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

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## 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 waste water treatment (Cham & Brownstein, 1991). 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 (Uhlhorn et al., 1987; Zespalis et al., 1989; Cot, 1998). Clay minerals have well-known structural adsorption, rheological and thermal properties (Jones & Galan, 1988; Pérez, 1994). Research on clay as a membrane material has concentrated mainly on pillared clays (Mishra & Parida, 1997; Cool et al., 1997). Studies of membranes prepared entirely from clay have just started (Messaoudi et al., 1995; Ishiguro et al., 1995; Le Van Mao et al., 1999; Rakib et al., 2000). The industry of conservation of sea products is very important in Tunisia. It produces a great amount of waste water which is generally rejected in the littoral and then is responsible for an enormous pollution, by supporting the eutrophication phenomenon (Dégrement, 1978). 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 (Abdelmouleh, 1997).

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.

New microfiltration membranes from Tunisian natural materials are obtained using ceramic method. Paste from Tunisian silty marls refereed (M<sub>11</sub>) 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 9.2µm 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<sub>18</sub>) is performed by slip casting method. The heating treatment at 900°C leads to an

average pore size of  $0.18\mu\text{m}$ . 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 waste water treatment.

## 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 (Guizard et al., 1997) deposited on a silty marls support.

### 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.

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

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

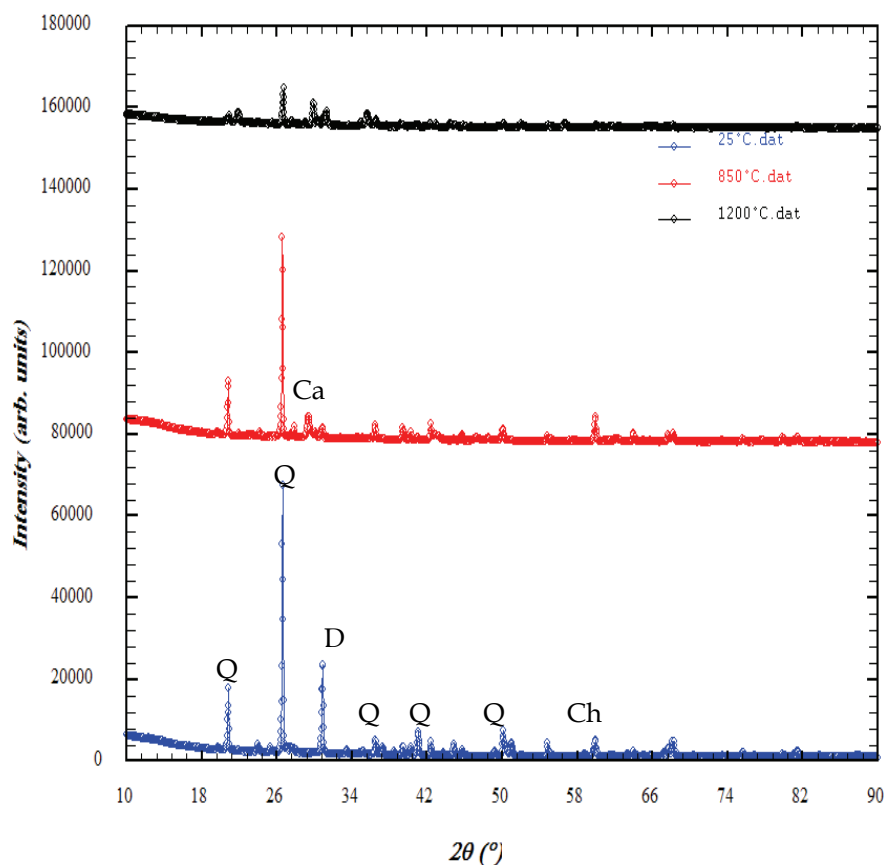


Fig. 1. X-ray diffractograms of the silty marls sample at different temperatures (Q=quartz, Ca=calcite, Ch=chlorite, D=dolomite).

The chemical analysis reveals that this kind of silty marls is essentially formed with a great amount of silica and calcium oxide. Figure 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 $\mu$ m was determined using a Particle Sizing Systems (Inc. Santa Barbara, Calif., USA Model 770 AccuSizer). The particle diameters range varied from 0.5 to 54 $\mu$ m. (Fig 2).

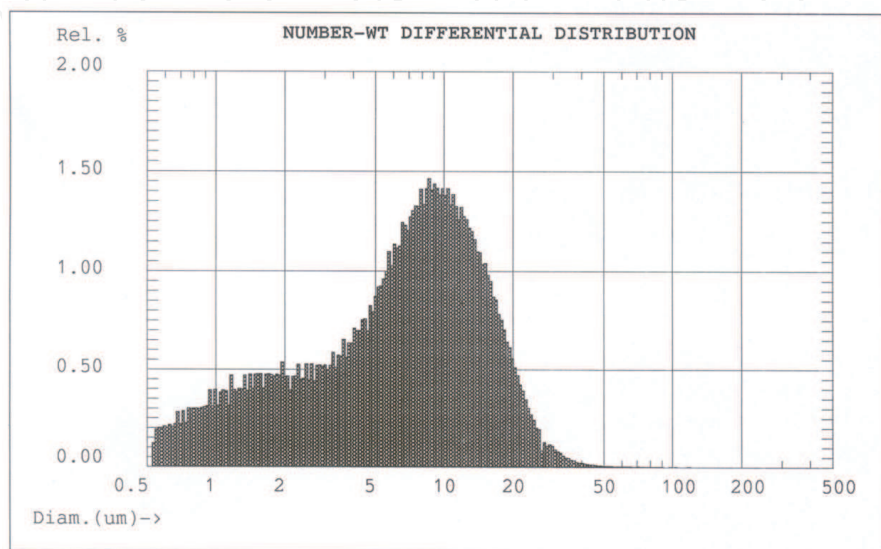


Fig. 2. Silty marls (M<sub>11</sub>) particle-size distribution.

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

- 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 (Khemakhem et al., 2006). Figure 3 shows the different configurations of tubes extruded in our laboratory (Two monochannel of different diameter and one multichannel tube).



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

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.

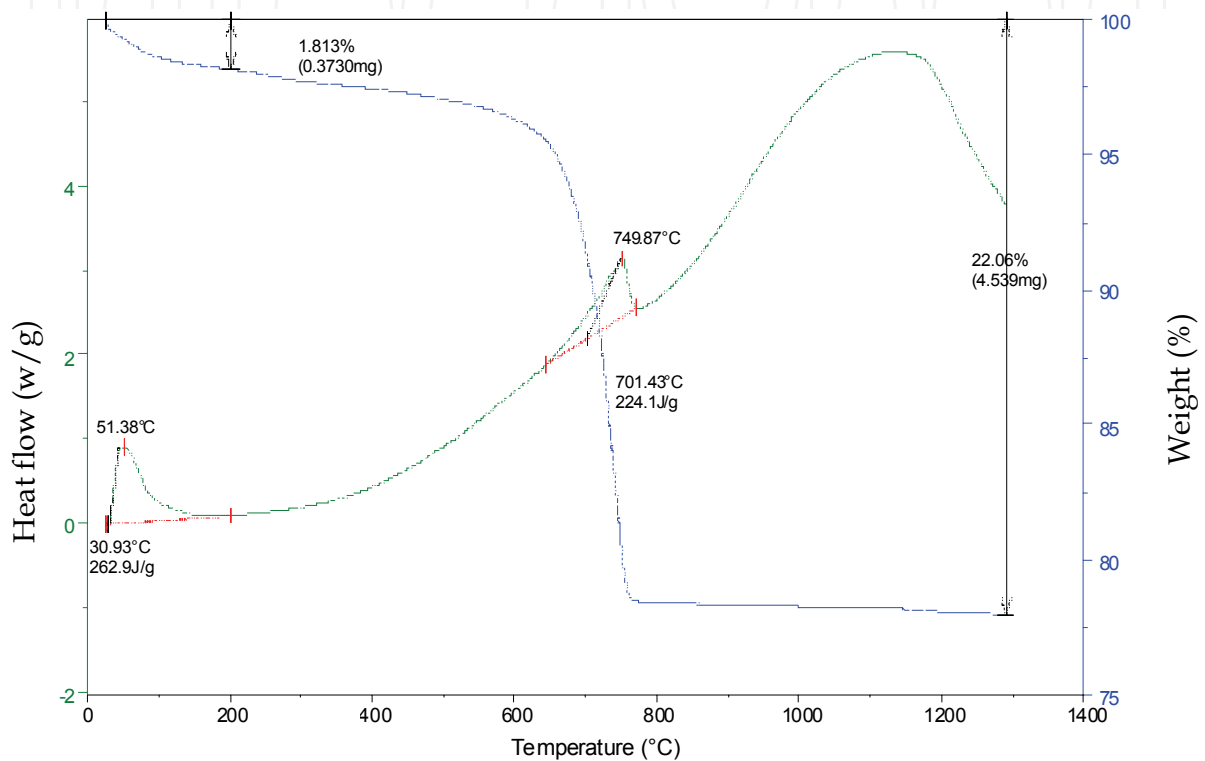


Fig. 4. Thermal analysis curve: DSC and TGA for silty marls powder.

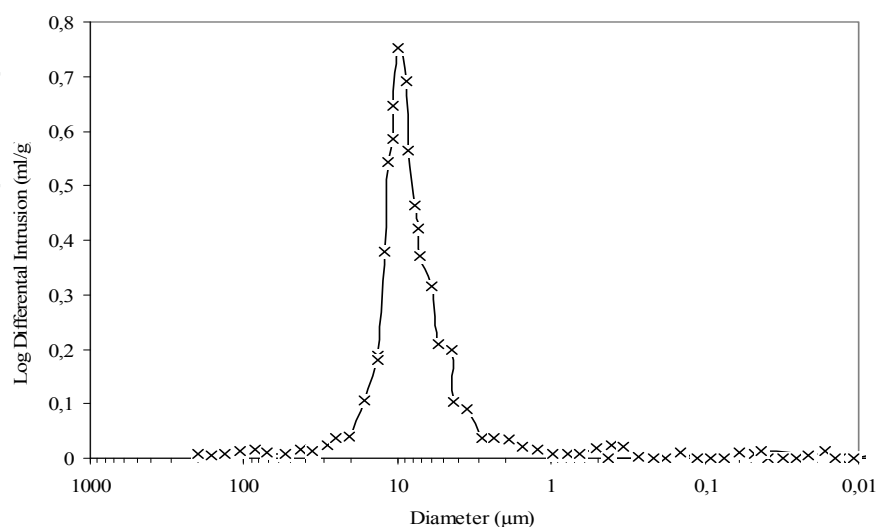


Fig. 5. Pore diameters of the silty marls supports.

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 9.2µm and 49% respectively (Fig.5).

Powders	Temperature (°C)	Pore size (µm)	Porous Volume (%)
Crushed during one hour 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 two hours 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

Table 2. Variation of pore size and porous volume according to the powder particle sizes for the silty marls (M11).

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:

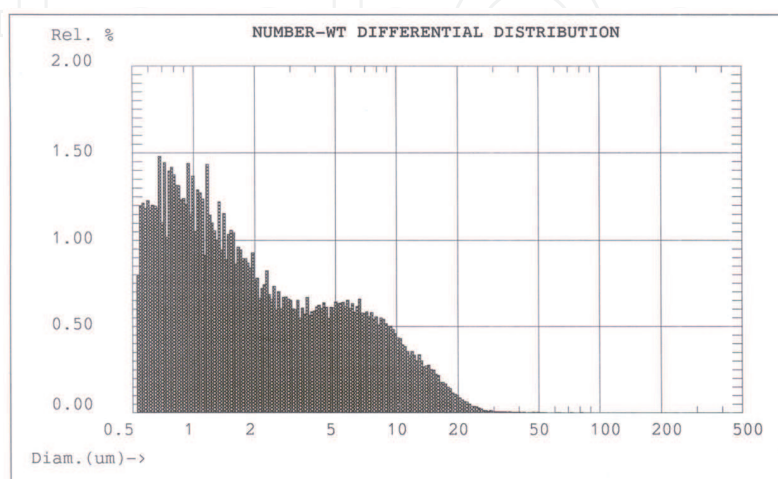


Fig. 6. Clay (JM<sub>18</sub>) particle-size distribution.

The material used for the membrane preparation is a Tunisian clay powder (JM<sub>18</sub>) taken from the area of Sidi Bouzid (Central Tunisia). This powder is crushed for 4 hours with a planetary crusher at 250 revolution/min and calibrated with 50 $\mu$ m. The obtained particle diameters range from about 0.5 to 23 $\mu$ m. (Fig 6).

The chemical composition of the clay (JM<sub>18</sub>) is shown in Table 3. It reveals that this material is essentially formed with a large amount of silica 62.64%.

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

Table 3. Composition of clay (JM<sub>18</sub>).

For preparing a microfiltration layer with JM<sub>18</sub>, the suspended powder technique was used. A deflocculated slip was obtained by mixing 5% w/w of JM<sub>18</sub>, 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.

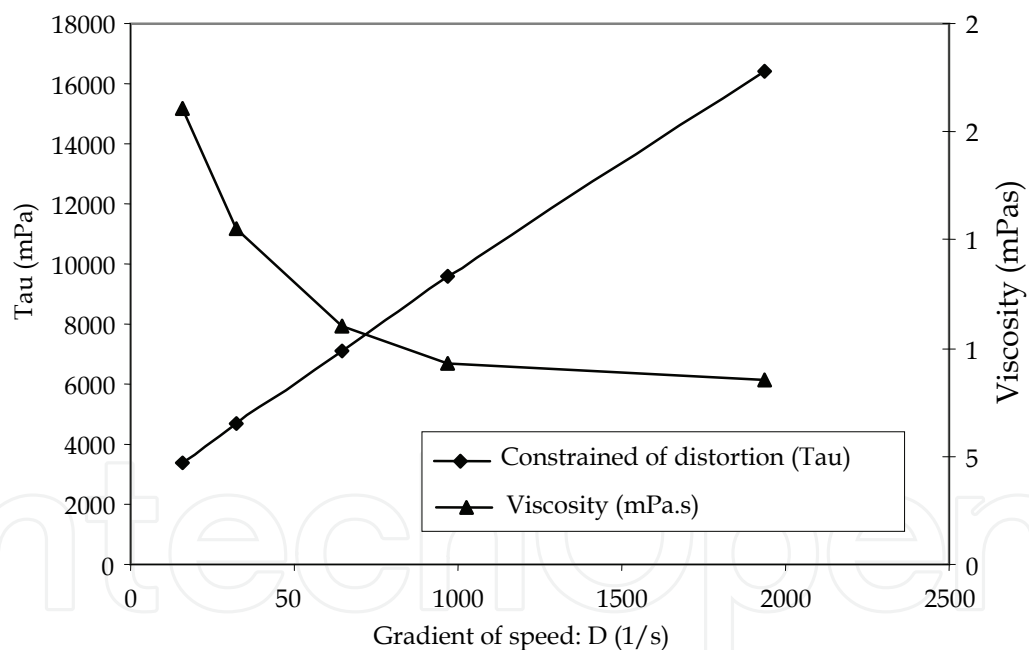


Fig. 7. Evolution of the stress ( $\tau$ ) and the viscosity ( $\mu$ ) vs. deformation of clay (JM 18) slip.

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.

Figure 7 shows the rheogram of the slip used. It is done by the curve of shear stress ( $\tau$ ) versus speed of rotation (D). The slip 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 M<sub>11</sub> support was performed by slip casting using a deposition time between 10 and 15 min. After drying at room temperature for 24h. The clay membrane was sintered at 900°C for 2h, after debonding at 250°C for 1h.

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 0.18μm (Fig. 8).

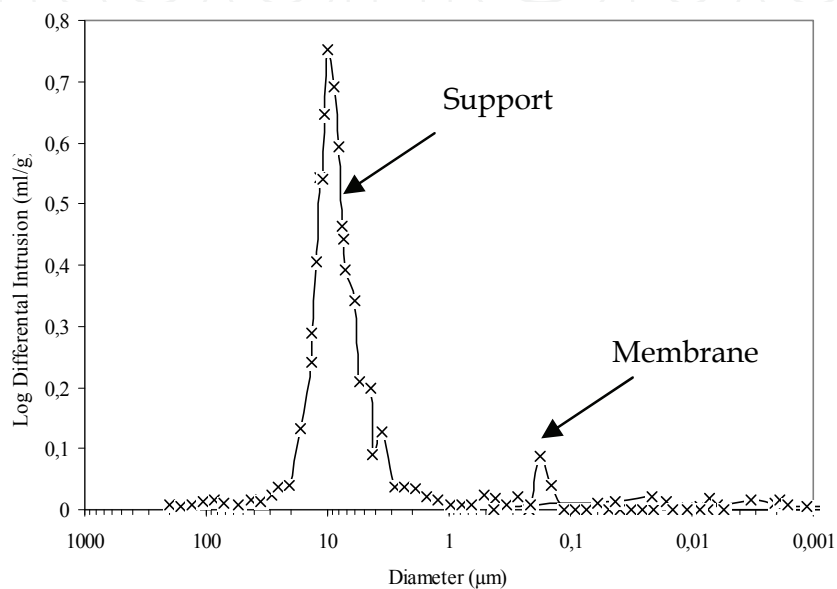
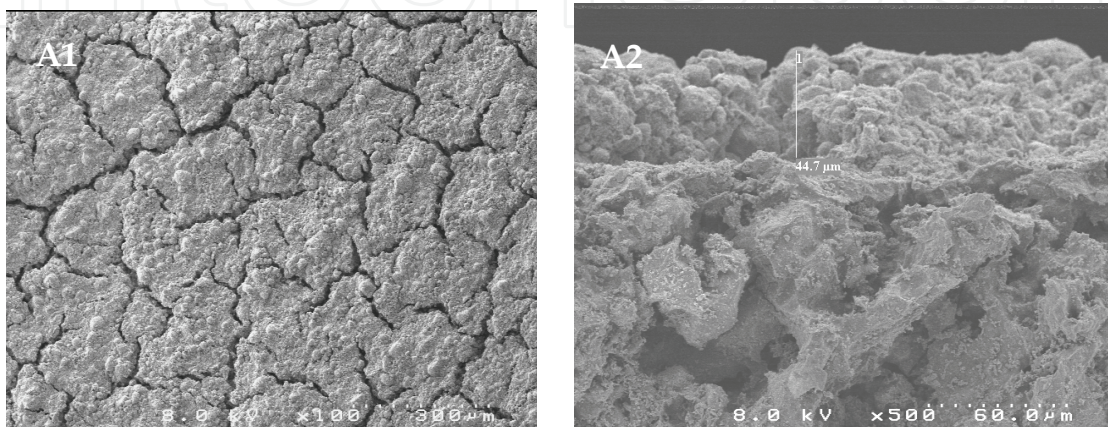


Fig. 8. Pore diameters of the clay (JM<sub>18</sub>) membrane.

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 50μm) were prepared. SEM (scanning electron microscopy) images of the resulting membranes are shown in Figure 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 10μm (in order to 7μm).





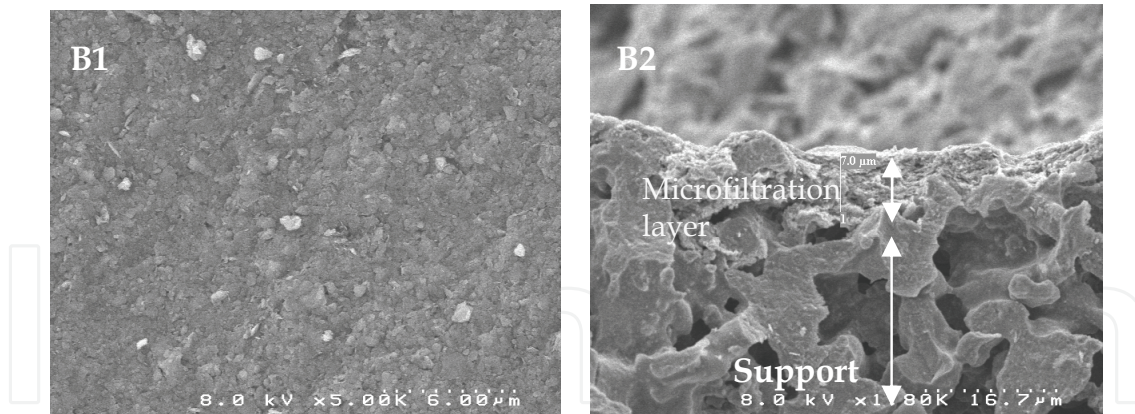


Fig. 9. Scanning electron micrographs of clay (JM<sub>18</sub>) membrane: (A: Membrane thickness upper than 10 μm, B: Membrane thickness less than 10 μm, 1: surface, 2: cross section)

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 bars.

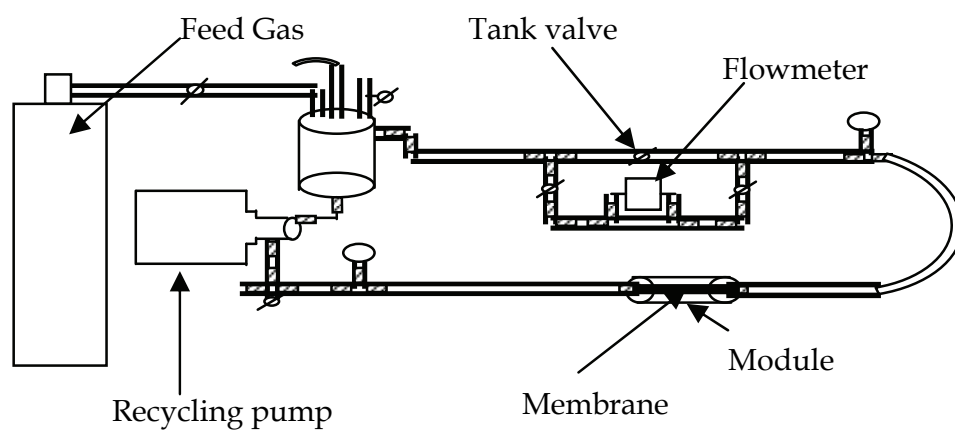


Fig. 10. Flow schema of experimental apparatus.

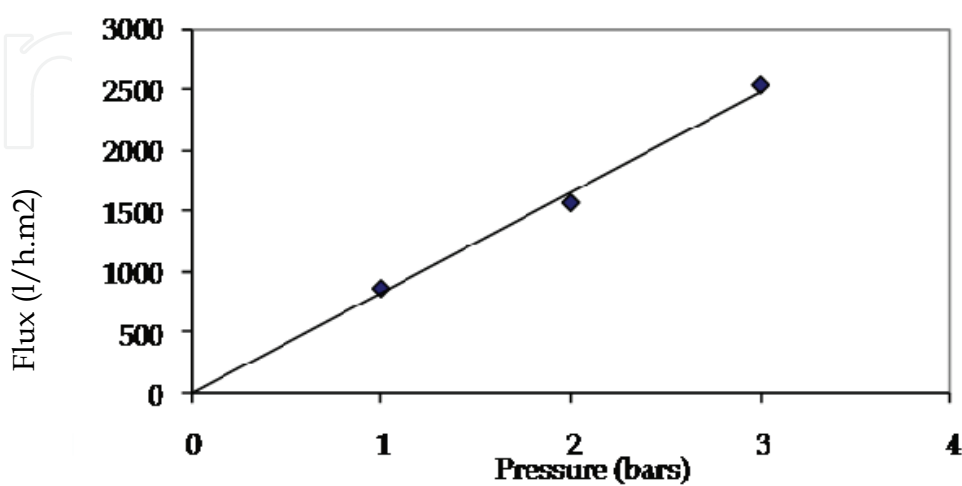


Fig. 11. Water fluxes vs. working pressure.

The flow rate was fixed at 2.5 m.s<sup>-1</sup>. 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<sup>-1</sup>.m<sup>-2</sup>.bar<sup>-1</sup> (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 (Afonso et al., 2002). 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 nm and 161 nm (Flood et al., 1993).

Figure 12 gives the variation of permeate flux with transmembrane pressure which is done by:  $(P_{inlet} + P_{outlet})/2 - P_f$  where:  $P_{inlet}$  and  $P_{outlet}$  are respectively the inlet and the outlet pressures across the filtration module.

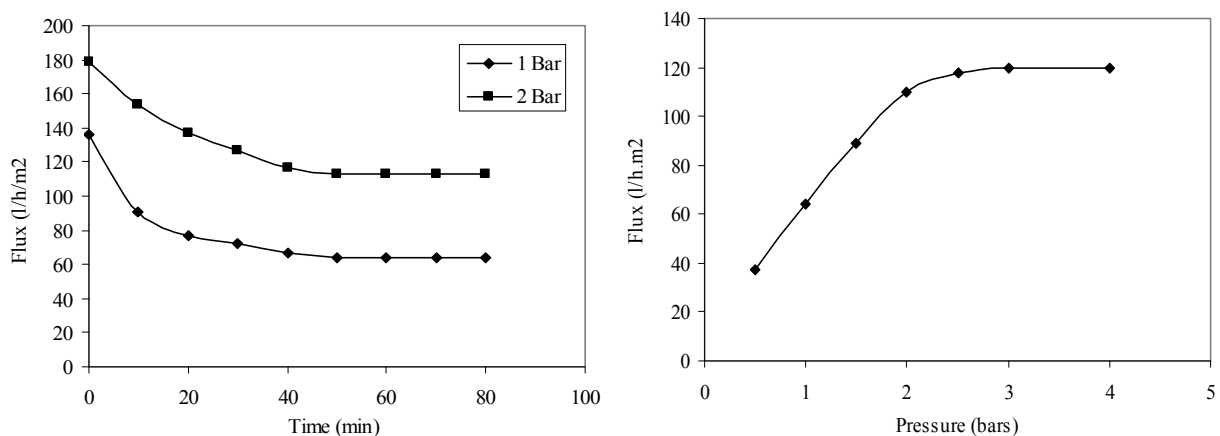


Fig. 12. Variation of flow according to the use pressure and time of filtration.

Permeate flux increased linearly with transmembrane pressure until a value of 2 bars and then stabilized at a value of 120 l/h.m<sup>2</sup>. 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, figure 13 shows a noticeable elimination of suspended matter illustrated by the change of the effluent colour as well as the elimination of the turbidity.

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

Table 4. Characteristics of the effluent before and after filtration.

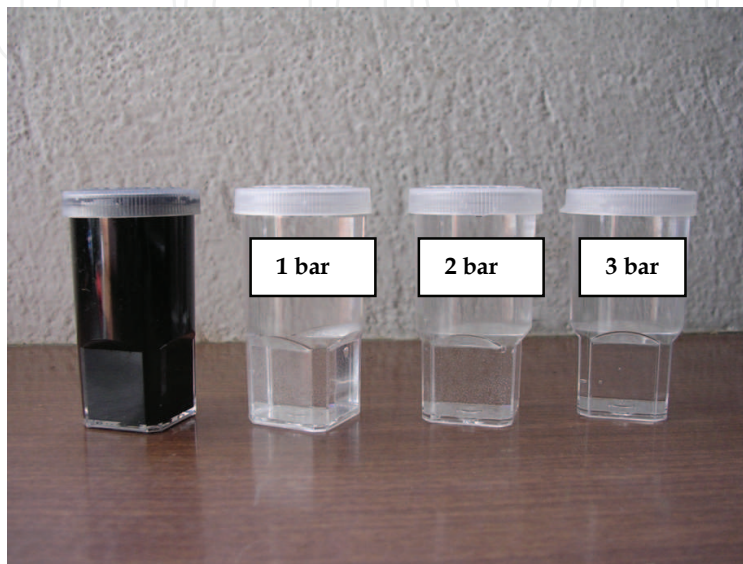


Fig. 13. A photograph of cuttlefish effluent before and after MF treatment.

### 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<sub>11</sub>). The microfiltration layer based on clay (JM<sub>18</sub>), 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 $\mu$ m) were achieved by optimisation of the calcination temperatures. Microfiltration membranes from Tunisian clay with pore sizes as small as 0.18  $\mu$ m could be then produced. This membrane has a water permeability of 870 l.h<sup>-1</sup>.m<sup>-2</sup>.bar<sup>-1</sup>.

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

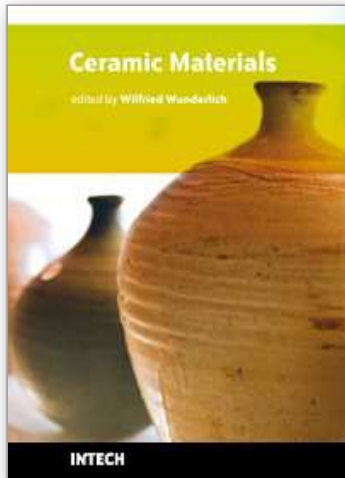
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