Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1110722

57 (2016) 20298–20306
September

Taylor & Francis
Taylor & Francis Group

Elaboration and characterization of flat membrane supports from Moroccan clays. Application for the treatment of wastewater

H. Elomari[a,*], B. Achiou[a], M. Ouammou[a], A. Albizane[a], J. Bennazha[a], S. Alami Younssi[a], I. Elamrani[b]

[a]*Laboratory of Materials, Membranes and Environment, Faculty of Sciences and Technologies, University Hassan II Casablanca, BP 146 Mohammedia 20650, Morocco, Tel. +212 523314705; emails: hananeelomari85@hotmail.fr (H. Elomari), achiou.brahim@gmail.com (B. Achiou), mouammou@yahoo.fr (M. Ouammou), albizane@yahoo.com (A. Albizane), jbennazha@yahoo.fr (J. Bennazha), alamiyounssisaad@yahoo.fr (S. Alami Younssi)*
[b]*Department of Earth Sciences, Geomaterials and Geo-Environment Team (Geo M&E), University Mohammed V Agdal, Scientific Institute, Rabat, Morocco, email: izdinelamrani@gmail.com*

Received 4 February 2015; Accepted 7 October 2015

ABSTRACT

In this work, ceramic supports for microfiltration have been made and thoroughly characterized from three Moroccan clays: clay of Meknes (CM), fine clay of Fès (FCF), and granular clay of Fès (GCF). X-ray fluorescence (XRF), X-ray diffraction, and thermogravimetric analysis (TGA) techniques were used to characterize the raw material. Flat disks of 3.6 cm of diameter and 1.5 mm in thickness were prepared from the natural clays: the powder was crushed and sieved to 63 μm. The obtained powder was then pressed without organic additives and without water addition to elaborate a porous structure. Finally, a thermal treatment was carried out in a programmable oven at different final temperatures; the best firing temperature of the support is 950°C. The resulting supports have been characterized by scanning electron microscopy, water porosity, corrosion resistance and mechanical strength. The porosity of the supports CM, FCF, and GCF was, respectively, 28.1, 30.8 and 40%, and the average pore diameter was 1.8 μm for the CM support, 1.50 μm for FCF support and 2.84 μm for GCF support. Elaborated flat supports have been used to treat colored solutions to verify the suitability of such filters in the preclarification step in wastewater treatment for Moroccan industry. Results showed a good retention of turbidity and conductivity for the three elaborated supports.

Keywords: Moroccan clay; Ceramic supports; Microfiltration; Wastewater treatment

1. Introduction

The considerable growth in water consumption in the industry causes significant wastewater production. Several physical, chemical, and biological processes of varying effectiveness can be used to remove pollutants from wastewater without danger to human health or unacceptable damage to the natural environment.

Ceramic membranes are increasingly used in many economic sectors because of their attractive advantages such as, a better chemical and thermal stability, a worthier mechanical resistance, long lifetime and little pollution impact on our environment [1–7].

*Corresponding author.

Research is based on the development of low-cost membranes from natural materials, such as clays, that are in abundance and which need lower firing temperature in comparison with metal oxide materials (alumina, silica, zircon, etc.) and have high flux performance to treat large volumes of liquid effluent [8–13].

The development of microfiltration membranes supported by clay materials, their characterization and valorization in the treatment of solutions containing metal salts and organic dyes has undergone several works of our team [14–19].

Our purpose in this work is to develop new filters made from Moroccan clays. These filters are intended to be used in the industrial wastewater treatment, especially in relevant Moroccan industries such as textiles and tannery.

2. Material and methods

2.1. Clay sampling

The flat membrane supports were elaborated from natural clays extracted from the northern part of Morocco: FCF and GCF belong to a deposit from Fès region located in the eastern lowest part of Saiss basin and CM from Meknès region situated in the center of the same basin. After collecting the raw clay, an important quantity of each sample was crushed for homogenization to provide statistically valid samples. Small quantities were dried at 60°C for 48 h and grounded in an agate mortar for further analysis.

2.2. Preparation of support

The process of the ceramic preparation is described in Fig. 1. The powder was crushed and sieved to 63 μm. The obtained powder was spread out in a stainless steel mold then pressed without any additives at 10 kg/m^2 using a hydraulic press for 15 min.

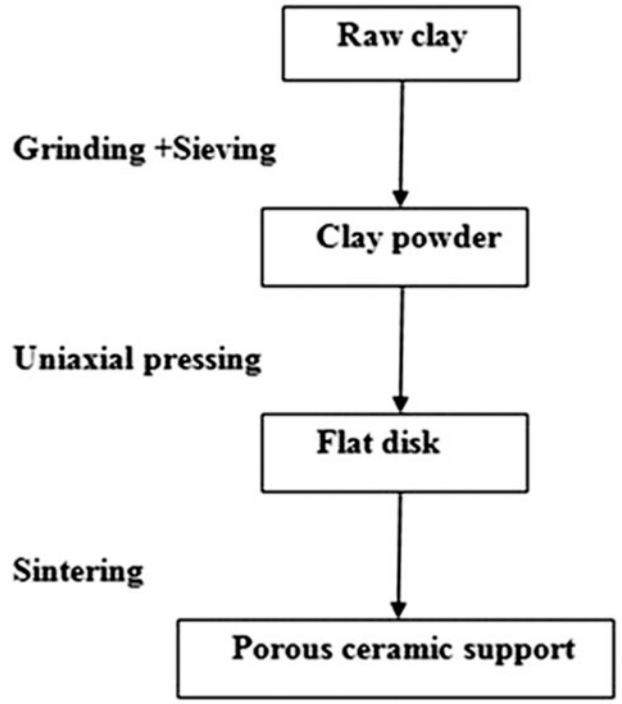

Fig. 1. Simplified diagram for elaboration of porous supports by uniaxial pressing method.

The porosity and mechanical strength are strongly related to the sintering process, the main factors that influence this step are the final temperature of sintering and final sintering time. The thermal program used in this work is shown in Fig. 2. The heating program ended at 950°C, with plateaus at 250, 750, and

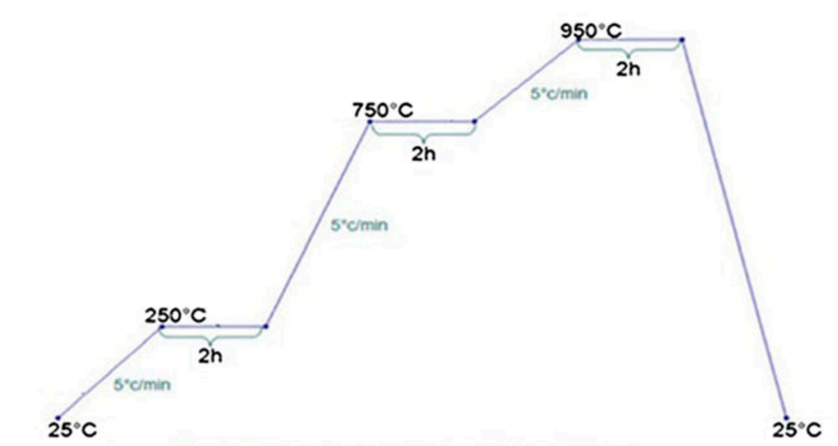

Fig. 2. Diagram of the thermal program.

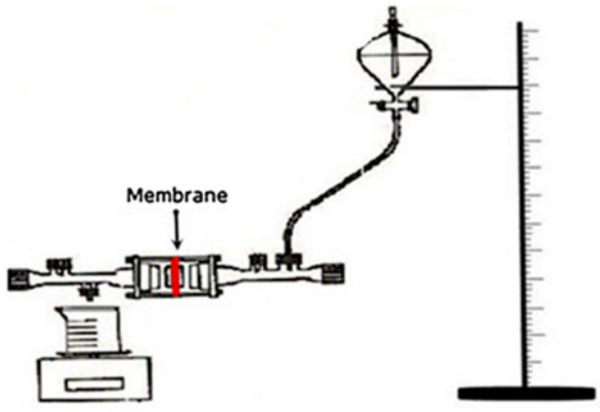

Fig. 3. Laboratory setup for low-pressure MF.

Table 1
Chemical composition of the clays (wt.%)

Clay	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	Lo.I[a]
CM [20]	47.17	10.88	4.98	2.80	1.39	14.62	19.4
FCF	41.28	12.29	4.131	2.803	1.736	14.23	20.2
GCF	46.76	10.07	3.976	2.462	1.502	14.58	18.2

[a]Lo.I: loss on ignition at 1,000˚C.

950˚C, being enough to get a stable structure using a programmable oven (Nabertherm L9/13/P320).

2.3. Filtration test

The filtration tests were performed on a laboratory-scale filtration pilot shown in Fig. 3. The support

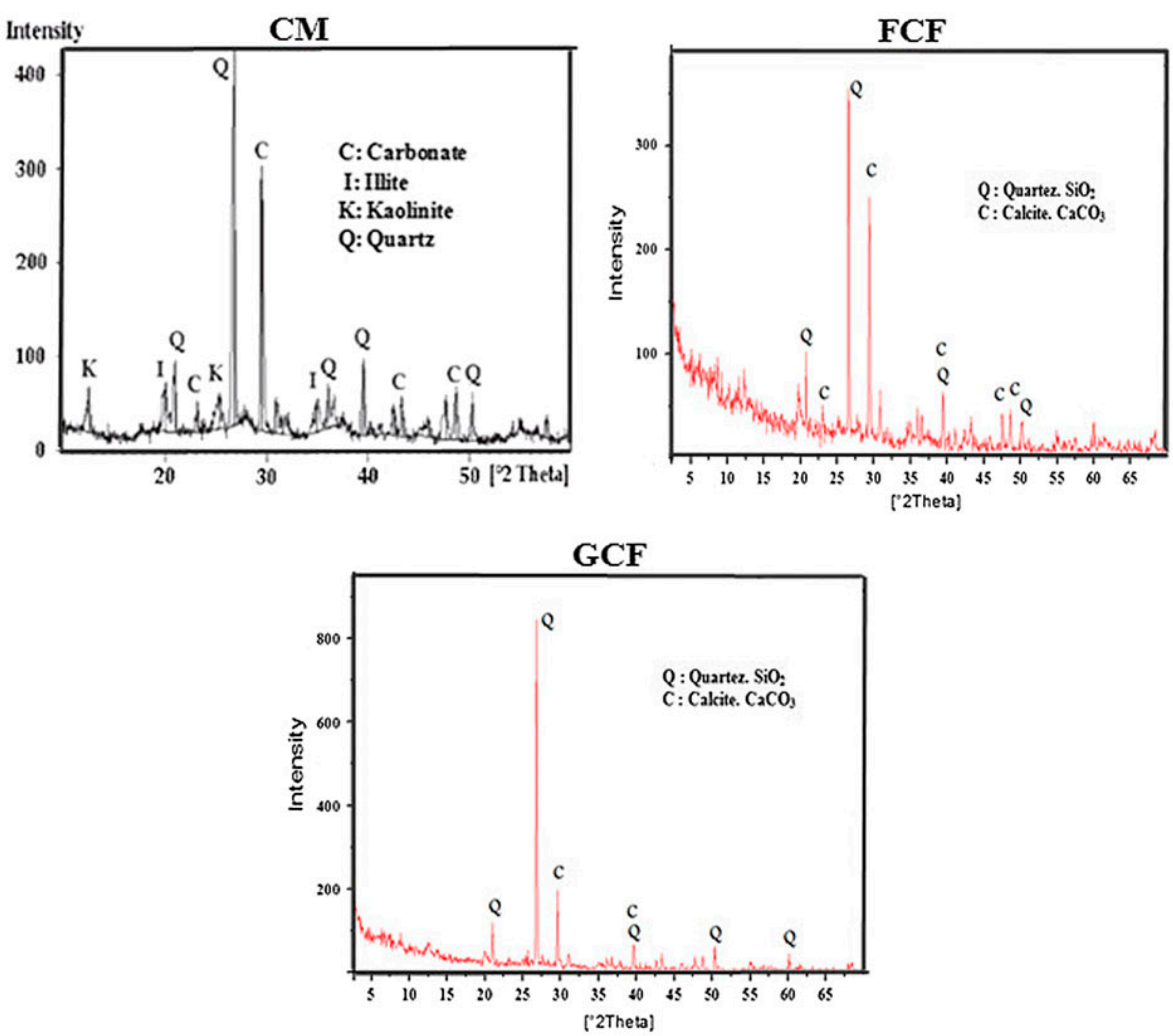

Fig. 4. X-ray diffractograms of clays (CM Anbri et al. [20], FCF and GCF).

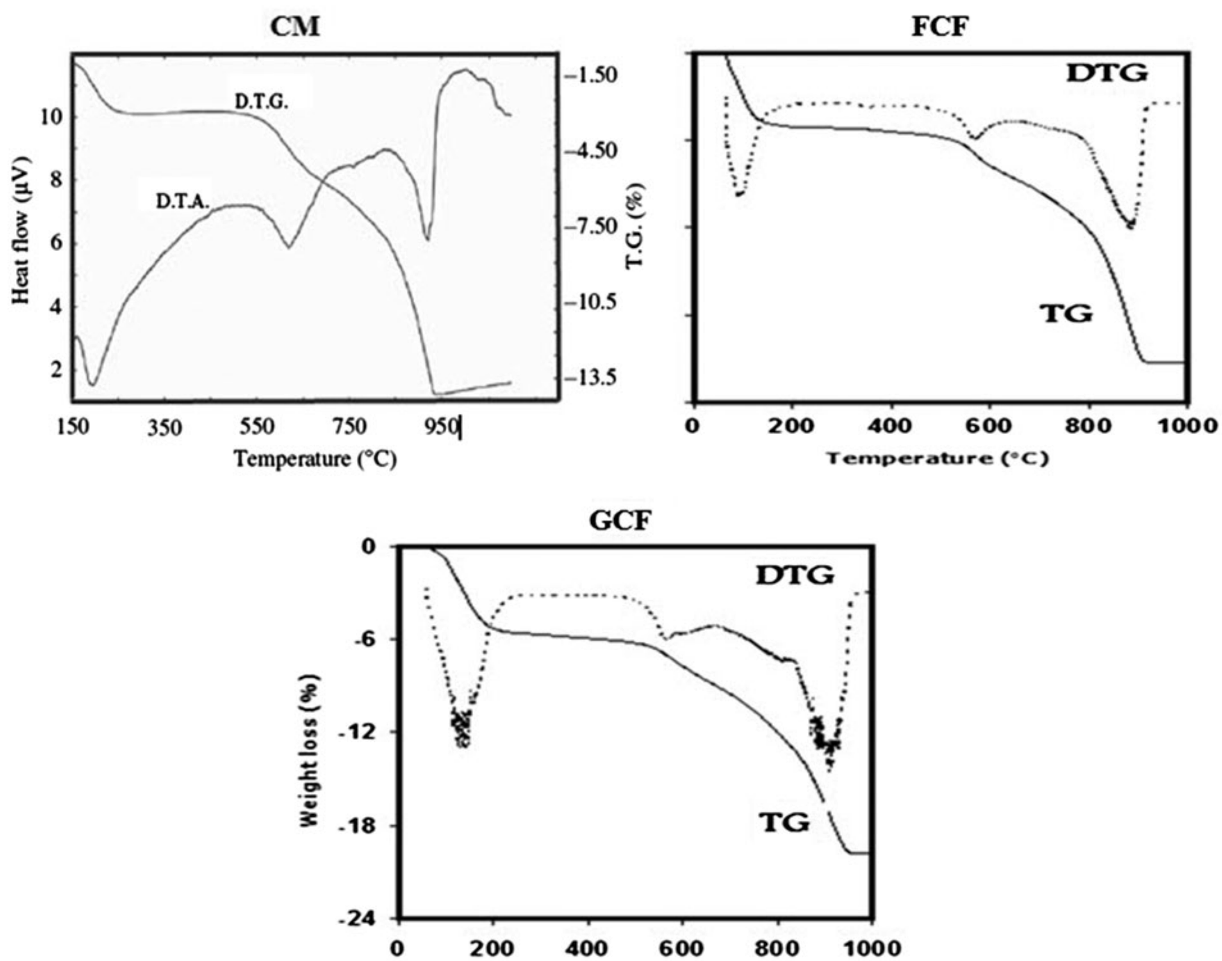

Fig. 5. Thermogravimetric analysis of clays (CM [Anbri et al. [20]], FCF and GCF).

with a filtration area of 10.2 cm^2 and a thickness of 1.5 mm is placed in the membrane housing and the water is filled in the system from the top. The supports were conditioned by immersing them in pure deionized (DI) water for 24 h before filtration tests. The temperature was set to 25 ± 2˚C. The pure water permeability of support was first studied. This test is carried out with distilled water to prevent clogging of the pores and hence decreased permeability. The fluxes were measured at different pressures (0, 0.04, 0.06, 0.08, 0.1, and 0.12 bar). The clarification of tanning industry effluent was carried out in the flat support at Δp = 0.12 bar for two hours.

2.4. Analyses

For CM clay, X-ray diffraction (XRD), differential thermal analysis (DTA), gravimetric thermal analysis (GTA) and fluorescence data already obtained by Anbri et al. in a previous work [20]. CM clay was extracted from the same deposit that has been the subject of those analyses.

Powders of FCF and GCF of Fès region were characterized by XRD, chemical analysis, and thermogravimetric analysis (TGA/DTG). The XRD analysis were carried out using a Philips X'Pert PRO diffractometer operating with Cu Kα radiations (Kα = 1.5418 Å). The chemical composition of samples FCF, and GCF was determined by X-ray fluorescence. A sequential spectrometer of XRF based on a scattering of wavelength was used. It is equipped with a channel of measure based on only one goniometer covering the complete range of measure of (Be to U). The sample preparation is based on the pearls protocol. Thermogravimetric analysis (TGA/DTG) studies were performed using a thermobalance of Versa Therm type. The temperature was increased from room temperature to 1,000˚C at a constant rate of 10˚C/min.

Apparent porosity was measured in accordance with ASTM C373-88 method [21]. Mechanical strength was measured in a three-point bending load method according to ASTM C674-88 [22].

Chemical resistant of supports was evaluated by weight loss in hydrochloric acid and soda solutions at 0.1 M.

The morphology and surface quality of elaborated supports were examined by scanning electron microscopy (SEM) (Hitachi, S-4500). The pore size was estimated by image processing of SEM pictures using ImgeJ software (Version 1.44e).

The microfiltration membrane tests have been applied to wastewater treatment coming from the tanning industry. Turbidity was measured using HACH 2100Q is Portable Turbidimeter. pH and conductivity of the effluent and permeate solution were measured directly using a Fisher Scientific accumet BasicAB15 pH Meter (USA) and a Conductivity Meter Model 101 (Orion Research, Cambridge, MA, USA), respectively.

3. Results and discussion

3.1. Clay powder characterization

Chemical analysis of raw clays was determined by X-ray fluorescence. Table 1 shows that samples CM, FCF, and GCF have a similar chemical composition with slightly higher quantities of SiO_2 for CM and Al_2O_3 for FCF. Besides, the presence of the iron oxide (4.98% in CM, 4.131% in FCF, and 3.976% in GCF) explains the rust color of the clays (CM, FCF, and GCF, respectively).

XRD diffractograms of the three clays (Fig. 4) indicate that Quartz and calcite are the major constituents of the minerals present in these clays.

The thermogravimetric analysis of samples CM, FCF, and GCF, shown in Fig. 5, indicates three important weight losses: The first one is located between 25 and 200˚C, the second one between 250 and 750˚C, and the third one between 800 and 950˚C. The first loss is due to the removal of adsorbed surface water and the second one corresponds to the loss of the water of structure, whereas the third loss is due to the decomposition of carbonates.

3.2. Characterization of the supports

Table 2 shows that the diameter of the elaborated flat supports (CM, FCF, and GCF) decreases from 4 cm to 3.8, 3.9, and 3.88 cm, respectively, after sintering at 950˚C; this is due to the shrinkage phenomena. While the loss in mass does not exceed 25% for the three supports. Fig. 6 shows the change of the coloration caused by the oxidation of the Fe^{2+}.

Table 2
The shrinkage and loss in mass of the elaborated supports after sintering at 950˚C

Parameter	CM (%)	FCF (%)	GCF (%)
Shrinkage	5.26	2.5	3
Loss in mass	21	22	25

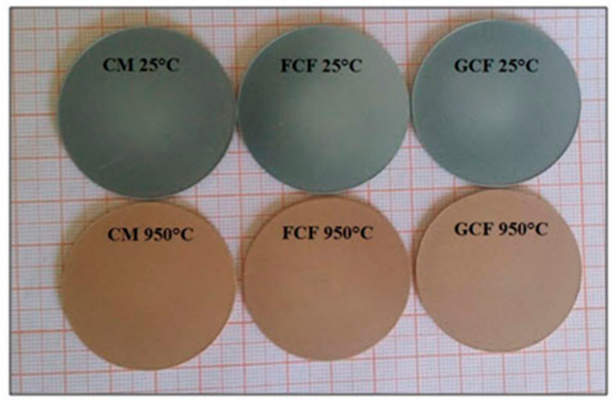

Fig. 6. Flat supports views after pressing (25˚C) and after sintering at 950˚C.

The porosity of the supports (CM, FCF, and GCF) (Fig. 7) increases from 28.15, 28.4, and 27.2%, respectively, at the temperature of 850˚C to 31.1, 31.8, and 40%, respectively, at the temperature of 950˚C, then decreases to 24.7, 25.3, and 26.5%, respectively, at the temperature of 1,050˚C. The first part of the curves

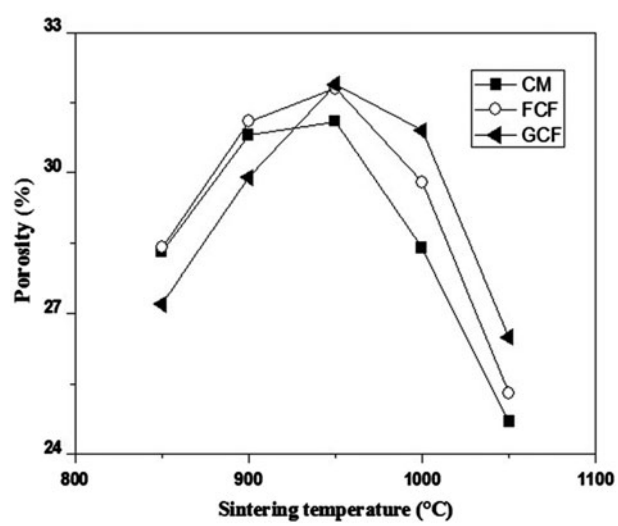

Fig. 7. Variation of porosity vs. the sintering temperature of CM, FCF, and GCF supports.

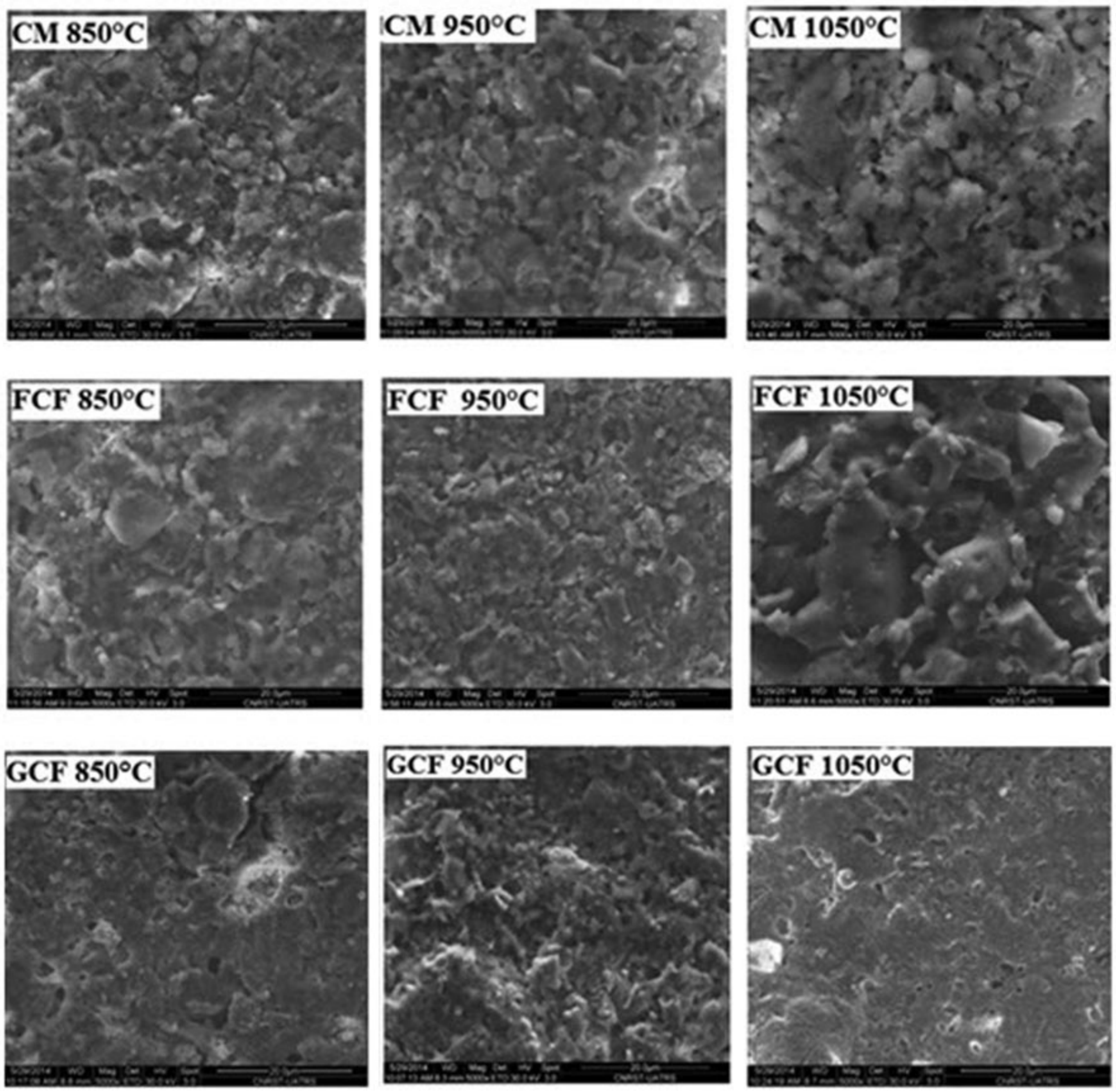

Fig. 8. SEM images of (CM, FCF, and GCF) supports sintered at 850, 950, and 1,050˚C.

corresponds to an opening of the pores with temperature, whereas the last part is caused by the beginning of the material densification [23].

The SEM micrographs reported on Fig. 8 show the surface of flat supports sintered at different temperatures and give information on the texture of the surface of the elaborated supports as a function of the temperature treatment (850, 950, and 1,050˚C). Micrographs indicate that the effect of sintering is very marked; a progressive reduction of porosity can be observed when temperature increases. At 1,050˚C, the phenomenon of melting starts and an important decrease in the porous volume is observed.

In order of evaluating the corrosion resistance parameter of the sintered supports (CM, FCF, and GCF) at 950˚C, two different solutions were used: hydrochloric acid and soda solutions at 0.1 M. The results reported in Fig. 9 show that flat supports (CM, FCF, and GCF) present a good chemical resistance in basic medium than in acidic medium. For a week of treatment, the weight loss for the flat supports CM, FCF, and GCF does not exceed, respectively, 3, 2, and 1 wt.% in basic medium, however, in acid medium, the weight loss can reach, respectively, 10, 11, and 14 wt.%. This is in agreement with typical physical properties of clays that they are effervescent with acids due to the strong presence of limestone.

The mechanical strength of the supports CM, FCF, and GCF is performed using the three points bending

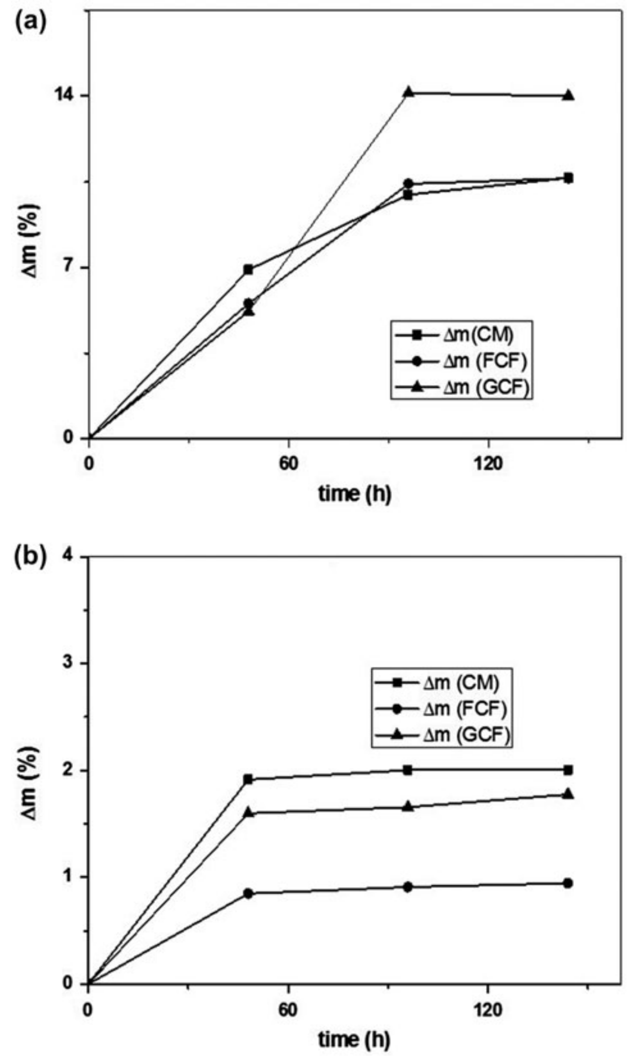

Fig. 9. Weight loss of samples in acidic medium (a) and basic medium (b).

strength method, it was respectively: 14.80, 16.13, and 14.42 MPa.

3.3. Determination of support permeability

Water permeability is a crucial parameter for defining the operating conditions. This test is carried out with distilled water to prevent clogging of the pores, hence the decease in the permeability. The fluxes are measured at different pressures (0, 0.04, 0.06, 0.08, 0.1, and 0.12 bar). The stabilization of the water flux through the support takes approximately 100 min. Experiments show also that the water flux through the support depends on the applied pressure. The average support permeability determined using pure distilled water for the flat supports CM, FCF, and GCF is, respectively: 353, 453, and 850 L/h m^2 bar (Fig. 10).

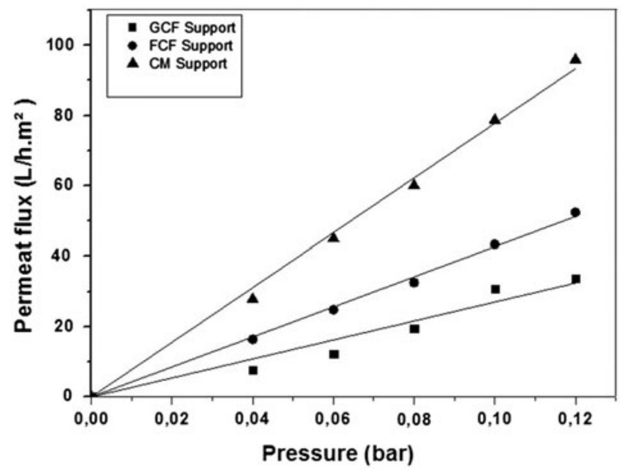

Fig. 10. Variation of water flux as a function of pressure.

3.4. Application to the treatment of dye tannery wastewater

The clarification of tanning industry effluent was carried out in the flat supports at $\Delta p = 0.12$ bar for two hours. This test was performed as a clue to determine the response of membranes to waste water filtration. Permeate was characterized by measuring pH, turbidity, conductivity and absorbance at 540 nm. The average effluent quality (before and after microfiltration treatment) is illustrated in Table 3. Microfiltration using FCF support proved to be effective in removing the turbidity, the pH remains unchanged (in the field of neutrality) for microfiltration using CM support; however, it will increase using FCF and GCF supports.

Table 3
Characteristics of the effluent before and after microfiltration at 0.12 bar with the CM, FCF, and GCF membranes

Sample	Conductivity (μs/cm)	Turbidity (NTU)	pH
Effluent	13.7	600	7.35
CM membrane	5.47	57	7.74
FCF membrane	3.4	29	9.91
GCF membrane	6.55	97	11.4

The elimination of conductivity is important: 60% for CM, 75% for FCF, and 52% for GCF.

4. Conclusion

In this work, low-cost ceramics support of microfiltration were prepared from Moroccan clays that are in abundance and need lower firing temperature in comparison with metal oxide materials. Several techniques were used to characterize the raw material (XRF, XRD, and TGA). After the step of grinding and sieving; the supports were elaborated from clays in powder state by uniaxial pressing method without organic additives and without water addition. Resulting disks were sintered at 950˚C.

The structural properties of CM, FCF, and GCF supports are satisfying in terms of porosity (28.1, 30.8, and 40%, respectively), and pore diameter (1.8, 1.50, and 2.84 μm respectively) were so attractive. The supports present a well chemical resistance in basic medium than in acidic medium. The SEM analysis shows that the surface of the elaborated supports has a good morphology without defects, more over the effect of sintering is very marked, a progressive reduction in volume porous is observed when the temperature increases, the phenomenon of fusion starts at 1,050˚C leading to an important decrease of the porous volume.

Result of the filtration test showed a good retention of turbidity and conductivity for the three elaborated supports.

The objective of our works in course is, on the one hand, the study of the effect of the addition of natural ash and fly ash on the characteristics of membrane supports CM, FCF, and GCF (porosity, permeability, …) and, on the other hand, the deposition of oxides materials layer on elaborated support surface to obtain ultrafiltration membrane.

References

[1] R. Sahnoun, S. Baklouti, Characterization of flat ceramic membrane supports prepared with kaolin-phosphoric acid-starch, Appl. Clay Sci. 83–84 (2013) 399–404.

[2] A. Harabi, F. Zenikheri, B. Boudaira, F. Bouzerara, A. Guechi, L. Foughali, A new and economic approach to fabricate resistant porous membrane supports using kaolin and $CaCO_3$, J. Eur. Ceram. Soc. 34 (2014) 1329–1340.

[3] J. Fang, G. Qin, W. Wei, X. Zhao, L. Jiang, Elaboration of new ceramic membrane from spherical fly ash for microfiltration of rigid particle suspension and oil-in-water emulsion, Desalination 311 (2013) 113–126.

[4] R.D. Colle, C.A. Fortulan, S.R. Fontes, Manufacture and characterization of ultra and microfiltration ceramic membranes by isostatic pressing, Ceram. Int. 37 (2011) 1161–1168.

[5] S. Jana, M.K. Purkait, K. Mohanty, Preparation and characterization of low-cost ceramic microfiltration membranes for the removal of chromate from aqueous solutions, Appl. Clay Sci. 47 (2010) 317–324.

[6] Y. Dong, X. Feng, D. Dong, S. Wang, J. Yang, J. Gao, X. Liu, G. Meng, Elaboration and chemical corrosion resistance of tubular macro-porous cordierite ceramic membrane supports, J. Membr. Sci. 304 (2007) 65–75.

[7] B.K. Nandi, R. Uppaluri, M.K. Purkait, Preparation and characterization of low cost ceramic membranes for micro-filtration applications, Appl. Clay Sci. 42 (2008) 102–110.

[8] I. Barrouk, S. Alami Younssi, A. Kabbabi, M. Persin, A. Albizane, S. Tahiri, New ceramic membranes from natural Moroccan phosphate for microfiltration application, Desalin. Water Treat. 55(1) (2015) 53–60.

[9] N. Baraka, N. Saffaj, R. Mamouni, A. Laknifli, S. Younssi, A. Albizane, M. El Haddad, Elaboration of a new flat membrane support from Moroccan clay, Desalin. Water Treat. 52 (2014) 1357–1361.

[10] S. Khemakhem, A. Larbot, R. Ben Amar, New ceramic microfiltration membranes from Tunisian natural materials: Application for the cuttlefish effluents treatment, Ceram. Int. 35 (2009) 55–61.

[11] Y. Dong, J. Zhou, B. Lin, Y. Wang, S. Wang, L. Miao, Y. Lang, X. Liu, G. Meng, Reaction-sintered porous mineral-based mullite ceramic membrane supports made from recycled materials, J. Hazard. Mater. 172 (2009) 180–186.

[12] S. Masmoudi, A. Larbot, H. El Feki, R. Ben Amar, Elaboration and properties of new ceramic microfiltration membranes from natural and synthesised apatite, Desalination 190 (2006) 89–103.

[13] S. Masmoudi, R. Ben Amar, A. Larbot, H. El Feki, A. Salah, L. Cot, Elaboration of inorganic microfiltration membranes with hydroxyapatite applied to the treatment of wastewater from sea product industry, J. Membr. Sci. 247 (2005) 1–9.

[14] A. Majouli, S. Younssi, S. Tahiri, A. Albizane, H. Loukili, M. Belhaj, Characterization of flat membrane support elaborated from local Moroccan Perlite, Desalination 277 (2011) 61–66.

[15] L. Palacio, Y. Bouzerdi, M. Ouammou, A. Albizane, J. Bennazha, A. Hernández, J.I. Calvo, Ceramic membranes from Moroccan natural clay and phosphate for industrial water treatment, Desalination 245 (2009) 501–507.

[16] N. Saffaj, M. Persin, S. Younssi, A. Albizane, M. Bouhria, H. Loukili, H. Dach, A. Larbot, Removal of salts and dyes by low ZnAl2O4–TiO2 ultrafiltration membrane deposited on support made from raw clay, Sep. Purif. Technol. 47 (2005) 3642.

[17] N. Saffaj, S. Younssi, A. Albizane, A. Messouadi, M. Bouhria, M. Persin, A. Larbot, Elaboration and properties of TiO_2–$ZnAl_2O_4$ ultrafiltration membranes deposited on cordierite support, Sep. Purif. Technol. 36 (2004) 107–114.

[18] N. Saffaj, S. Younssi, A. Albizane, A. Messouadi, M. Bouhria, M. Persin, A. Larbot, Preparation and characterization of ultrafiltration membranes for toxic

removal from wastewater, Desalination 168 (2004) 259–263.

[19] H. Loukili, S. Alami Younssi, M. Ouammou, A. Albizane, M. Persin, A. Larbot, Filtration de solutions salines et de colorants sur membranes d'ultrafiltration en $ZnAl_2O_4$–TiO_2 déposée sur support d'argile (Filtration of saline solutions and dye on ultrafiltration membranes $ZnAl_2O_4$–TiO_2 deposited on clay support), Récent. Prog. Gén. Proc. 93 (2006) P37-1, P37-8.

[20] Y. Anbri, N. Tijani, J. Coronas, E. Mateo, M. Menéndez, J. Bentama, Clay plane membranes: Development and characterization, Desalination 221 (2008) 419–424.

[21] ASTM C674-88, Standard test method for water absorption, bulk density, apparent porosity, and apparent specific gravity of fired white ware products.

[22] ASTM C674-88, Standard test methods for flexural properties of ceramic white ware.

[23] N. Saffaj, M. Persin, S. Younsi, A. Albizane, M. Cretin, A. Larbot, Elaboration and characterization of microfiltration and ultrafiltration membranes deposited on raw support prepared from natural Moroccan clay: Application to filtration of solution containing dyes and salts, Appl. Clay Sci. 31 (2006) 110–119.