

New ceramic microfiltration membranes from Tunisian natural materials: Application for the cuttlefish effluents treatment

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Received 3 November 2006; received in revised form 18 April 2007; accepted 12 September 2007

Available online 1 February 2008

Abstract

New microfiltration membranes from Tunisian natural materials are obtained using ceramic method. Paste from Tunisian silty marls refereed (M_{11}) is extruded to elaborate a porous tubular configuration used as supports. The support heated at 1190 °C, shows an average pore diameters and porosity of about 9.2 μm and 49%, respectively. The properties in term of mechanical and corrosion resistances are very interesting. The elaboration of the layer based on Tunisian clay refereed (JM_{18}) is performed by slip-casting method. The heating treatment at 900 °C leads to an average pore size of 0.18 μm . The water permeability determined of this membrane is 867 $\text{l h}^{-1} \text{m}^{-2} \text{bar}^{-1}$. This membrane can be used for crossflow microfiltration. The application to the cuttlefish effluent clarification shows an important decrease of turbidity (inferior to 1 NTU) and chemical organic demand (COD) values (retention rate of about 65%). So, it seems that the prepared membrane is suitable for such wastewater treatment.

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Keywords: D. Clay; E. Membrane; Ceramic; Microfiltration; Silty marls; Cuttlefish effluent

1. Introduction

Interest in separation by the use of membranes has rapidly increased during the last 10–15 years. The membrane technologies are utilized in various fields: chemistry, food, biotechnology and recently wastewater treatment [1]. For economic consideration, a great deal of research has been devoted to the development of new type of inorganic membranes, which have displayed improved resistance to heat, chemicals and corrosion. Rapid development and innovation have already been realised in this area [2–4].

Clay minerals have well-known structural adsorption, rheological and thermal properties [5,6]. Research on clay as a membrane material has concentrated mainly on pillared clays [7,8]. Studies of membranes prepared entirely from clay have just started [9–12].

The industry of conservation of sea products is very important in Tunisia. It produces a great amount of wastewater which is generally rejected in the littoral and then is responsible for an enormous pollution, by supporting the eutrophication phenomenon [13].

Before freezing, the cuttlefish must be washed to eliminate black colour caused by the ink contained in the animal bag, resulting in highly coloured wastewater [14].

In this study, we investigate the development of ceramic membranes based on Tunisian natural materials which are in abundance and need lower firing temperature in comparison with metal oxide materials. The prepared microfiltration membranes were used for the treatment and the decoloration of cuttlefish effluent.

2. Experimental results

Microfiltration ceramic membranes were developed and prepared in the laboratory. They consist of a clay skin layer prepared by slip-casting method [16,17] deposited on a silty marls support.

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Table 1
Composition of silty marls (M_{11})

Elements (%)	M_{11}
SiO ₂	31.61
Al ₂ O ₃	10.38
Fe ₂ O ₃	6.53
CaO	24.17
MgO	19.92
Na ₂ O	2.21
K ₂ O	3.43
TiO ₂	1.55

2.1. Support shaping and characterisation

For this study, the supports were prepared from Tunisian silty marls (M_{11}). The chemical composition of these materials is shown in Table 1. The chemical analysis reveals that this kind of silty marls is essentially formed with a great amount of silica and calcium oxide. Fig. 1 presents the XRD patterns of raw silty marls, it shows that quartz (Q) is the main crystalline mineral present in this powder.

The particle size analysis of the powder after crushing for 2 h with the assistance of a planetary crusher at a rate of 250 revolutions/min and calibrated with 100 μ m was determined using a Particle Sizing Systems (Inc. Santa Barbara, California, USA Model 770 AccuSizer). The particle diameters range varied from 0.5 to 54 μ m (Fig. 2).

Plastic pastes are prepared from ceramic powder of silty marls mixed with organic additives:

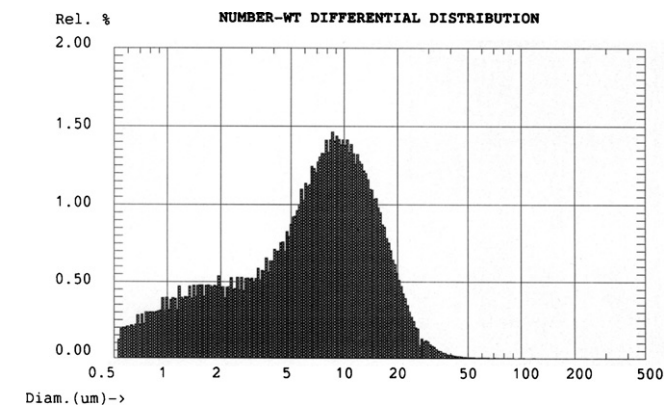


Fig. 2. Silty marls (M_{11}) particle size distribution.

- 4% (w/w) of Amijel: pregelated starch, as plasticizer (Cplus 12072, cerestar).
- 4% (w/w) of Methocel: cellulose derivative, as binder (The Dow Chemical Company).
- 8% (w/w) of starch of corn as porosity agent (RG 03408, Cerestar).
- 25% (w/w) of water.

The rheological properties must be studied to obtain a paste allowing shaping by extrusion process [18]. Fig. 3 shows the different configurations of tubes extruded in our laboratory (two monochannel of different diameter and one multichannel tube).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with simultaneous DSC–TGA 2960 TA instrument. The sample was heated at room temperature to 1250 °C at a rate of 5 °C/min under static atmospheric conditions. Two endothermic peaks were detected (Fig. 4). First peak appears at 51.38 °C, due to a weight loss of 1.81% of the initial weight. It corresponds to the departure of water (moisture or adsorption) due to attraction on the surface of the sample and zeolitic water inserted between the layers or in the cavities of the crystalline structure. Second peak which maximum appears toward 749.87 °C corresponds to the dehydroxylation.

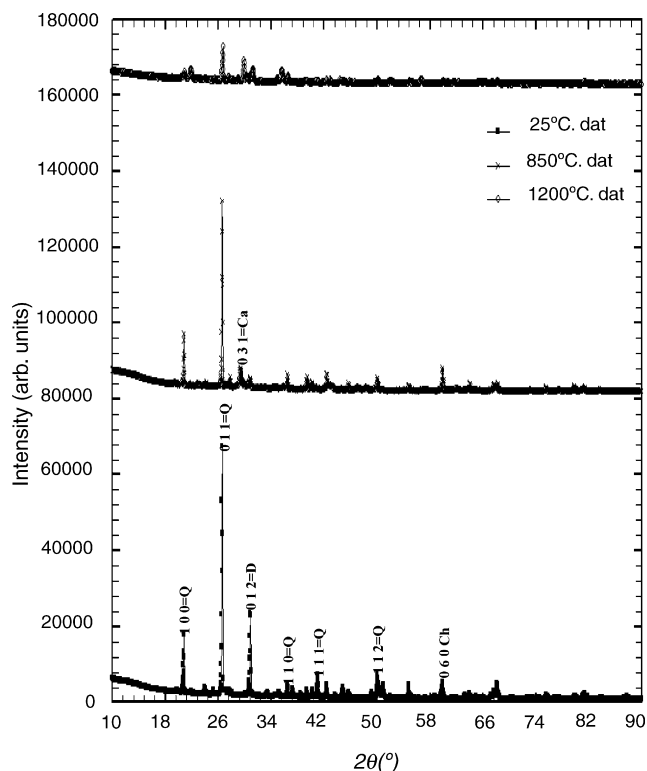


Fig. 1. X-ray diffractograms of the silty marls sample at different temperatures (Q = quartz, Ca = calcite, Ch = chlorite, D = dolomite).



Fig. 3. A photograph of variety of configurations of porous ceramic supports.

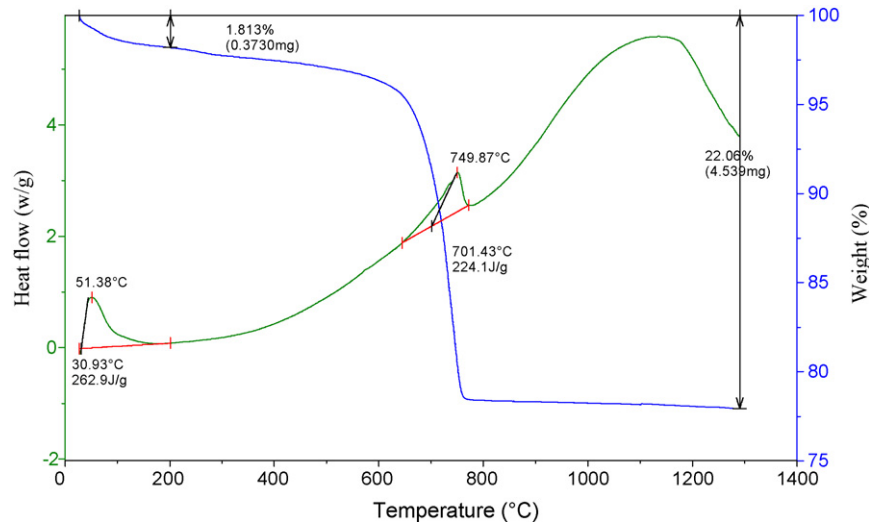


Fig. 4. Thermal analysis curve: DSC and TGA for silty marls powder.

Sintering experiments of the support were carried out in air. Two steps has been realised: the first for the elimination of organic additives at 250 °C, and the second for the sintering at 1190 °C. The temperature–time schedule not only affects the pore diameters and porous volume of the final product but also determines the final morphology and mechanical strength. By controlling the sintering temperature of the ceramic, it is possible to increase the pore size and to obtain a higher mechanical strength. We have also observed that the obtained silty marls support presents the highest mean pore diameter for the highest mechanical strength: the support fired at 1190 °C and characterised by mercury porosimetry showed mean pore diameters and porosity of about 9.2 μm and 49%, respectively (Fig. 5). It can also be observed that the porosity and the pore size parameters are strongly dependent on the sintering temperature and particle size of the powders (Table 2).

2.2. Membrane shaping and characterisation

The material used for the membrane preparation is a Tunisian clay powder (JM₁₈) taken from the area of Sidi Bouzid

(Central Tunisia). This powder is crushed for 4 h with a planetary crusher at 250 revolutions/min and calibrated with 50 μm . The obtained particle diameters range from about 0.5 to 23 μm (Fig. 6).

The chemical composition of the clay (JM₁₈) is shown in Table 3. It reveals that this material is essentially formed with a large amount of silica 62.64%.

For preparing a microfiltration layer with JM₁₈, the suspended powder technique was used. A deflocculated slip was obtained by mixing 5% (w/w) of JM₁₈, 30% (w/w) of polyvinyl alcohol (PVA) (12% w/w aqueous solution) as binder and water (65% w/w). The thickness of microfiltration layer can be controlled by the percentage of the clay powder added to the suspension and the deposition time.

The viscosity of the slip elaborated according to the protocol described previously has been studied right before deposition. The used viscosimeter (LAMY, TVe-05) permits to use 5 speeds of rotation for the determination of the dynamic viscosity of the substance to characterize.

Fig. 7 shows the rheogram of the slip used. It is done by the curve of shear stress (τ) versus speed of rotation (D). The slip

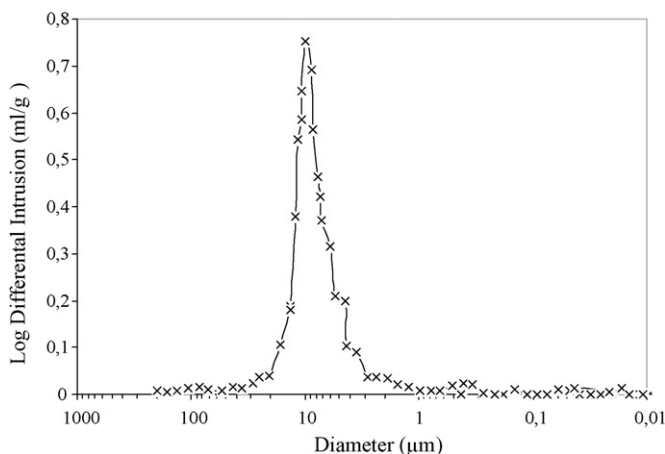
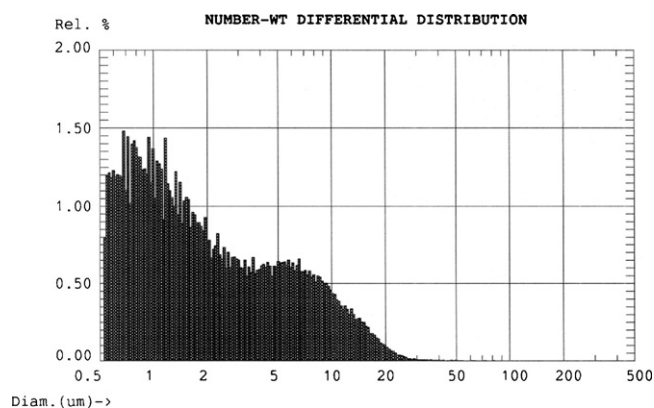
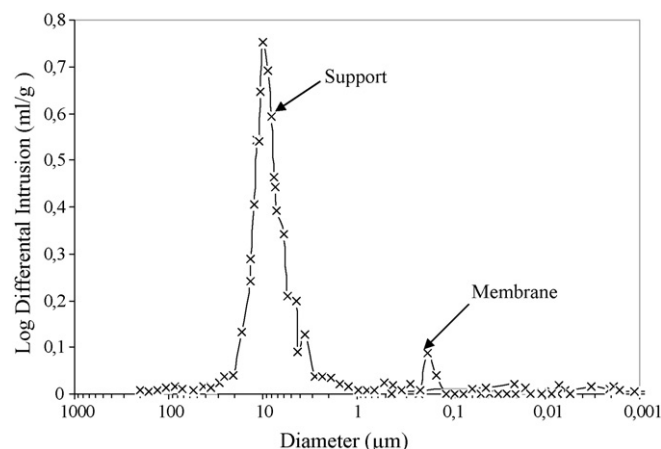


Fig. 5. Pore diameters of the silty marls supports.

Table 2

Variation of pore size and porous volume according to the powder particle sizes for the silty marls (M₁₁)

Powders	Temperature (°C)	Pore size (μm)	Porous volume (%)
Crushed during 1 h and calibrated with 125 μm	1160	9.6	58
	1170	10.9	56
	1180	12.8	53
	1190	14.3	52
	1200	16.5	51
Crushed during 2 h and calibrated with 100 μm	1160	5.9	52
	1170	7.3	50
	1180	8.5	49
	1190	9.2	49
	1200	12.5	46

Fig. 6. Clay (JM₁₈) particle size distribution.Fig. 8. Pore diameters of the clay (JM₁₈) membrane.Table 3
Composition of clay (JM₁₈)

Elements (%)	JM ₁₈
SiO ₂	62.64
Al ₂ O ₃	17.09
FeO ₃	8.5
MgO	0.07
Na ₂ O	0.32
K ₂ O	4.8
Mn ₂ O ₃	0.02
SO ₃	0.4
Loss on the ignition	6.16

has a plastic behaviour of Bingham, controlled by the presence of PVA; the value of the limiting shear stress is 4 mPa. Such behaviour permits the maintenance of particles in a stable suspension.

The deposition of the slip on the M₁₁ support was performed by slip-casting using a deposition time between 10 and 15 min. After drying at room temperature for 24 h. The clay membrane was sintered at 900 °C for 2 h, after debonding at 250 °C for 1 h.

Total porous volume and pore size distribution are measured by mercury porosimetry. This technique relies

on the penetration of mercury into a membrane's pores under pressure. The intrusion volume is recorded as a function of the applied pressure and then the pore size was determined. The pore diameters measured were centered near 0.18 μm (Fig. 8). The pore size in the microfiltration layer can also be varied using powders with different particle size distributions.

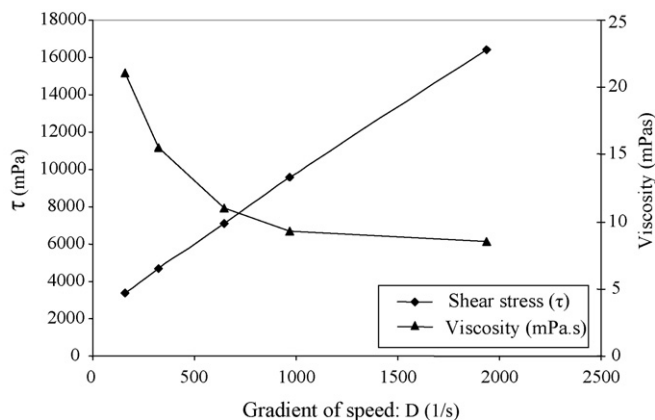
Different microfiltration membranes with different layers thickness (between 5 and 50 μm) were prepared. SEM (scanning electron microscopy) images of the resulting membranes are shown in Fig. 9. This figure gives information on the texture of the elaborated membrane surface. A defect free membrane was only obtained for membrane thickness less than 10 μm (in order to 7 μm).

Crossflow microfiltration tests were performed using a home-made pilot plant (Fig. 10) at a temperature of 25 °C and transmembrane pressure (TMP) range between 1 and 4 bar. The flow rate was fixed at 2.5 m s⁻¹. Before the tests, the membrane was conditioned by immersion in pure deionised water for a minimum of 24 h. The working pressure was obtained using a nitrogen gas source. The membrane was initially characterized by the determination of water permeability which was 870 l h⁻¹ m⁻² bar⁻¹ (Fig. 11).

2.3. Application for cuttlefish effluents treatment

Membrane processes can be used for the treatment of wastewater produced by the sea products conditioning [19]. In our case, the prepared microfiltration membranes have been applied to the cuttlefish effluent produced from cuttlefish conditioning and freezing process. The used samples were collected from a sea product-freezing factory located in Sfax (Tunisia). The dark colour in this type of effluent was due to the presence of particles in suspension (sepia ink), which has a size range between 56 and 161 nm [15].

Fig. 12 gives the variation of permeate flux with transmembrane pressure which is done by: $(P_{\text{inlet}} + P_{\text{outlet}})/2 - P_f$ where: P_{inlet} and P_{outlet} are respectively the inlet and the outlet pressures across the filtration module. Permeate flux increased linearly with transmembrane pressure until a value of 2 bar and

Fig. 7. Evolution of the stress (τ) and the viscosity (μ) vs. deformation of clay (JM₁₈) slip.

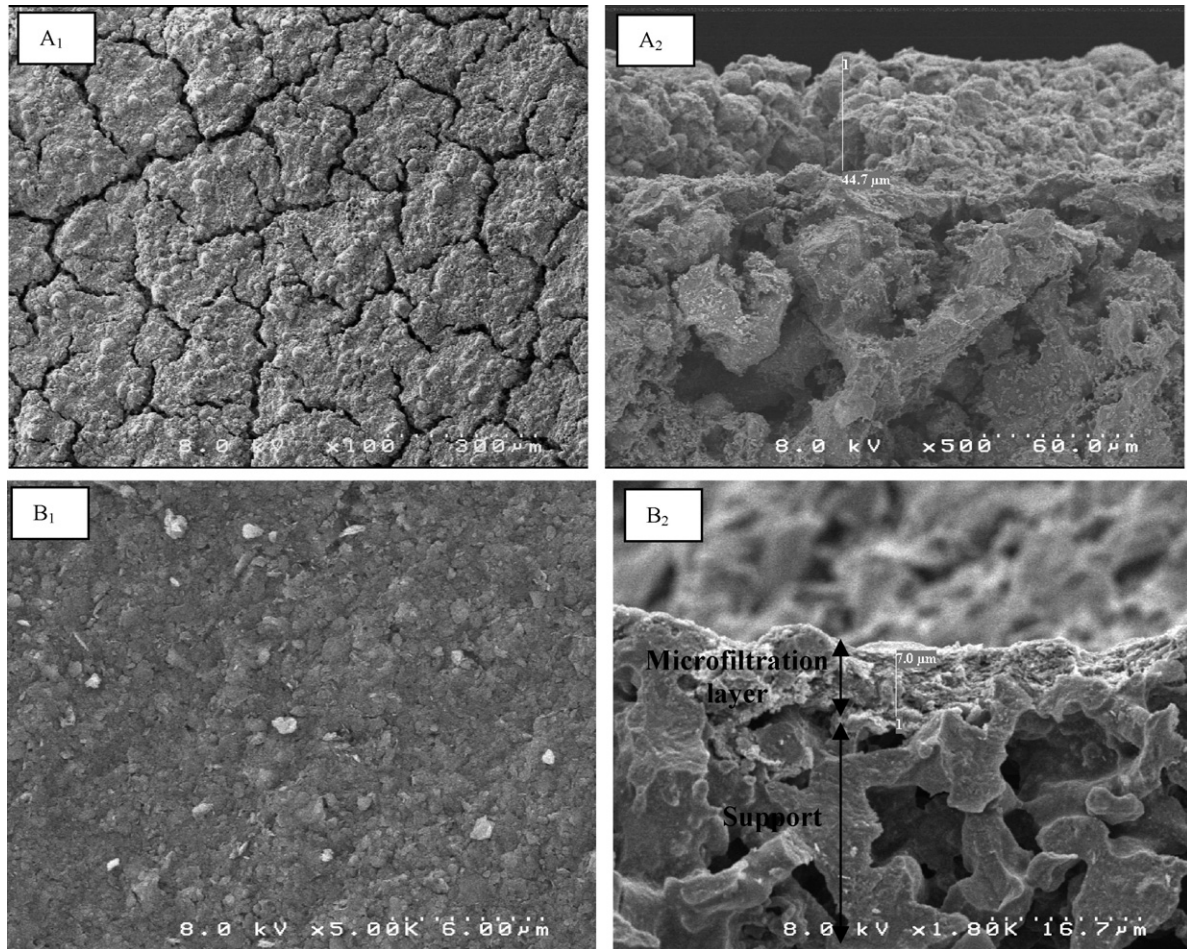


Fig. 9. Scanning electron micrographs of clay (JM₁₈) membrane (A: membrane thickness upper than 10 μm , B: membrane thickness less than 10 μm , 1: surface, 2: cross-section).

then stabilized at a value of $120 \text{ l h}^{-1} \text{ m}^2$. This behavior can be explained by the formation of a concentrated polarization layer. The variation of permeate flux with time shows that the fouling phenomenon is not very important: the permeate flux decreased by only 33%.

Table 4 gives the main characteristics of the raw and treated effluent. It can be observed that the permeate turbidity determined by using a Turbidimeter (HACH RATIO 2100A); is very low (inferior to 1 NTU) and that the COD retention rate

(COD is chemical organic demand determined by colorimetric method) is superior to 65%. These results confirm the efficiency of these microfiltration prepared membranes to cuttlefish effluent treatment.

In term of quality, Fig. 13 shows a noticeable elimination of suspended matter illustrated by the change of the effluent colour as well as the elimination of the turbidity.

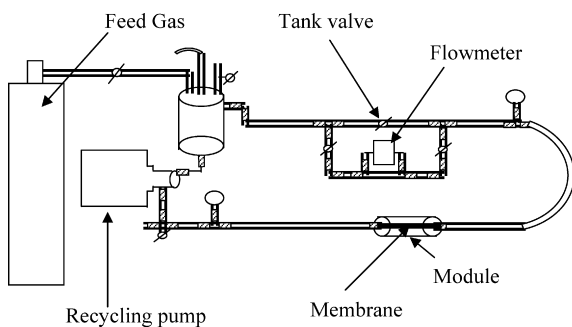


Fig. 10. Flow schema of experimental apparatus.

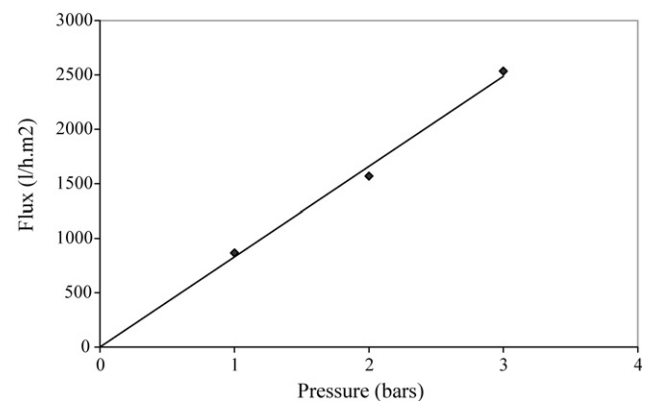


Fig. 11. Water fluxes vs. working pressure.

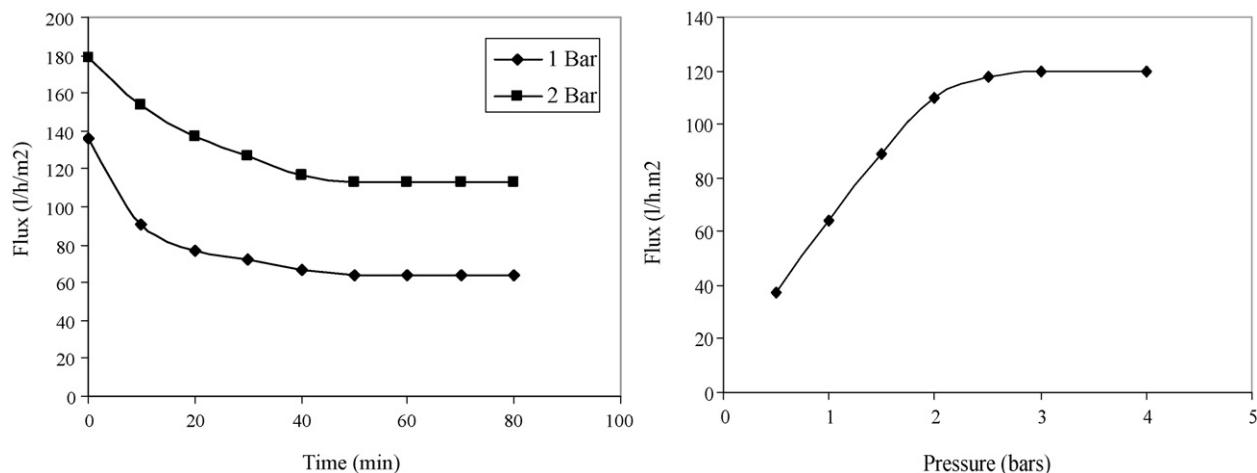


Fig. 12. Variation of flow according to the use pressure and time of filtration.

Table 4
Characteristics of the effluent before and after filtration

Sample	Conductivity (mS/cm)	Turbidity (NTU)	DCO (mg/l)
Raw effluent	80	>2000	6000–6500
Filtrate ($P = 1$ bar)	72	0.89	2460
Filtrate ($P = 2$ bar)	70.5	0.62	1930

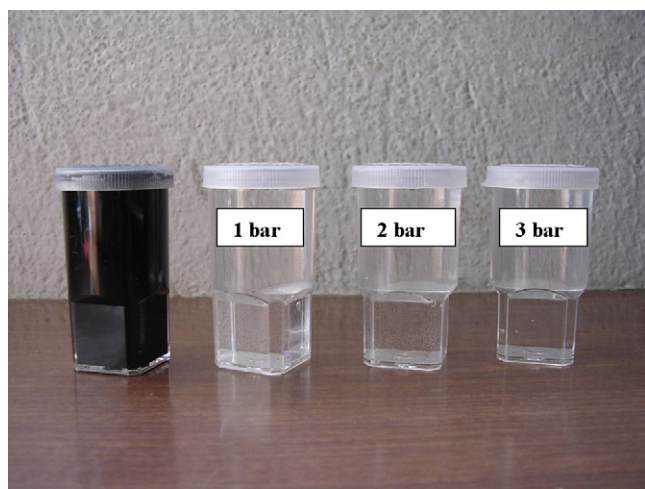


Fig. 13. A photograph of cuttlefish effluent before and after MF treatment.

3. Conclusion

In this work we have prepared new microfiltration membranes using natural powder derived from Tunisian natural material. The ceramic support was formed by the extrusion of a ceramic paste of silty marls (M_{11}). The microfiltration layer base on clay (JM_{18}), deposited onto the supports, was obtained by slip-casting method. An excellent link between the support and the microfiltration layer was obtained.

The support pore sizes could be carefully controlled by the choice of the particle diameters sizes of natural materials (silty

marls). The desired pore sizes of the microfiltration layer ($<1 \mu\text{m}$) were achieved by optimisation of the calcination temperatures. Microfiltration membranes from Tunisian clay with pore sizes as small as $0.18 \mu\text{m}$ could be then produced. This membrane have a water permeability of $870 \text{ l h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$.

One application of these membranes is the washing cuttlefish effluent treatment. These membranes can also be used as a support for ultrafiltration layer.

References

- [1] K.K. Cham, A.M. Brownstein, Ceramic membranes growth prospects and opportunities, *Am. Ceram. Soc. Bull.* 70 (1991) 703–707.
- [2] R.J.R. Uhlhorn, M.H.B.J. Huis in't Veld, K. Keizer, A.J. Burggraaf, *Sci. Ceram.* 14 (1987) 551–556.
- [3] V.T. Zespilis, W. Van Praag, K. Keizer, J.G. Van Ommen, J.R.H. Ross, A.J. Burggraaf, Modified Alumina Membranes as Active Materials in Catalytic Processes, First Intern ICIM, Montpellier, 1989, 3–6 July, pp. 367–372.
- [4] L. Cot, Inorganic membranes: academic exercise or industrial reality, inorganic membranes, in: *Proceedings of the Fifth Internal Conference on Inorganic Membranes*, Nagoya, 22–26 June, 1998.
- [5] B.F. Jones, E. Galan, Sepiolite and palygorskite, in: S.W. Bailey (Ed.), *Reviews in Mineralogy, Hydrous Phyllosilicates*, 19, Mineralogical Society of America, Washington, 1988, pp. 631–674.
- [6] J.L. Pérez-Rodríguez, E. Ga, Determination of impurity in sepiolite by thermal analysis, *Thermal Anal.* 42 (1994) 131–141.
- [7] T. Mishra, K. Parida, Transition-metal oxide pillared clays. Part 2. A comparative study of textural and acidic properties of manganese(III) pillared montmorillonite and pillared acid-activated montmorillonite, *J. Mater. Chem.* 7 (1) (1997) 147–152.
- [8] R. Cool, A. Clearfield, V. Mariagnanam, L.J.M. Ellistrem, R.M. Crooks, E.F. Vansant, Self-assembly of aluminium-pillared clay on a gold support, *J. Mater. Chem.* 7 (3) (1997) 443–448.
- [9] L. Messaoudi, A. Larbot, M. Rafiq, L. Cot, Mise au point d'une membrane de microfiltration sur supports tubulaires à base d'une argile marocaine, *Ind. Ceram. Ver.* 12 (910) (1995) 831–835.
- [10] M. Ishiguro, T. Matsuura, C. Detellier, Reverse osmosis separation for a montmorillonite membrane, *J. Membr. Sci.* 107 (1995) 87–92.
- [11] R. Le Van Mao, E. Rutinduka, C. Detellier, P. Gougay, V. Hascoet, S. Tavakoliyan, S.V. Hoa, T. Matsuura, Mechanical and pore characteristics of zeolite composite membrane, *J. Mater. Chem.* 9 (1999) 783–788.

- [12] S. Rakib, M. Sghyar, M. Rafiq, A. Larbot, L. Cot, Elaboration et caractérisation d'une céramique macroporeuse à base d'argène granitique, *Ann. Chim. Sci. Mater.* 25 (2000) 567–576.
- [13] L. Dégremont, *Mémento technique de l'eau*, Paris, (1978), pp. 232–965.
- [14] A. Abdelmouleh, Etude expérimentale de la valorisation de l'allache et de la seiche en Tunisie, Thèse de doctorat, 1997, pp. 130–135.
- [15] R. Flood, D. Deibel et C. Morris, *Oikopleura Vanhoeffeni* Using Sepia Ink, *Biol. Bull.* 178 (1990) 118–125.
- [16] V. Thoraval, B. Castelas, J.P. Jolin, A. Larbot, L. Cot, Preparation and Characterisation of Microporous Ceramic Media, *Key Engineering Materials*, vol. 61, Trans. Tech. Pub. Ltd., Switzerland, 1991, p. 118–213.
- [17] C. Guizard, A. Julbe, A. Larbot, L. Cot, in: B.I. Lee, E.J. Pope (Eds.), *Chemical Processing of Ceramics*, Marcel Dekker Inc., New York, 1994, p. 501.
- [18] S. Khemakhem, R. Ben Amar, A. Larbot, A. Ben Salah, L. Cot, Fabrication of mineral supports of membranes for microfiltration/ultrafiltration from Tunisian clay, *Ann. Chim. Sci. Mater.* 31 (2) (2006) 169–181.
- [19] M.D. Afonso, R. Borquez, Review of the treatment of seafood processing waste-waters from the fish meal industry, *Desalination* 142 (2002) 29–45.