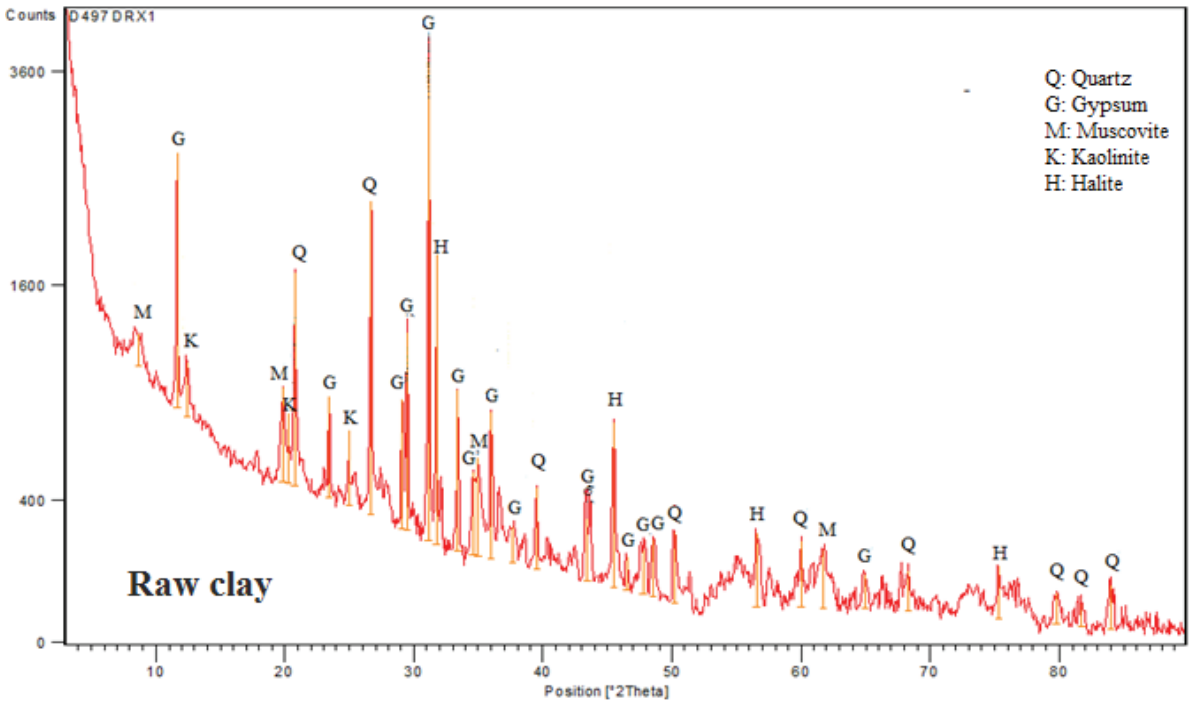

Fig. 4. Diffractogram of natural clay.

sample (Table 1). The particle diameter (Table 2) ranges from 1 to 36 μm. More than 70% of the particles present a diameter <5 μm.

Fig. 4 presents the XRD patterns of raw Sahara clay; it shows that kaolinite (K), muscovite (M), gypsum (G) and quartz (Q) are the main minerals present in the raw clay sample.

TGA and DTA are shown in Fig. 5. There are four endothermic peaks and one exothermic peak. The TGA curve, indicates weight loss of about 8 wt% at low temperature (<100°C). That is attributed to the evaporation of the intercalated or adsorbed water in the powder sample. The small weight loss of 4 wt% seen in the TGA curve between 100°C and 200°C can be attributed to the removal of structural water from the ceramic material. This is confirmed by the corresponding DTA peak at about 140°C or 150°C. The temperature range between 200°C and 400°C is associated to the endothermic reaction. Regarding the TGA thermogram, 4% can be attributed to the removal of structural water. The temperature range between 500°C and 600°C is associated to the endothermic reaction. Such thermodynamic change corresponds to a sample mass loss of about 10 wt%. This process arises from the dehydration (structured water) of kaolinite, accordingly the structural hydroxyls are eliminated leading to the transformation of kaolinite to a new metakaolinite amorphous phase and/or the decomposition of carbonates in the high temperature regime, structural reorganization processes of the ceramic materials occur as suggested by the presence of a succession of exothermic phenomena located between 900°C and 950°C due to the structural reorganization of metastable metakaolin transitional phase.

Table 1
Chemical analysis of the clay

Oxides	Clay
SiO_2	47.17
Al_2O_3	10.88
Fe_2O_3	4.98
MgO	2.80
K_2O	1.39
CaO	14.62
LoI	19.4

Table 2
Particle size distribution of clay

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

The spectrum of natural clay given in Fig. 6 shows a band which is located at 3,625 cm^{-1} corresponding to stretching vibrations of the OH groups of constitutions of water and one located at 3,415 cm^{-1} corresponds to the vibration of the OH bond of water adsorbed. The other band is approximately 1,632 cm^{-1} refers to the –OH deformation vibration. The margins of the strips located between 1,010; 1,100 and 1,150 cm^{-1} corresponding to the Si–O bond and two weak bands at 777 and 870 cm^{-1} attributed to carbonates. The vibration of Si–O–Al occurs for muscovite by a peak at 550 cm^{-1}. Around 600, 650 and 800 cm^{-1} is suitable for the group of bending vibration metal–OH in the case of kaolinite. The sample also contains free crystalline silica (quartz) of which the most intense absorption band is at 1,080 cm^{-1}. It is hardly demonstrated as masked by the binding of Si–O band (at about 1,000 cm^{-1}).

3.2. Characterizations of the supports

3.2.1. Visual inspection of supports

Fig. 7 shows visual inspection of raw support and sintered at 950°C, the support conserved its configuration. The membranes gradually changed their color from gray at 25°C to a darker red color at 950°C. This change of color could be due to the oxidation of Fe.

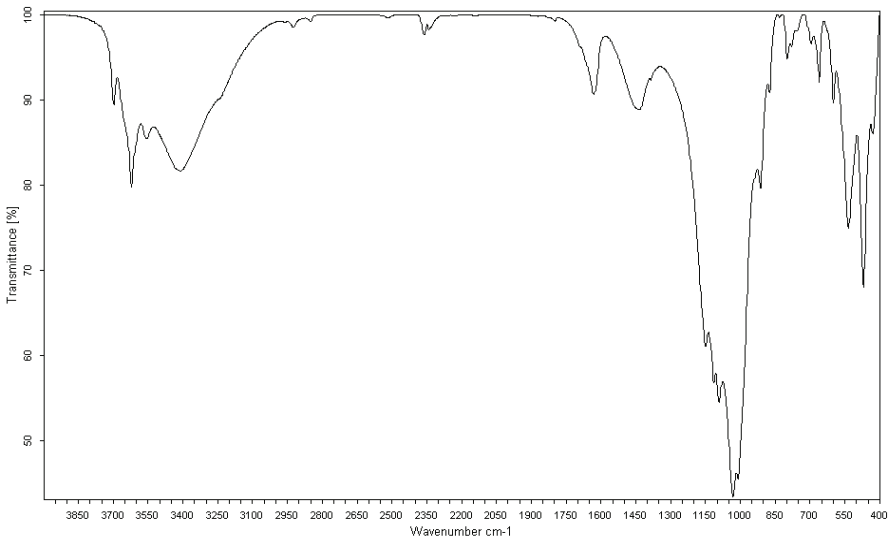

Fig. 6. Infra-red spectrum of natural clay.

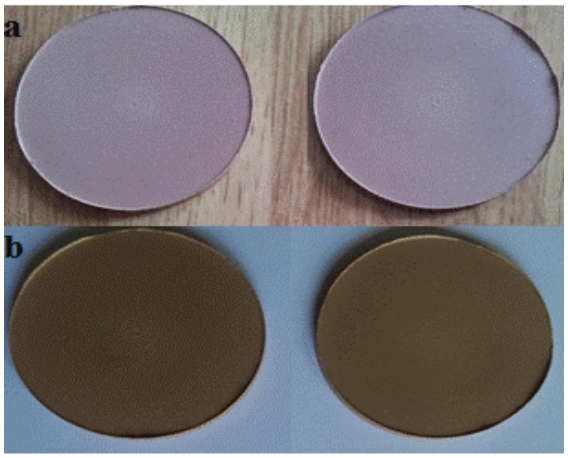

Fig. 7. Flat supports views: before sintering (25°C) and after sintering 950°C.

3.2.2. Scanning electron microscopy

The evolution of surface morphology and densification of the sintered support at different temperatures were determined by scanning electron microscopy. Fig. 8 shows the morphology and surface character of the membrane materials produced at various sintering temperatures. The surface of the supports sintered at temperatures from 900°C to 1,100°C give information about the texture of the developed media. According to the micrographs of the heat treatment effect is very marked when the temperature increases is observed a gradual reduction of the porosity. The verification phenomenon (melting of the vitreous phase) begins at 1,100°C, which explains the observed significant decrease in the pore volume.

3.2.3. Pore size distribution

The average pore size was estimated by image processing of SEM pictures using ImageJ analysis. The average pore diameter (d) was calculated by the following equation:

$$d = \sqrt{\frac{\sum_{i=1}^{n} n_i \cdot d_i^2}{\sum_{i=1}^{n} n_i}} \quad (1)$$

where n_i is the number of pores and d_i is the pore diameter (μm).

The distribution of pores size seen on the surface of the supports sintered at different temperature (from 900°C to 1,100°C) is shown by Fig. 9. The result shows a unimodal distribution of the pore size for sintering temperatures at 900°C and 1,100°C. The average pore diameter decreased from 2.80 to 0.8 μm when temperature increases from 900°C to 1,100°C. This behavior corresponds to an opening of the pores at low temperature. The average pore size diameter of the support is found to be around of 2.75 μm. However, the majority of pores (about 94%) have a diameter < 2.26 μm. At the temperature of 1,050°C, it is observed that there is a decrease of the pores diameter because of the material densification when the temperature increases to 1,100°C and the connectivity between pores decreases at a higher temperature.

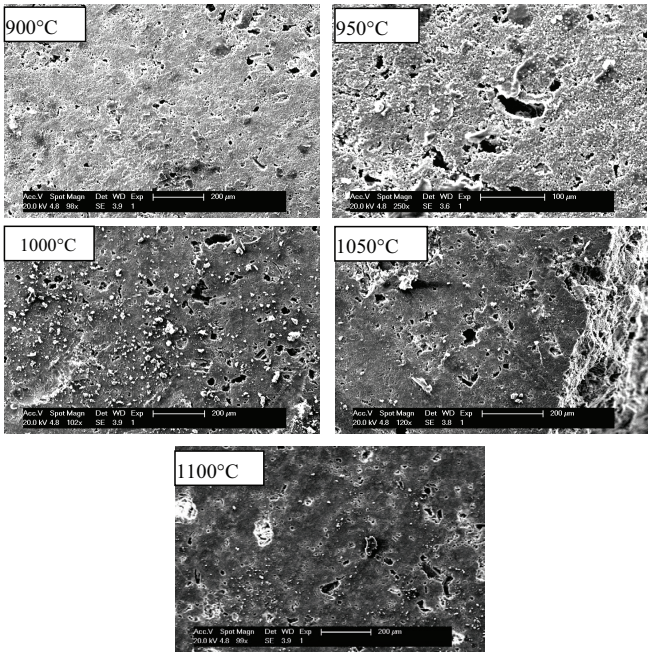

Fig. 8. SEM of supports sintered at different temperatures.

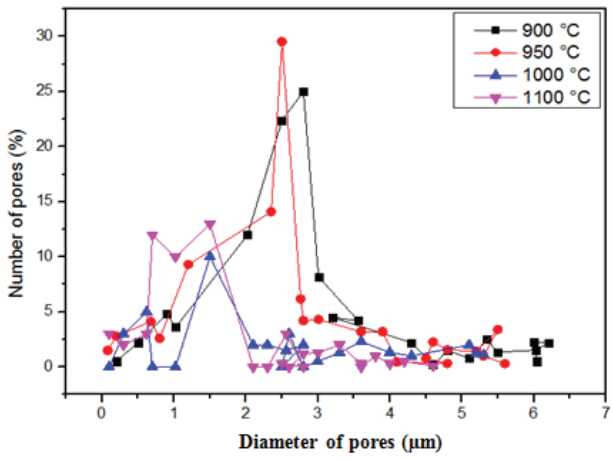

Fig. 9. Flat supports views after sintering at various temperatures.

3.2.4. Porosity of supports

The evolution of apparent porosity of the supports with a sintering temperature is shown in Fig. 10. The porosity of the supports was studied at temperature range between 900°C and 1,100°C. The porosity increased from the minimum value found at 900°C (38%) to achieve a maximum at 950°C (40.81%), followed by a sharp decrease of 18% of porosity when temperature reaches 1,100°C.

3.2.5. Mechanical strength

The mechanical strength and the porosity are strongly related to temperature changes, mainly the final sintering temperature. Mechanical resistance variation is indicated in Fig. 11.

3.2.6. Chemical resistance

The support sintered at 950°C was soaked at room temperature using acid medium of HCl solution at pH 1.01 and basic medium of NaOH solution at pH = 13.5 for 8 d. The results reported in Fig. 11 show that the flat supports present a good chemical resistance in basic medium than in acid one. The weight loss does not exceed 2.3 wt% in basic medium. However, in basic medium, the weight loss reaches 5.5 wt%.

3.3. Filtration test

3.3.1. Determination of support permeability

The pure water permeability of support was first studied. The support was conditioned by immersion in pure deionized water for a minimum of 24 h before filtration test. Support was first characterized by their water permeability. The fluxes were measured at different pressures (0.04, 0.06, 0.08, 0.1 and 0.12 bar). The stabilization of the water flux through the support is shown in Fig. 12. Experiments show also that the water flux through the support depends on the applied pressure. The average support permeability determined using distilled water is 121 L/h m² bar (Fig. 13).

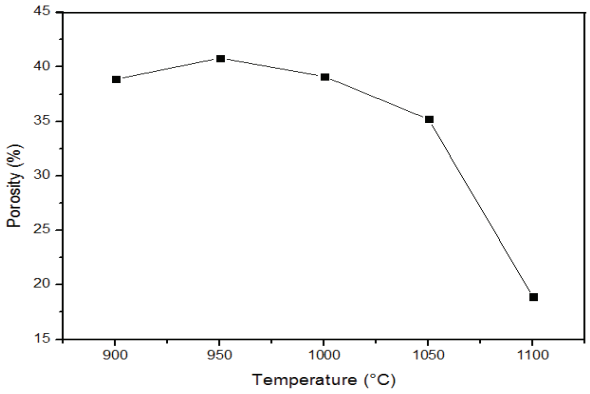

Fig. 10. Evolution of the apparent porosity as a function of sintering temperature.

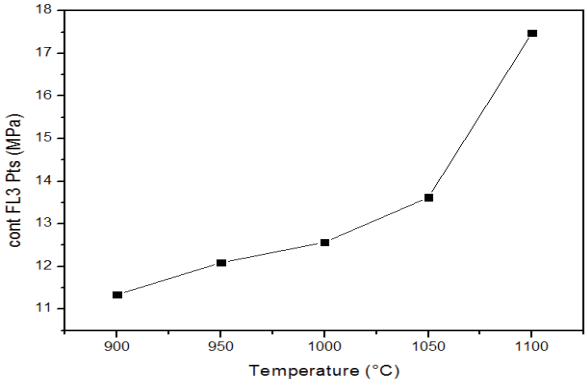

Fig. 11. Variation of the mechanical strength vs. sintering temperature.

3.3.2. Filtration of textile effluents

Most of industries such as textiles, paper, plastics, leather, food and cosmetics industries use dyes or pigments to color their product. Such extensive use of color often poses problems in the form of colored wastewater that require pre-treatment for color prior to disposal into receiving water bodies or publicly owned treatment works. The removal of such compounds at such low levels is a difficult problem. Among the methods employed are the adsorption onto sludge of wastewater treatment plant, as well as other physicochemical techniques as coagulation, flocculation, ozonation and adsorption. Membrane support process can be used to reduce the effluent contaminants.

The filtration test on the support membrane developed from natural Moroccan Sahara clay was achieved by measuring the turbidity, the conductivity and pH of this textile effluents by using a TN-100/T-100, Fisher Scientific Accumet BasicAB15 pH meter (USA) and a conductivity measurement model 101 (Orion Research, Cambridge, MA, USA), respectively. The results obtained are reported in Table 3.

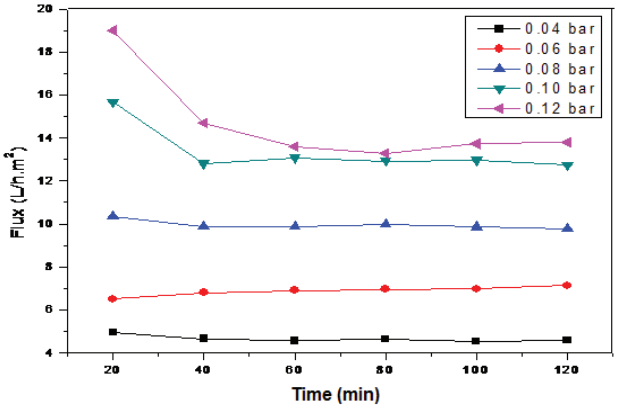

Fig. 12. Water flux vs. operating time.

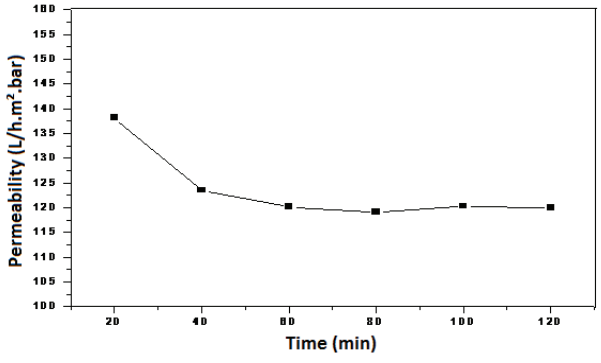

Fig. 13. Permeability vs. operating time.

Table 3
Filtration test on the materials developed

pH		Conductivity (μS/cm)		Turbidity (NTU)	
Effluent	Permeate	Effluent	Permeate	Effluent	Permeate
7.05	8.26	1,553	1,128	181	6.04

Membrane supports based on Moroccan Sahara clay are shown an important removal efficiency to reduce suspended solids. The conductivity of the filtrate remains normal access from the national standard of drinking water (2,700 μS/cm), the decrease in this parameter is due to the elimination of some of the dissolved salts.

4. Conclusion

The clay of Moroccan Sahara could be considered as effective source materials for the development of ceramic membrane media with its abundance in nature Sahara and low cost compared with other frequently used materials. The flat support exhibit good characteristics regarding the porosity and permeability as well as the tests of filtration allows clarification of used effluents.

To improve better efficiency performance materials were developed. Further study will be conducted before a competitive application can be proposed for other more powerful separation processes such as microfiltration, ultrafiltration and nanofiltration.

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