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Ceramic filters for oil emulsion treatments

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ABSTRACT

This work focused on obtaining low-cost macroporous ceramic tubes to be used as filters or as supports for the preparation of multilayer ceramic membranes. A Tunisian natural clay was used as raw material and cellulose as porogen agent. Cellulose fibers obtained from paper were used. The tubular supports were shape formed by extrusion in order to obtain a low-cost material with high porosity low shrinkage. The characterization of the process has been carried out studying the phase evolution, microstructure, pore structure, mechanical strength, and water permeability at various sintering temperatures. The porosity was improved adding 10 wt.% of cellulose to the clay and sintering temperatures were between 800 and 900˚C. The sintered macroporous support with 10 wt.% cellulose, sintered at 850˚C exhibited good performance such as porosity 40%, mechanical strength 6.5 MPa, and water permeability 8.5 L/h m^3. Finally, an emulsion of oil was significantly cleaned. A rejection rate of 50% for 10 min of treatment time was obtained. This work shows the possibility to develop cost-effective ceramic support with controllable pore size, porosity, and high strength for high performance membranes.

Keywords: Clay; Membrane; Cellulose; Ceramic; Porosity

1. Introduction

Ceramic membranes have been gaining more attention in industrial applications, such as pharmaceutical and electronic industries, in food, biochemistry, and waste water treatment [1], etc. Compared to the organic membranes, ceramic membranes have superior mechanical, chemical, and thermal stabilities, higher separation efficiency, longer life time, and ease of cleaning.

However, the application of ceramic membranes is greatly restricted by the high cost of both the starting materials and the sintering process [2,3]. In many applications, the configuration usually have either flat-plate or tubular which increase a lot to the cost of such membranes.

In general, performance of many ceramic membranes depends strongly on the porous support. An excellent membrane support should have high mechanical strength, high permeability, narrow pore size distribution, and low manufacturing cost. The aforesaid parameters depend mainly on the starting raw materials, sintering temperature and the manufacturing method.

In recent years, many researchers have focused on the development of new types of inorganic membranes, most ceramic membranes have been prepared

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from alumina (Al_2O_3) [4], zirconia (ZrO_2) [5], titania (TiO_2) [6], and silica (SiO_2) [7] as well as carbon [8], zeolite [9] and coal fly ash [10]. Nowadays, microfiltration ceramic membranes are commercially available for some industrial separation applications.

For this membrane type, single layer or multi-layer membrane is obtained by coating the macro-porous support by the membrane. By this way, an asymmetric structure is obtained with a gradient in pore size. Such kinds of support should offer sufficient mechanical strength for the system to withstand pressure gradients imposed during the practical applications.

Some efforts have been made to prepare porous ceramic support by pressing and extrusion, using clay as main raw material. However, these prepared supports showed some shortcomings such as low porosity, small pore size, low strength, or large shrinkage [3].

However, no elaborate and comprehensive research has been done to investigate the substantial influence of use cellulose as porogen agent [11,12] on the structure and properties of ceramics supports. The cellulose fiber which is a raw material for paper production remains reusable for manufacturing new products.

The membrane filtration has large potential for the efficient separation of oil/water emulsions and reuse of treated water. The separation properties of oil/water emulsions by cross-flow microfiltration were studied with ceramic microfiltration membranes [13]. The effects of pore size; applied pressure, cross-flow velocity, transmembrane pressure, and flux were systematically studied.

The objective of this work was to develop new tubular porous support from a local natural clay and using cellulose cellulose fibers as porogen agent. We will also examine an application in treating oil/water emulsion with membrane support. In this work, cellulose fibers obtained from paper were used. The fibers were recovered from paper, after a mechanical treatment, and directly added to the clay formulation. The tubular supports were shape formed by extrusion in order to obtain a low-cost material with high porosity low shrinkage.

2. Experimental

2.1. Materials and methods

An Oligocene clay collected from the Tabarka region located in the northwest of Tunisia was used as the main raw material. Due to its plasticity, no plasticizer was required for the extrusion.

Cellulose fibers were selected as porogen agent. They were obtained from commercial white paper for printing. The papers are cut into small pieces 2–3 mm which were placed in distilled water then soaked overnight in the ultrasonic basin. They were covered with water (preferably hot). Therefore, the cellulose fibers were released.

The plastic paste was prepared from the clay powder with the cellulose used as porogen agent (10 wt.%) and then with water in the proportion of 20–25 wt.% of the powder weight. This ratio was selected in order to add an extra porosity (in the order of 25% in volume considering nominal densities) that we considered to be sufficient for the purpose of these filters.

After mixing, the obtained clay formulation was then extruded in a homemade extruder. Ceramic tubes of 4 mm of internal diameter and 8 mm of external diameter were obtained. After drying, the support was sintered at 800, 850, and 900˚C for 2 h using 3˚C/min as heating rate and 10˚C as cooling rate.

Synthetic oily water was prepared in the laboratory. The preparation procedure consisted of the emulsification of the oil (0.2 wt.%) with water in an ultrasonic bath for 30 min which was enough to obtain emulsion.

2.2. Technical characterization

In order to characterize the support, different techniques were used. Chemical analysis of clay was determined by X-ray Fluorescence using a Bruker spectrometer type S4 Pioneer, equipped with an X-ray anode Rh (60 kV, 150 mA). The phase composition of the original clay was semi-quantitative calculated using the most intense diffraction peaks of each phase with the help of a facility of X'Pert High Score software.

The study of the plasticity was carried out by the Casagrande method, using the Atterberg limits, defining a range of percentage of water in which the mixture is plastic. The determination of the plastic limit has been defined using the procedure described by the Spanish standard UNE103-103-93.

Apparent densities of sintered materials were calculated geometrically, obtained from 5 samples for each temperature. Pore volume and size distribution of sintered materials were determined by Mercury porosimetry with a Pore Sizer 9300 from Quantachrome Corp. The surface area of the clay was determined with a Monosorb Surface Area Analyzer MS-13 from Quantachrome Corp. Morphology of ceramic membranes were studied by scanning electron

Table 1
Chemical analysis of the clay

SiO_2	Al_2O_3	MgO	MnO_2	Na_2O	K_2O	TiO_2	P_2O_5	CaO	Fe_2O_3	L.O.I
56.9	27.6	0.5	0.002	0.1	1.8	1.5	0.3	0.1	2.0	8.7

microscopy (SEM) using a TM 1000 HITACHI microscope. The mechanical resistance was evaluated through the diametral compression test using an Universal Testing Machine (INSTRON, UK). 10 samples were measured with 30 mm length, 4 mm of internal diameter, and 8 mm of external diameter.

The system of water depuration treatment consists of separate oil from water using the prepared tubular support, 15 cm length, as a semi-permeable barrier [4].

Permeability was evaluated through the flux per surface unit and time.

In addition to its permeability, the support is characterized by a retention rate (TR) defined as follows:

$$TR = 1 - \frac{C_p}{C_o} \quad (1)$$

where C_p the solute concentration in the permeate, and C_o is the concentration solute in the feed solution.

3. Results and discussion

3.1. Starting materials

The chemical analysis of the clay (oxide percentages) is shown in Table 1.

The results shown in oxide percentages, confirm the presence of silica (57%) from clay minerals and quartz. The alumina (28%) comes from clay minerals and feldspar. Alkaline elements, mainly potassium oxide, are associated with illite content of the clay. The alkalis content ($K_2O + Na_2O$) is relatively low (~1.9%).

The iron oxide content 2% is considered acceptable, which is in agreement with the range used in the literature for ceramic production.

Phases' quantification showed that the studied clay is mainly composed of kaolinite (57%), with minor amounts of illite (8%). The associate mineral is essentially the quartz (35%) in concordance with the high amount of SiO_2 reported by the chemical analysis (shown in Table 2).

Table 2
Mineralogical analysis of the clay

Mineralogy (wt.%)	
Kaolinite	57
Illite	8
Quartz	35

3.2. Plasticity

The plasticity index is a parameter of plasticity that shows the position of these clays. This clay can be considered in the category of plastic clay. Clay provides important plasticity with a plasticity index Ip = 26.

The mineralogical analyses are reasonably consistent with plasticity results which are in agreement with the range defined in the literature for ceramic production [14].

3.3. Mechanical strength

After removing water, the supports were sintered at 800, 850, and 900°C. These temperatures were selected considering a previous dilatometric study. In Table 3, apparent density values of sintered materials are shown. There is a decreasing in density at 850°C, compatible with decomposition of clay minerals and the consequent thermal expansion. After that, the shrinkage takes place.

Fig. 1 shows the evolution of the mechanical strength as a function of sintering temperature, as the resistance increases with temperature. This result is in good agreement with the trend observed in the literature; this behavior is closely related to the microstructure tubular support, its densification and, in particular, to the formation of the glassy phase.

Temperature of 850°C was selected to perform filtration experiments considering the behavior of density and mechanical resistance. The support sintered at 850°C has a diametral compression modulus of 6.5 MPa. Such resistance is enough for testing the tangential filtration.

Table 3
Apparent density values of materials sintered at different temperatures

Temperature (°C)	800	850	900
Density (g/cm^3)	1.95 ± 0.05	1.80 ± 0.05	1.94 ± 0.05

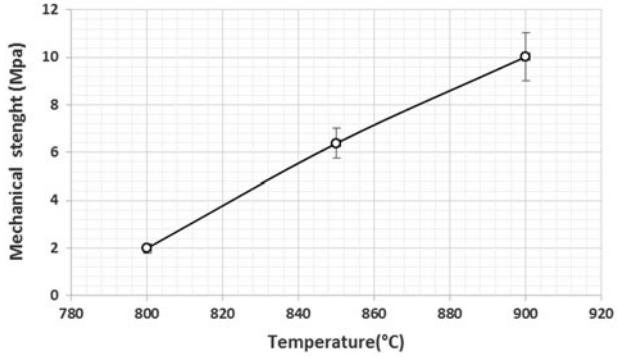

Fig. 1. Mechanical strength vs. firing temperature of the porous ceramic tubes.

3.4. SEM

The evolution of the material with the temperature was characterized also by SEM. Fig. 2 shows the support surface which is homogeneous and does not present any macro defects (cracks, etc.). At 800 and 850°C (Fig. 2(a) and (c)). The laminar morphology of clays remains visible. At 900°C the morphology change, the lamellar structures, from the original clays that remain at 800 and 850°C, has disappeared and less porosity can be observed. The best sintering temperature for a ceramic filter, from SEM observations and considering densities (Table 3), looks to be 850°C.

3.5. Mercury porosimetry

Fig. 3 shows the distribution of pore diameter after thermal treatment at 850°C. The result shows a bimodal distribution of the pore size. This means that there are two classes of pore distribution with pore diameter of 2.5, 0.07 μm, respectively. The biggest in size would match the porosity created by cellulose fibers and smaller to porosity among clay particles.

An important point is the total volume of porosity that is 40%. This value is not so high, but considering that the permeability will be mainly limited by the pore size, it is enough.

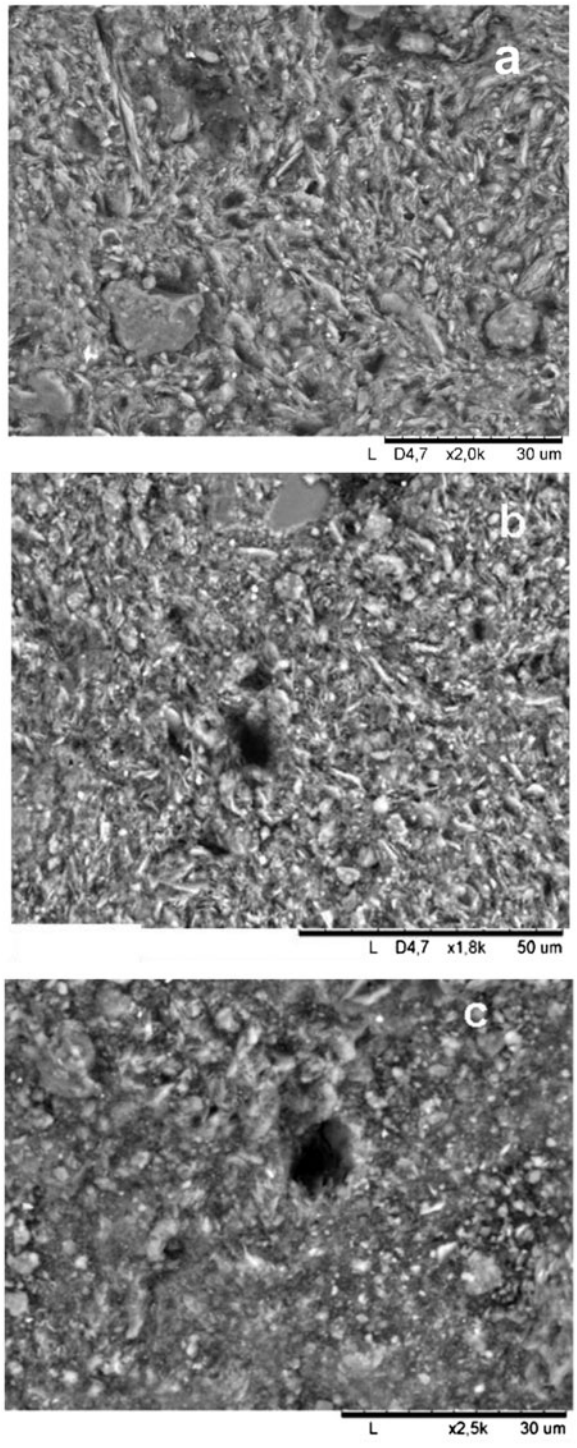

Fig. 2. Micrographs obtained by SEM of supports sintered at: (a) 800°C, (b) 850°C, and (c) 900°C.

3.6. Study of deionized water permeability

The cross flow filtration setup (shown in Fig. 4) was used to measure the water flux of the support

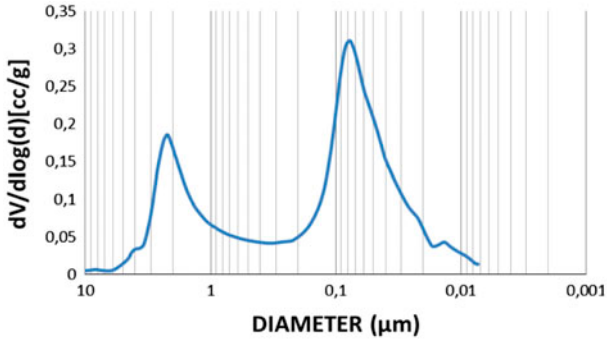

Fig. 3. Pore size distribution of ceramic tubes sintered at 850 ℃ for 2 h.

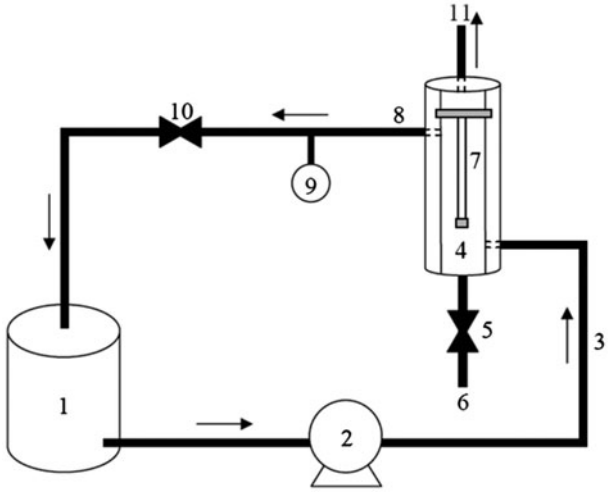

Fig. 4. Schematic representation of cross flow microfiltration setup. Equipment permeability/water filtration.
Notes: (1) the feed tank, (2) pump pressure, (3) feed line, (4) membrane module, (5) valve 1, (6) draining, (7) tubular membrane, (8) the recirculation line (retentate flow line), (9) pressure transducer, (10) valve 2, and (11) the permeate flow line.

tubular. For each support, the water fluxes were measured at different applied pressures (1, 2, and 3 bar) for 1 h (Fig. 5). Deionized water was used in these permeability measurements and it has not been subjected to any treatment to increase its purity.

It should be noticed that the flux decreases very fast in the first 20 min. A stable flux is obtained after 40 min, the relatively low water permeate flux value is as what is expected, because of its relatively low pore size. Additionally, the effect of the applied pressure on water permeate flux has been taken evaluated. The flux increases linearly with the applied pressure. Values of flux obtained are similar to membranes prepared with similar natural clays [14].

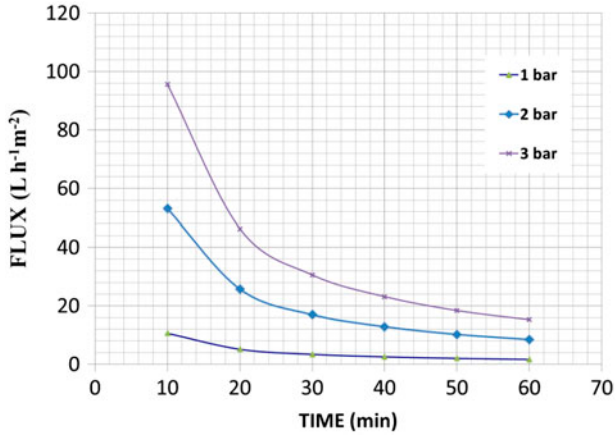

Fig. 5. Flux of distilled water through the support vs. time at different pressures.

3.7. Filtration of oil/water emulsion

The filtration of oil/water emulsions was carried out to evaluate the efficiency of the tubular supports as semi-permeable barrier. The pressure used for these tests was 2 bar. The flux was similar that with deionized water. Membrane filtration has large potential for the efficient separation of oil/water emulsion for the reuse of treated water.

The concentration of oil in feed, permeate, and retentate was determined using ultraviolet spectroscopy (UV) using the absorption band centered at 206.52 nm. The retention rate attained 50% after 10 min of treatment.

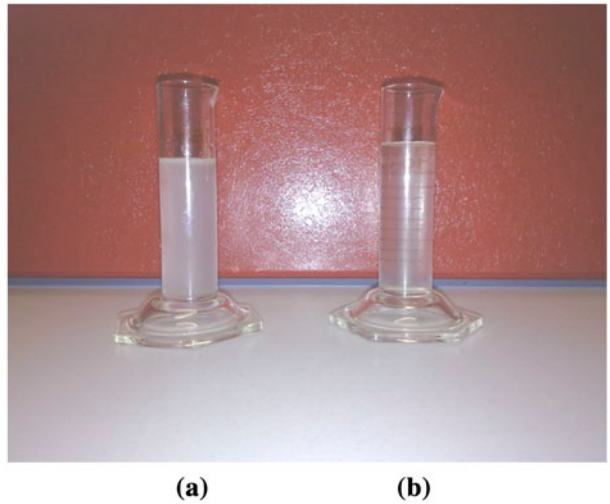

Fig. 6. The turbidity of the "water" (a) before and (b) after passing through the membrane.

As can be observed in Fig. 6, a decreasing in the turbidity of the water is observed only passing through the support.

4. Conclusions

In this paper, it has been mainly studied the addition of cellulose to a local natural Tunisian clay in order to be used as support for micro-filtration membranes.

Based on the results obtained, the following conclusions can be drawn:

(1) A sintering temperature of 850°C was considered optimum for the supports made by the optimized composition 10% of cellulose.
(2) These tubular supports have advantageous textural characteristics namely a 40% porosity, with a bimodal porosity distribution, centered at 2.5 and 0.07 μm, respectively.
(3) The tubular support has shown good performance in terms of mechanical resistance (6.5 MPa).
(4) The support presents interesting retention properties with regard to emulsion oil/water. The retention rates attained 50% after 10 min of treatment.

Acknowledgements

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References

[1] P. Pandey, R. Chauhan, Membranes for gas separation, Prog. Polym. Sci. 26 (2001) 853–893.
[2] 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.
[3] F. Bouzerara, A. Harabi, S. Achour, A. Larbot, Porous ceramic supports for membranes prepared from kaolin and doloma mixtures, J. Eur. Ceram. Soc. 26 (2006) 1663–1671.
[4] J.M. Benito, A.J. Conesa, F. Rubio, M.A. Rodríguez, Preparation and characterization of tubular ceramic membranes for treatment of oil emulsions, J. Eur. Ceram. Soc. 25 (2005) 1895–1903.
[5] T. Van Gestel, H. Kruidhof, D.H.A. Blank, H.J.M. Bouwmeester, ZrO_2 and TiO_2 membranes for nanofiltration and pervaporation. Part 1. Preparation and characterization of a corrosion-resistant ZrO_2 nanofiltration membrane with a MWCO < 300, J. Membr. Sci. 284 (2006) 128–136.
[6] M. Zhou, S. Roualdès, A. Ayral, New photocatalytic contactors obtained by PECVD deposition of TiO_2 thin layers on the surface of macroporous supports, Eur. Phys. J. 224 (2015) 1871–1881.
[7] N.C. Nwogu, M. Kajama, E. Gobina, A study of gas diffusion characteristics on a micro porous composite silica ceramic membrane, Compos. Struct. 134 (2015) 1044–1050.
[8] A.F. Ismail, L.I.B. David, A review on the latest development of carbon membranes for gas separation, J. Membr. Sci. 193 (2001) 1–18.
[9] H. Maghsoudi, Defects of zeolite membranes: Characterization, modification and post-treatment techniques, Sep. Purif. Rev. 45 (2016) 169–192.
[10] J. Liu, Y. Dong, X. Dong, S. Hampshire, L. Zhu, Z. Zhu, L. Li, Feasible recycling of industrial waste coal fly ash for preparation of anorthite-cordierite based porous ceramic membrane supports with addition of dolomite, J. Eur. Ceram. Soc. 36 (2016) 1059–1071.
[11] S.K. Nataraj, S. Roy, M.B. Patil, M.N. Nadagouda, W.E. Rudzinski, T.M. Aminabhavi, Cellulose acetate-coated α-alumina ceramic composite tubular membranes for wastewater treatment, Desalination 281 (2011) 348–353.
[12] M. Zafar, M. Ali, S. Khan, T. Jamil, M. Taqi Zahid Butt, Effect of additives on the properties and performance of cellulose acetate derivative membranes in the separation of isopropanol/water mixtures, Desalination 285 (2012) 359–365.
[13] J.M. Benito, M.J. Sánchez, P. Pena, M.A. Rodríguez, Development of a new high porosity ceramic membrane for the treatment of bilge water, Desalination 214 (2007) 91–101.
[14] W.E. Worrall, Clays and Ceramic Raw Materials, second ed., Elsevier Applied Science, London, UK, 1986.