J. Mater. Environ. Sci. 7 (1) (2016) 196-204
ISSN : 2028-2508
CODEN: JMESC

Elaboration and characterization of flat ceramic microfiltration membrane made from natural Moroccan pozzolan (Central Middle Atlas)

B. Achiou[1,*], H. Elomari[1], M. Ouammou[1], A. Albizane[1], J. Bennazha[1], S. Alami Younssi[1], I. E. El Amrani[2], A. Aaddane[1]

[1] *Laboratory of Materials Membranes and Environment, Department of Chemistry, Faculty of Sciences and Technologies, University Hassan II, Mohammedia – Casablanca, Morocco.*
[2] *Department of Earth Sciences. University Mohammed V Agdal, Scientific Institute. Rabat, Morocco.*
**Corresponding author: E-mail: achiou.brahim@gmail.com; Phone: +212650822811*

Abstract

This work reports the elaboration of ceramic microfiltration membranes made by dry process and based on different Moroccan pozzolans (Pozzolan of N'Aid Said (PN), Black Pozzolan of Hebri (BPH) and Red Pozzolan of Hebri (RPH)). Raw pozzolans were characterized by XRF, XRD and TGA analysis. Disks of 40 mm in diameter and 2±0.2 mm in thickness were elaborated by uniaxial pressing method and then sintered at 950 °C. Elaborated membranes were characterized by SEM analysis, shrinkage measurement, water porosity, mechanical strength, and chemical resistant. The morphology of top surface of membranes was homogenous and free from cracks. Results showed that the average pore diameter was approximately 2.84, 2.20 and 2.36 µm for PN, BPH and RPH membranes respectively. In the other hand, the optimized water permeability was 1424, 843 and 1952 L/m^2.h.bar respectively, after two hours of filtration. The elaborated membranes were tested to treat water washing of Jeans and they were able to remove approximately 99% of turbidity.

Key Words: Geo-material, Natural pozzolan, Flat ceramic membrane, Microfiltration, Textile effluent.

1. Introduction

Recently, ceramic membranes have been used intensively because of their attractive advantages such as better chemical and thermal stability, better mechanical resistance and long life. In general, these membranes are made from expensive metal oxides such as Alumina, Silica, Zircon and Titanium [1-9]. Using cheaper raw materials is very recommended to manufacture and develop new ceramic membranes, especially for emerging countries, where many environmental problems need to be solved at low cost [10-17]. In that sense, as geo-materials are abundant in a country like Morocco, they can be used as alternative to classic ceramic membranes.

In our laboratory, several works where local geomaterials were used as microfiltration and ultrafiltration membranes are reported in the literature. Moroccan clays were used to elaborate ceramic membranes for microfiltration and ultrafiltration and used to treat solutions containing dyes and salts [18-20]. Natural phosphate was used as raw material to manufacture tubular membrane [21]. Perlite was also used to prepare flat and tubular ceramic membrane for microfiltration of industrial wastewaters [22-23].

Natural pozzolan is siliceous or siliceous and aluminous materials. The pozzolan is a pyroclastic volcanic rock, resulting from explosive eruptions (Strombolian). The rock is soft and is presented in an accumulation of granules with an average diameter less than 2 cm. Pozzolan is formed around the volcanic crater of the deposits up to several tens of meters in thickness, depending on the amount of magma projected into the air during the volcanic eruption. It is generally presented in black color, due to the important amount of iron and magnesium present in the magma. However, the pozzolan in the crater is acquired a reddish color which is explained by oxidation of iron due to release of gases rich on steam.

This paper describes elaboration of new porous ceramic membranes made from natural Moroccan pozzolan. The choice of this geomaterial is, principally due to its abundance in Morocco, its relatively low cost and its behavior as friendly environmental raw material. Elaborated membranes could be potentially used for microfiltration and ultrafiltration.

2. **Experimental**

2.1 Raw material sampling

Pozzolan of different origin could have different properties because of the differences in their chemical composition and forming conditions. Pozzolans used in this work were extracted from the volcanic province of Central Middle Atlas. This region in Morocco was the seat during Neogene (-23 to -1.8 million years) of important volcanic activity that allowed the emission of a huge amount of pozzolan, and a large flowed lava which covered all the region between the cities of Ifrane, Azrou and Timahdite.

Three Moroccan pozzolans were selected for elaboration of microfiltration membranes. They were collected from two sites of Azrou region in Morocco: Pozzolan career of Jbel Hebri (Black Pozzolan of Hebri (BPH) and Red Pozzolan of Hebri (RPH)), located at the east of national road (N13) connecting Azrou and Timahdite (x: 33° 21'29.27 "N; y 5° 9'3.68" W). The second pozzolan career of N'Ait Said (Pozzolan of N'Aid Said (PN)) is the biggest one and it's located at about 10 km of Jbel Hebri (x : 33° 23'5.63"N ; y : 5° 3'35.05"O). N'Ait Said and Jbel Hebri career were exceeded 20 meters in thickness.

2.2. Experimental protocol

The pozzolan samples were directly used as raw material to elaborate ceramic membrane without any add of chemical agent. The raw material was dried in stove at 110 °C for 24 h then it was crashed in ball mill at 240 rpm for 30 min. The resulting powder was sieved using standard screen. Only fractions lower than 63 µm were used to prepare the membrane.

The shaping of macroporous flat disks of 40 mm diameter and 2±0.2 mm thickness was fabricated by hydraulic uniaxial pressing method. Pozzolan powder was spread out in a stainless steel mold then pressed at 12 tones using a hydraulic press for 15 minutes. The green membranes were sintered at 950 °C in a programmable furnace (Nabertherm L9/13/P320) according to thermal program shown in Figure 1. Cooling of the furnace from sintering temperature to room temperature was carried out by simple automatic heating shutdown.

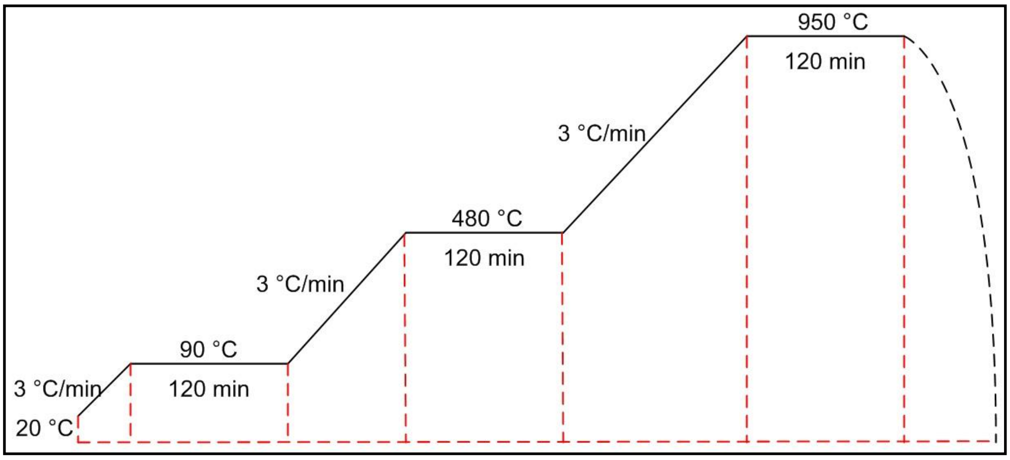

Figure 1: Thermal program used for sintering membrane.

2.3 Test of filtration

Filtration test at lower pressure from 0 to 0.12 bar was carried out in a laboratory microfiltration pilot made from glass (Figure 2). The membrane was placed in vertical position and perpendicular to flow direction of filtering solution. The working pressure ΔP was controlled by variation of height of water between membrane surface and level of liquid in separating funnel. Appling pressure on membrane surface is given by following formula:

$$\Delta P = \rho g h$$

Where ρ is the water density, g is gravitational acceleration, and h is the height of water. All filtration experiments were conducted at room temperature (25±2 °C).

Water permeability was measured for several elaborated membranes using bidistilled water during two hours of filtration. Performance of membranes was provided by clarification of effluent generated by local textile industry, specially washing water effluent of Jean process that was previously filtered by a sieve of 45 µm. The effluents were characterised by measuring pH, conductivity, turbidity and absorbance at maximum wavelength absorption λ_{max} of 664 nm which was determined by scanning the visible range from 400 nm to 750 nm. The filtration performance of elaborated membranes was determined using rejection factor of turbidity R_T and rejection factor of soluble dyes R_{ABS}. R_T and R_{ABS} are respectively defined as:

$$R_T = \frac{(T_{effluent} - T_{permeate})}{T_{effluent}} \times 100$$

$$R_{ABS} = \frac{(ABS_{effluent} - ABS_{permeate})}{ABS_{effluent}} \times 100$$

$T_{effluent}$ and $T_{permeate}$ are turbidity in the effluent and permeate, and $ABS_{effluent}$ and $ABS_{permeate}$ are absorbance at 664 nm in the effluent and permeate.

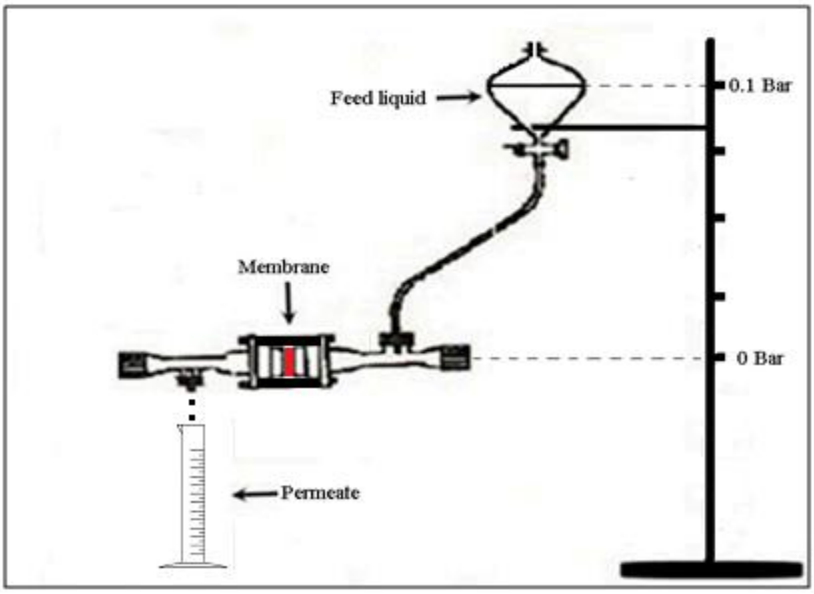

Figure 2: Laboratory setup for microfiltration at low pressure.

2.4 Analyses

The samples of pozzolan were characterized using different techniques. Particle size distribution was carried out by laser particle size analyzer (Malvern Mastersizer 2000). The chemical composition was determined by X-Ray fluorescence using sequential spectrometer of X fluorescence (Bruker S8) based on a scattering of wave length. Thermo-gravimetric analysis (TGA) study was performed using a thermobalance of VersaTherm type under air and αAl_2O_3 as reference. The temperature is increased from room temperature to 1000 °C at a rate of 10 °C/min. The mineralogical analyses of the raw pozzolans and pozzolans sintered at 950 °C were carried out by X-ray diffraction techniques (XRD). The XRD patterns were obtained with Philips X'Pert PRO using CuKα 1 radiation source (α=1.54060 Å).

Weight and dimensions of flat membranes were measured before and after thermal treatment in order to evaluate mass loss and shrinkage. Water porosity, water adsorption and apparent density were measured in accordance with ASTM C373-88 method. Mechanical strength was measured in a three point bending load method according to ASTM C674-88 (Instron 3369). Morphology of elaborated membrane was observed by Scanning Electron Microscopy (SEM) operating at 10 kV (FEI Company, Quanta 200) and average pore size was estimated by image processing of SEM pictures using ImgeJ software (Version 1.44e). Chemical resistant of membranes was evaluated by weight loss in HCl solution pH=1.5 and NaOH solution pH=13 [24].

3. **Results and discussion**

3.1 Pozzolan powder characterization

The chemical composition of three pozzolans is displayed in Table 1 (given in weight percentage (wt.%) of oxides). This analysis shows that the three pozzolans are essentially composed of silica, alumina, ferric oxide, lime and magnesia.

Natural pozzolan is essentially composed by amorphous phase and presence of small crystals which are dispersed in glassy amorphous groundmass. Figure 3 shows the X-ray diffraction pattern of natural and sintered pozzolans at 950 °C. All crystalline phases are reported in Table 2. Magnetite in raw pozzolans (NP and RPH) is transformed to hematite after sintering. Augite and forsterite phases preserve their structure during thermal treatment of NP and BPH. For RPH, we can note the disappearance of dioposite and the appearance of augite and albite mineral phases after applying thermal program. Quartz phase is detected in fired NP and could be explained by the crystallization of amorphous silica.

Table 1: Chemical composition of natural pozzolans.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_3O	P_2O_5	L.I*
PN	39.04	13.42	12.14	11.52	8.20	0.20	1.30	2.19	1.09	5.99
BPH	40.76	13.26	11.93	10.38	9.24	0.21	1.36	2.99	0.98	4.09
RPH	40.70	13.39	12.14	8.45	9.04	0.17	0.86	1.49	0.77	9.29

*Loss on ignition at 1000 °C

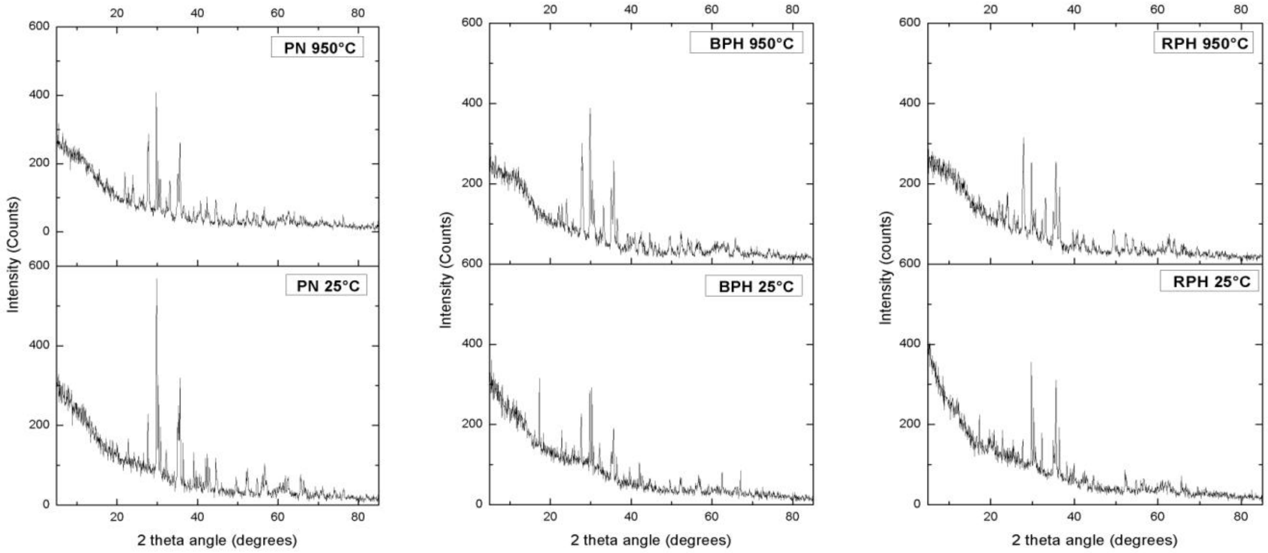

Figure 3: X-Ray diffractograms of natural and sintered pozzolans at 950 °C.

Table 2: Crystalline phases presented in natural pozzolan and pozzolan sintered at 950 °C.

Sample	Phase name	Chemical Formula	Reference code	Strongest pic (°2Theta)
PN 25 °C	Magnetite	$Fe_{2.94}O_4$	01-086-1355	62.3
	Augite, aluminian	$Ca[Mg, Fe, Al][Si, Al]_2O_6$	00-041-1483	29.8
	Forsterite	$Mg_{1.63} Fe_{0.37} [Si O_4]$	01-079-1210	36.4
BPH 25 °C	Hematite, syn	Fe_2O_3	01-073-0603	35.6
	Augite, aluminian	$Ca[Mg , Al , Fe]Si_2O_6$	00-024-0202	29.8
	Forsterite	$Mg_{1.62} Fe_{0.38} [Si O_4]$	01-080-1633	35.5
RPH 25 °C	Magnetite	Fe_3O_4	01-089-0951	29.7
	Diopside	$CaMgSi_2O_6$	01-075-1092	29.8
PN 950 °C	Hematite	Fe_2O_3	01-089-2810	33.1
	Augite, aluminian	$Ca[Mg, Al, Fe]Si_2O_6$	00-024-0202	29.8
	Quartz	SiO_2	01-083-0541	27.8
BPH 950 °C	Hematite, syn	Fe_2O_3	01-079-1741	33.2
	Augite, aluminian	$Ca[Mg, Al, Fe]Si_2O_6$	00-024-0202	29.8
	Forsterite	Mg_2SiO_4	00-021-1260	36.6
RPH 950 °C	Hematite	Fe_2O_3	00-024-0072	33.1
	Augite, aluminian	$Ca[Mg, Al, Fe]Si_2O_6$	00-024-0202	29.8
	Albite, ordered	$NaAlSi_3O_8$	00-009-0466	27.8

To understand all the physical and chemical transformations that occur in the material within the studied temperature range, thermal analysis proves to be the suitable technique. Figure 4 presents TGA and DGA analysis of pozzolan samples from room temperature to 1000 °C at a heating rate of 10 °C/min. There are two weight losses corresponding to total weight of initial weight of samples 4.91, 5.61 and 9.45% respectively for PN, BPH and RPH. The first weight loss from 25 °C to 380 °C is due to the elimination of free and adsorbed water. The second weight loss from 390 °C to 550 °C corresponds to the dehydroxylation of structural hydroxyl groups. It is about 0.91, 1.61 and 2.65% respectively for PN, BPH and RPH. TGA results inferred that minimum sintering temperature for the membrane fabrication should be above 850 °C.

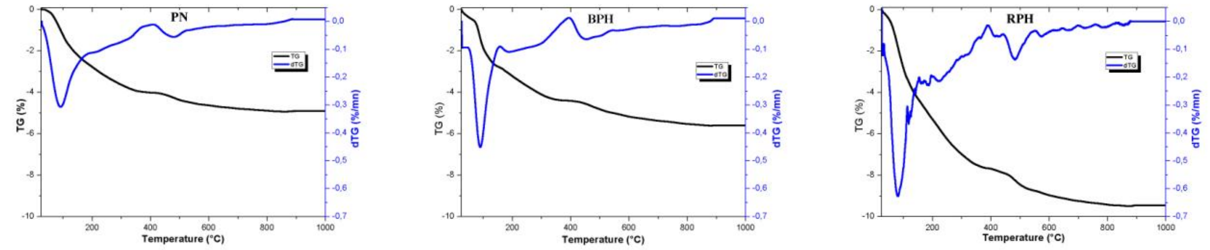

Figure 4: TGA and DGA of natural pozzolans.

Particle size distribution of natural pozzolan powders sieved by a sieve of 68 µm is shown in Figure 5. 90% of particles have 34.0, 38.7 and 34.5 µm in diameter respectively for PN, BPH and RPH. The average particle size of the three pozzolan samples is 9.72, 9.48, and 9.25 µm respectively.

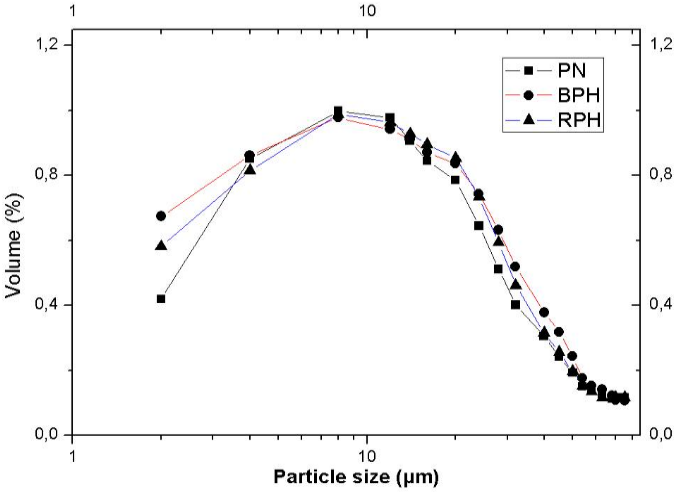

Figure 5: Particle size distribution of pozzolan powders.

3.2 Membrane characterization

Morphology and texture of elaborated membranes were investigated by using Scanning electron microscopy (SEM). Figure 6 shows the micrographs relating to evolution of the microstructure with the increasing of sintering temperature from 850 to 1050 °C. At temperature of 850 °C, the grains are not well consolidated and intergranular contacts are so large. The membranes sintered at 950 °C are free of macro defect and present good consolidation between particles. Their top surface is characterized by a rough morphological structure. The increase of the sintering temperature to 1050 °C generated partial vitrification of the ceramic material and therefore decreasing of porous volume.

The membranes sintered at 950 °C were chosen as the optimal membranes and were used to investigate their properties. Figure 7 shows that obtained membranes changed their color from grey (PN and PBH) and light brown (RPH) to dark brown after thermal treatment and sintering. This change in color is probably due to the iron oxidation. Table 3 reports the physical characteristics of elaborated membranes at 950 °C.

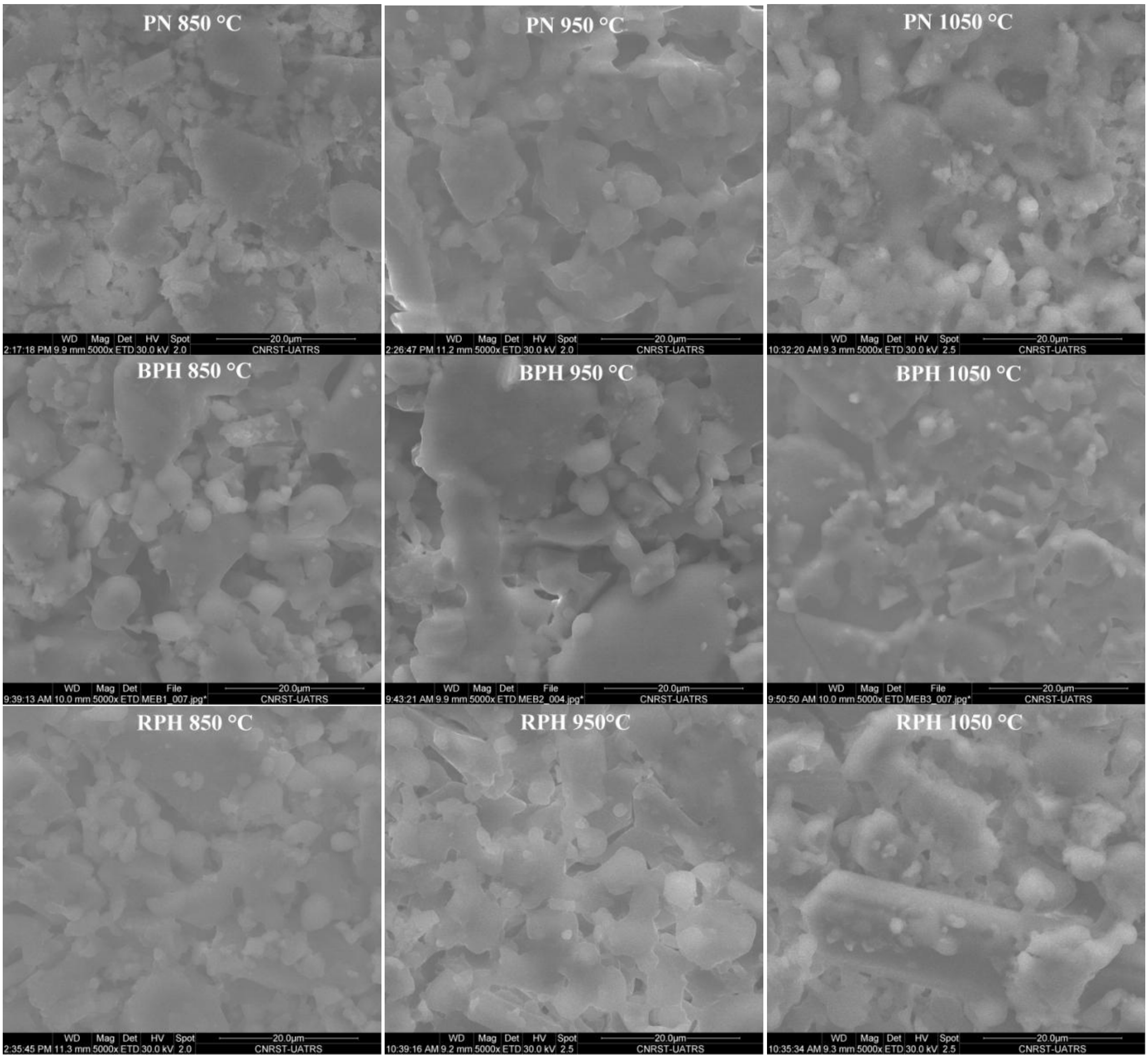

Figure 6: SEM images of membranes sintered at 850 °C, 950 °C and 1050 °C.

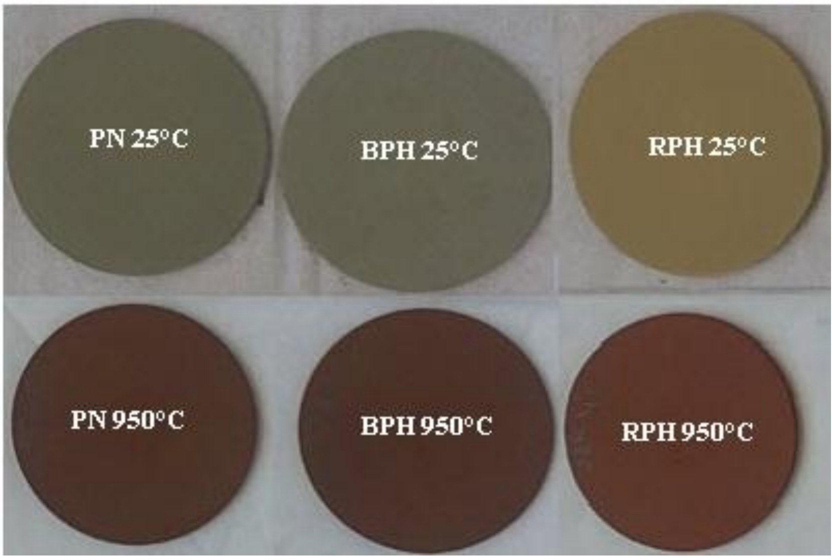

Figure 7: Views of elaborated membranes before and after sintering at 950 °C.

Table 3: Physical characteristics of elaborated membranes at 950 °C.

Parameter	PN	BPH	RPH	Unit
Shrinkage	2.14	4.95	2.17	%
Porosity	32.4	29.6	33.0	%
Apparent density	2.1	2.1	1.9	--
Water absorption	14.6	12.8	15.2	%
Flexural strength	14.80	18.58	19.16	MPa

The average pore size of membran es sintered at 950 °C is measured using ImgeJ software that localizes all visible pores in the SEM pictures. The software measures the area of each pore presented on the surface. The diameter of each pore is given by the diameter of a circle that has the same area. The average pore size d (µm) is calculated using the following formula:

$$d = \sqrt{\frac{\sum_{i=1}^{n} n_i \times d_i^2}{\sum_{i=1}^{n} n_i}}$$

Where n is the number of pores and d_i is the pore diameter (µm) of each pore. The average pore sizes of the three samples are 2.84, 2.20 and 2.36 µm for PN, BPH and RPH respectively.

Chemical stability of elaborated membranes was evaluated by mass loss in acid medium (HCl solution at pH=1.5) and basic medium (NaOH solution at pH=13) during seven days at the atmospheric conditions. Figure 8 and Figure 9 show that pozzolan membranes present a good resistance in basic medium (less than 0.7% for all membranes). However, in acid medium, BPH and RPH lost less than 2% of weight while PN lost about 3.14%. The stability of mass loss was obtained after three days for BPH and RPH, and five days for PN.

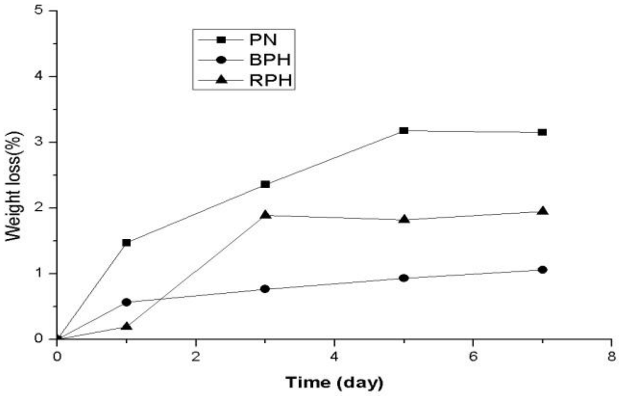

Figure 8: Weight loss of membranes in HCl solution at pH=1.5.

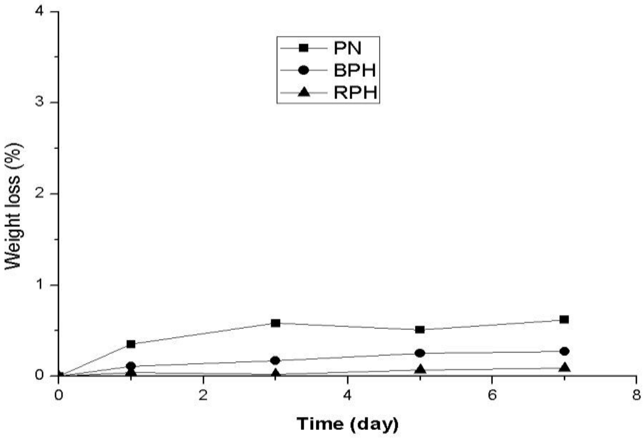

Figure 9: Weight loss of membrane in NaOH solution at pH=13.

3.3 Filtration test

Water permeability L_p (L/h.m^2.bar) is an intrinsic characteristic of membrane. Variation of the permeate flux J (L/h.m^2) with applied transmembrane pressure ΔP (bar) allows to determinate L_p value for all elaborated membranes using the following equation:

$$J = L_p \times \Delta P$$

Experimental results of flux as a function of transmembrane pressure presented in Figure 10 show a linear behavior for all membranes. The values of water permeability are 1467, 889 and 1982 L/h.m^2.bar for PN, BPH and RPH respectively.

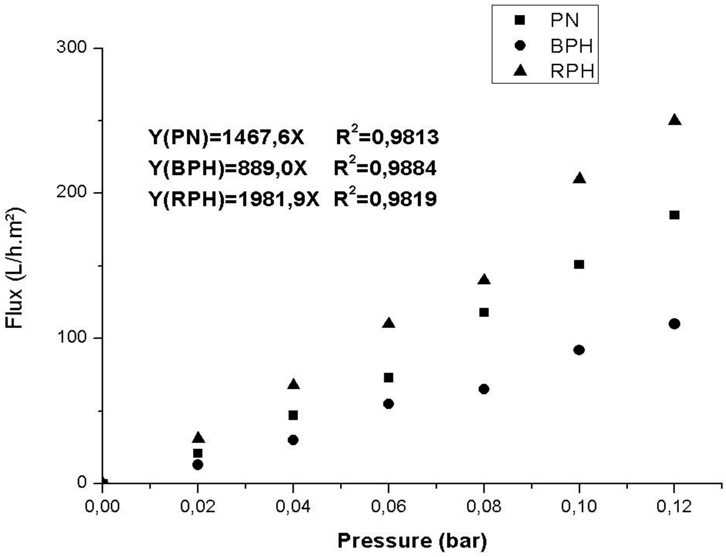

Figure 10: Variation of water flux as a function of transmembrane pressure.

Textile activities generate bearing discharges not only dyes but also other toxic substances, which cause environmental damage. For this reason, elaborated membranes are used to treat the wastewater coming from washing water effluent of Jean process. The test of tangential filtration of textile effluent was carried out using glass pilot. Figure 11 presents the change of permeate of textile effluent with filtration time at pressure of 0.12 bar. As seen for the three membranes, the permeate flux decreases continuously during filtration test. This flux decline is mainly due to the accumulation of suspended particles on the membrane surface. The characteristics of textile effluent before and after filtration are reported in Table 4. Filtration results show that membranes can remove 99.4% of turbidity which is due to suspended solids presented in the effluent, and 30.5% of soluble dyes are retained by these membranes. Values of pH and conductivity are not significantly changed.

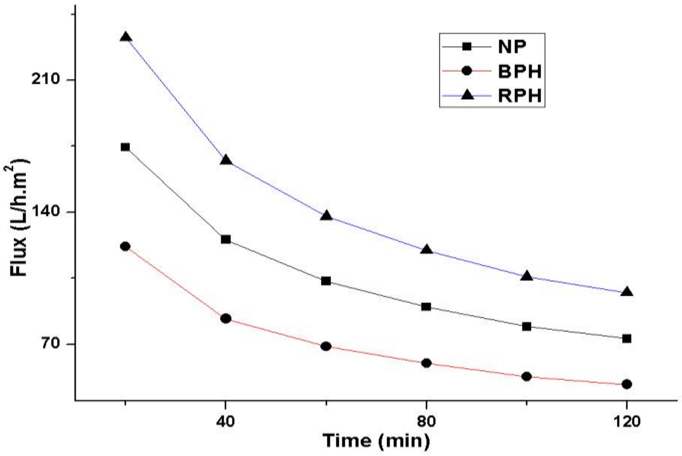

Figure 11: Permeate of textile effluent vs. filtration time.

Table 4: Characteristics of textile effluent before and after filtration.

Sample	pH	Conductivity (µS/cm)	Turbidity (NTU)	Absorbance at 664 nm	R_T (%)	R_{ABS} (%)
Textile effluent	7.70	680	152	0.118	0	0
PN permeate	7.56	661	0.87	0.087	99.4	26.3
BPH permeate	6.98	686	0.46	0.090	99.7	23.7
RPH permeate	7.18	683	0.68	0.082	99.5	30.5

Conclusions

This study reports the elaboration and the characterization of new fat ceramic microfiltration membranes made by a dry process and based on Moroccan natural pozzolans. The analyses of the three raw pozzolans show that all samples are siliceous and aluminous materials with a SiO2/Al2O3 ratio of 3:1. SEM analyses, porosity and mechanical strength results inferred that optimal fired temperature is 950 °C which leaded to a good porous ceramic body, free of defect. Membranes sintered at 950 °C for two hours presented less weight loss in both acid medium and alkali medium. A good mechanical strength was reached in comparison with the other membranes reported in the literature.

Filtration results show that membranes can be used for the treatment of textile effluents generated from Jean washing process and containing suspended solids. They can remove approximately 99% of turbidity. Also these membranes could be used for microfiltration membrane or support to develop ultrafiltration membrane that could be applied to eliminate the total soluble dyes from aqueous solutions.

Acknowledgements - The authors express their thanks to the Moroccan institution of “Hassan II Academy of Science and Technology” ID: ELA5580689, for their financial support. Project name: « Multidisciplinary research on geomaterials and the volcanic geosites of Morocco: Need for their valorization and their utilization in the perspective of a sustainable development » .2012-2015.

References

1. Yeung K.L., Sebastian J.M., Varma A., *J. Membr. Sci.* 131 (1997) 9.
2. Lee S.Y., Lee S.J., Kwon S.J., Yang S.M., Park S.B., *J. Membr. Sci.* 108 (1995) 97.
3. Del Colle R., Fortulan C.A., Fontes S.R., *Ceram. Int.* 37 (2011) 1161.
4. Nagasawa H., Shigemoto H., Kanezashi M., Yoshioka T., Tsuru T., *J. Membr. Sci.* 441 (2013) 45.
5. Falamaki C., Khakpour Z., Aghaie A., *J. Membr. Sci.* 263 (2005) 103.
6. Qiu M., Fan Y., Xu N., *J. Membr. Sci.* 348 (2010) 252.
7. Bouzerara F., Harabi A., Ghouil B., Medjemem N., Boudaira B., Condom S., *Procedia Eng.* 33(2012) 278.
8. Pan Y., Wang T., Sun H., Wang W., *Sep. Pur. Technol.* 89 (2012) 78.
9. Ahmad A.L., Sani N.A.A, Sharif Zein, S.H., *Ceram. Int.* 37 (2011) 2981.
10. Anbri Y., Tijani N., Coronas J., Mateo E., Menéndez M., Bentama J., *Desal.* 221 (2008) 419.
11. Tijani N., Ahlafi H., Smaihi M., El Mansouri A., *Med. J. Chem.* 2 (2013) 484.
12. Masmoudi S., Ben Amar R., Larbot A., El Feki H., Ben Salah A., Cot L., *J. Membr. Sci.* 247 (2005) 1.
13. Masmoudi S., Larbot A., El Feki H., Ben Amar R., *Desal.* 190 (2006) 89.
14. Khemakhem M., Khemakhem S., Ayedi S., Amar R., *Ceram. Int.* 37 (2011) 3617.
15. Li C.F., Zhong S.H., *J. membr. Sci.* 204 (2002) 89.
16. Dong Y., Zhou J., Lin B., Wang Y., Wang S., Miao L., Lang Y., Liu X., Meng G., *J. Hazardous Mater.* 172 (2009) 180.
17. Fang J., Qin G., Wei W., Zhao X., *Sep. Pur. Technol.* 80 (2011) 585.
18. Saffaj N., Alami Y.S., Albizane A., Messouadi A., Bouhria M., Persin M., Cretin M., Larbot A., *Sep. Pur. Technol.* 36 (2004) 107.
19. Saffaj N., Persin M., Younsi S.A., Albizane A., Cretin M., Larbot A., *Appl. Clay Sci.* 31 (2006) 110.
20. Palacio L., Bouzerdi Y., Ouammou M., Albizane A., Bennazha J., Hernández A., Calvo J.I., *Desal.* 245 (2009) 501.
21. Barrouk I, Younssi S.A., Kabbabi A., Persin M., Albizane A., Tahiri S., *Desal. Water Treat.* 55 (2014) 53.
22. Majouli A, Younssi S.A, Tahiri S., Albizane A., Loukili H., Belhaj M., *Desal.* 277 (2011) 61.
23. Majouli A., Tahiri S., Alami Y.S., Loukili H., Albizane A., *Ceram. Int.* 38 (2012) 4295.
24. Nandi B.K., Uppaluri R., Purkait M.K., *Appl. Clay Sci.* 42 (2008) 102.