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Study of Ceramic Membrane from Naturally Occurring-Kaolin Clays for Microfiltration Applications

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RESEARCH ARTICLE

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Abstract

The focus of this work is to assess the quality of porous membranes prepared from naturally occurring kaolin clays and to evaluate the performance of tubular ceramic membranes treating integrated raw effluents from seafood industry. This material has been chosen due to its natural abundance, its non-toxicity, low cost and its valuable properties. The preparation and characterization of porous tubular ceramic membranes, using kaolin powder with and without corn starch as poreforming agent, were reported. SEM photographs indicated that the membrane surface was homogeneous. The effects of material compositions, additives and the relatively lower sintering temperature, ranging from 1100° to 1250°C, on porosity, average pore size, pore-size distribution and mechanical strength of membranes have been investigated. A correlation between microstructure and mechanical properties of membranes has been discussed. The performance of the novel ceramic membranes thus obtained was determined by evaluating both the water permeability and rejection. The obtained membrane was used to treat cuttlefish effluents generated from the conditioning seawater product industry which consumes a great amount of water. Cross-flow microfiltration was performed then, in order to reduce the turbidity and chemical oxygen demand (COD).

Keywords

ceramic tubular membrane, kaolin-clays, sintering, filtration, cuttlefish effluent

1 Introduction

Water pollution is one of the most important crises in modern times because water is the most important basis of life. There is much current interest in the application of microfiltration and ultrafiltration membranes in separation procedures because of their potential for the treatment of large quantities of wastewater [1-5]. This is a successful way to solve water pollution crisis and to maintain the environment wellness.

The use of ceramic membranes has many advantages such as high thermal and chemical stability, pressure resistance, long lifetime, good resistance to fouling, and ease of cleaning [6-7]. Unfortunately, ceramic membrane fabrication, even though commercially available, still remains highly expensive from a technical and economic point of view due to the use of expensive powders such as alumina [8-10], zirconia, titania and silica [11, 12].

Recently, the development of low cost ceramic membranes based on natural materials such as apatite powder [13], natural raw clay [14-16], graphite [17], phosphates [18,19], dolomite, kaolin [20-24] and waste materials such as fly ash [25- 29], appeared as an efficient solution to treat waste water at a low cost. The properties of the ceramic membranes are mainly determined by their composition, the pore-former content and the sintering temperature.

MF is a membrane process for concentration, purification, and fractionation in diverse fields such as food, textile, pharmacy, chemical, paper, and leather industries. MF is often used to remove particles, microorganisms, and colloidal materials from suspensions [30-32].

Fouling would reduce productivity and potentially shorten membrane life. To understand the mechanisms of fouling, some researchers proposed various models to analyze and predict the flux decline behavior during filtration of macromolecular solutions, among them the resistance-in-series model. According to this model, the flux decline is due to the combined effects of irreversible membrane fouling which is not easy to remove [33,34] but with reversible fouling, rinsing with clean water can solve the problem. The main factors that influence fouling are the physicochemical properties of the membrane, feeding solution and operating conditions.

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According to this context, this study is related to the elaboration of tubular ceramic membranes using kaolin clays (chemical structure: $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ [35, 36]). Corn starch powder was added as pore-forming agent to produce sufficient porosity with acceptable mechanical property. Corn starch is a natural biopolymer that consists of carbon, hydrogen and oxygen. Besides, it is cheap, non toxic and environmental friendly. The porous structure takes place when the starch is burned out during the sintering process and leaves a pore in the membrane body.

The properties of the porous membranes formed were discussed as a function of sintering temperature in order to optimize the preparation conditions. Their structural and functional properties are determined by different techniques. The most important parameters used in the characterization of these substrates are: surface and internal morphology, mean pore size, pore size distribution, porosity and water permeability. Mechanical and chemical stability study of the membrane is also performed to verify its application in highly corrosive medium. The prepared microfiltration membranes were used for the treatment and the decoloration of cuttlefish effluent. Additionally, the effect of operating parameters such as transmembrane pressure, on the permeate flux and the fouling resistance are studied for microfiltration application.

1.1 Resistance fouling theory

The volume flux in a pressure driven membrane process depends on the hydraulic resistance of the used membrane and the pressure drop over the membrane. This is generally expressed by the following formula:

$$J_w = \Delta P / \eta_w R_m \quad (1)$$

where, R_m is the intrinsic hydraulic resistance of the membrane and η_w is the viscosity of water.

The permeate flux (J_s) after filtration of the solution can be expressed by the resistance-in-series model [34].

$$J_s = \Delta P / \eta_s R_t \quad (2)$$

in which η_s is the permeate viscosity and R_t is the total resistance that can be defined as:

$$R_t = R_m + R_p + R_f \quad (3)$$

where, R_p is the resistance due to polarization layer considered as reversible fouling (polarization concentration which can be removed by water) and R_f is the resistance caused by irreversible fouling.

Experimentally, the intrinsic membrane resistance R_m was calculated by measuring the pure water flux J_w and viscosity η_w .

Total resistance R_t was estimated from the solution flow rates under operating conditions using Eq. (4):

$$R_t = \Delta P / \eta_s J_s \quad (4)$$

Resistance, due to irreversible fouling R_f is determined from the pure water flux J'_w through the membrane after processing and rinsing with distilled water for 10 min:

$$R_f = (\Delta P / \eta_w J'_w) - R_m \quad (5)$$

This enables calculation of the resistance due to the concentration polarization R_p from Eq. (3). In order to obtain the resistance values in m^{-1} all variables used the SI units.

2 Materials and methods

2.1 Materials

In this study, both the supports and membranes were prepared from clay. The clay used in the present study is a kaolin Codex, it was recommended by the L.P.M Cerina (Laboratoire des Plantes Medicinales, Tunisia). Corn starch powder was used as a pore former.

2.2 Powder characterization

The chemical composition of the kaolin powder was determined by spectroscopic techniques, as X-ray fluorescence for metals and by atomic absorption for alkaline earth metals.

Phase identification was performed by XRD analysis (Philips X'Pert X-ray) diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), and the crystalline phases were identified by reference to the International Center for Diffraction Data cards.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out from ambient temperature to 1300°C at a rate of $10^\circ\text{C min}^{-1}$ under air, using a setaram SETSYS Evolution 1750.

The particle size distributions of kaolin were determined by the Dynamic Laser Scattering (DLS) technique using water as dispersing medium (Mastersizer 2000, Malvern Instruments).

The powder morphology as well as the microstructure formed in the sample was determined by SEM images obtained using a Hitachi scanning electron microscope.

2.3 Membranes elaboration

The elaboration of membranes implies the following sequence of operations:

- preparation of a plastic ceramic paste;
- shaping by extrusion;
- Consolidation by thermal treatment.

The process of the ceramic preparation was described in Fig. 1. Porous tubular membranes were fabricated from a mixture of kaolin and starch powders. The selected composition of powders used for the plastic paste preparation was 90 wt. % kaolin and 10 wt. % starch as a plasticizer. The powder mixture was aged with a progressive addition of water to obtain a plastic paste with a good homogeneity and to allow the shaping. Subsequently, the paste was left for 24 h under a high humidity to improve its rheological property. After that, an extrusion

technique is used to form some tubular samples. For good drying of these tubular samples, they are placed at room temperature on rotating aluminum rolls during 24h to ensure a homogeneous drying and to avoid twisting and bending.

Finally, a thermal treatment was carried out in an automatic and programmable furnace (Type 30400) at different final temperatures. Two steps have been determined. Subsequently, the membrane was heated up to 400°C for 2 h at a heating rate of 2°C min⁻¹ in order to eliminate the organic additive used as pore-forming agent. In a second step, the membrane was sintered at a temperature ranging from 1100 to 1250 °C with a ramping rate of 5°Cmin⁻¹ in order to avoid the formation of cracks during sintering of the samples. The final temperature was kept constant for 1 h. After that, the consolidated support was allowed to cool until the environmental temperature was reached.

The temperature–time schedule not only affects the pore diameters and porous volume of the final product but also allows obtaining the final morphology and mechanical strength. Tubular membranes were elaborated with external/internal diameter of 16/11mm and the length of 150 mm.

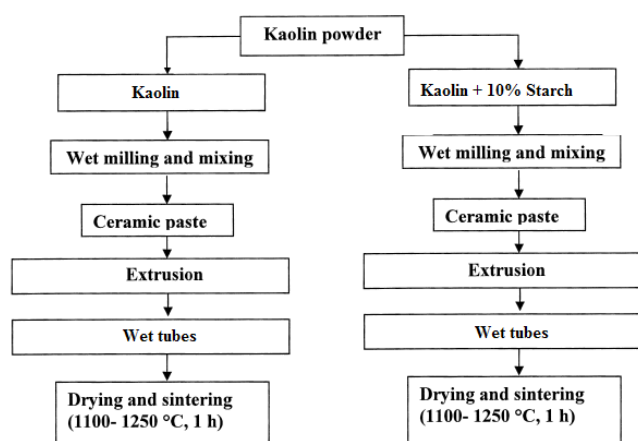


Fig. 1 Schematic diagram describing the procedures, used in this work, for membrane preparation

2.4 Membranes characterization

The evolution of densification and surface quality of the membranes sintered at different temperatures were determined by scanning electron microscopy.

Porosity and pore size distribution were measured by mercury porosimetry. This technique relies on the penetration of mercury into a membrane's pores under pressure [21, 23, 37]. The intrusion volume is recorded as a function of the applied pressure and then the pore size was determined.

The mechanical resistance tests were performed using the three points bending method (LLOYD Instrument) to control the resistance of the membranes fired at different temperatures.

The corrosion tests were carried out using aqueous solutions of nitric acid (pH=2.5) and sodium hydroxide (pH=12.5) at 45 and 80°C, respectively. All the samples were ultrasonically

rinsed in distilled water, dried at 110°C and stored in a dryer. The degree of corrosion was characterized by the percentage of the weight loss.

2.5 Filtration pilot

The laboratory pilot used for the filtration experiments was equipped with a cross-flow filtration system implementing tubular ceramic membrane of 15 cm length. The tubular membrane was placed in a stainless steel carter. The transmembrane pressure (TMP) can reach 6 bars. It was controlled by an adjustable valve on the retentate side. Temperature was kept at 25 °C by a thermal exchange system. The membrane was conditioned by immersion in pure deionized water for a minimum of 24 h before filtration tests. The determination of the water membrane permeability was performed with distilled water.

2.6 Effluent characterization

Wastewater samples were taken from the effluents produced by a sea-product freezing factory located in Sfax, Tunisia. The cuttlefish washing waters were characterized by a high organic load and a strong salinity [3]. The dark color in this effluent was due to the presence of sepia ink (containing melanin) as suspension particles [38]. The characterization by transmission electrons microscopy revealed that these granules of “melanin” are spheres with diameter values ranging from 56 to 161 nm [18, 39].

A large number of analyses were conducted on each sample and the following parameters were measured: turbidity, Chemical Oxygen Demand (COD), temperature and conductivity.

3 Results and discussion

3.1 Characterization of the starting materials

The chemical composition of kaolin is given in Table 1, where the main impurities are CaO, K₂O, TiO₂ and Fe₂O₃. It reveals that the major components were silica (SiO₂: 47.85%) and aluminium oxide (Al₂O₃: 37.60%).

Table 1 Chemical composition of the used kaolin (wt %).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	CaO	TiO ₂	LOI*
Kaolin(%)	47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27

*LOI: Loss on Ignition at 1000°C

Phase identification is of great importance before any membrane manufacturing. Fig. 2 presents the XRD patterns of the raw and thermally treated kaolin clay. Before applying heat treatment, it can be seen that kaolinite (K) was the major mineral component with a small amount of quartz (Q) and illite (I) impurities. No other components were observed, because the impurities are so tiny (see Table 1) and most of them are probably incorporated into the crystal structure of kaolinite. After calcinations of the sample at 600°C, all the peaks in the

diffractogram due to kaolinite disappeared. This is due to the transformation of kaolinite to amorphous metakaolinite. On the contrary, the peaks of quartz and illite did not change which means the kaolinite phase is only concerned by the thermal treatment at 600°C. At a temperature of 1,250°C, peaks of illite (I) disappeared too, whereas peaks of mullite (M) appeared due to the transformation of metakaolinite. The quartz (Q) peaks remained unchangeable in the diffractogram which confirms the thermal stability of this phase.

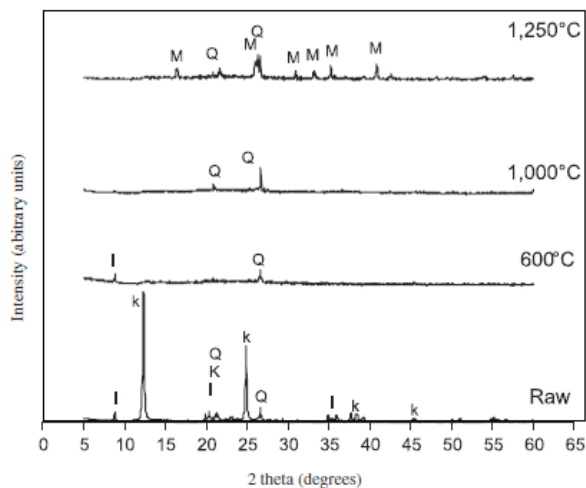


Fig. 2 XRD pattern of the pure kaolin before and after heat treatment (K=Kaolinite; Q=Quartz; I= Illite; M=Mullite)

The particle size distribution of kaolin was determined by the Dynamic Laser Scattering (DLS) technique. This method gave an average particle size in the order of 4 μm.

The scanning electron microscopy (SEM) examination of clay powder presented in Fig. 3 indicates that the clay powder is characterized by a platelet-like structure typical of lamellar clays.

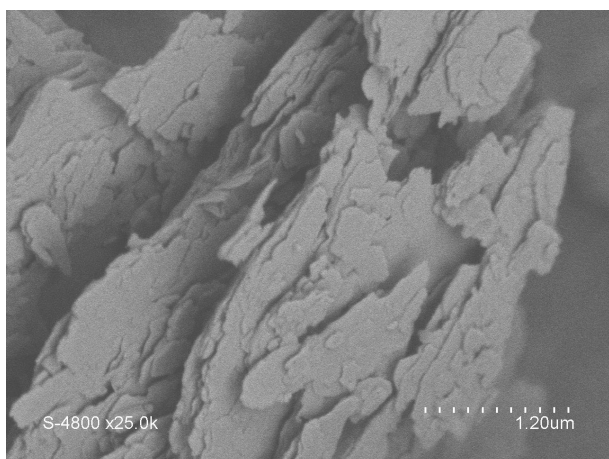


Fig. 3 SEM micrograph of the kaolin powder

A total weight loss is observed by TGA to be about 12.5% of kaolin (Fig. 4). In fact, the weight loss consists of two distinct stages: the first one is considered as a slight weight loss

between room temperature and 150°C, because of the dehydration of the kaolin-clay. The second mass loss detected between about 400 and 700°C is mainly due to the phenomenon of dehydroxylation of kaolinite confirmed by DTA (Fig. 5) which shows an endothermic peak at 580°C leading to the transformation of kaolinite to metakaolinite. A third stage, which is characterized by an exothermic reaction, appeared at about 980°C without any weight loss. The exothermic peak corresponds to the metakaolin–mullite transformation [40].

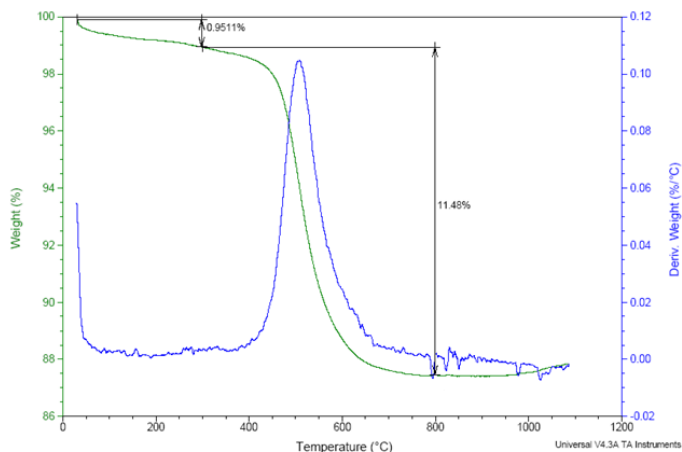


Fig. 4 TGA-DTG data of the kaolin powder

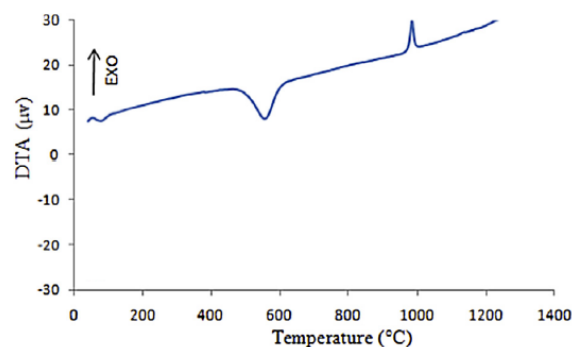


Fig. 5 DTA curve of the kaolin powder

3.2 Characterization of the membranes

For the development of high-quality membranes, the following properties are of major importance: pore size distribution, porosity, surface texture, mechanical properties and chemical stability.

3.2.1 Scanning electron microscopy (SEM)

Fig. 6 illustrates SEM pictures for the membrane sintered at the four different temperatures considered in this work. The optimal sintering temperature was determined by comparing the texture of the different obtained samples.

The ceramic substrates sintered at lower temperature (1100°C and 1150°C) show highly porous structure. Below 1100 °C, the presence of intergranular contacts are detected which are large enough to ensure ceramic cohesion (beginning of sintering).

The membrane sintered at 1200°C and 1250°C are more consolidated due to the fact that for sintering temperatures over 1200 °C, the particles agglomerate together creating more dense ceramic body. As a result the porosity of the membrane decreases with an increase in sintering temperature.

The obtained results (Fig. 7) show that the starch addition to kaolin has a positive effect on the porosity of membranes compared to those prepared from kaolin alone. More pores can be observed when starch corn is added to the composition, which leads to more porous structure.

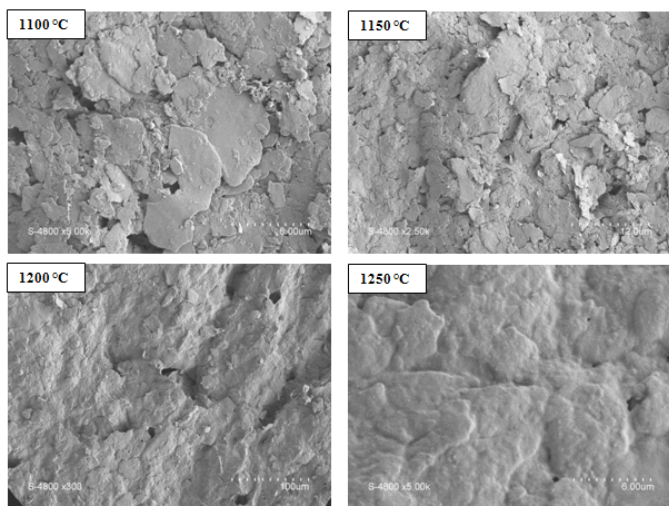


Fig. 6 SEM of membranes sintered at different temperatures

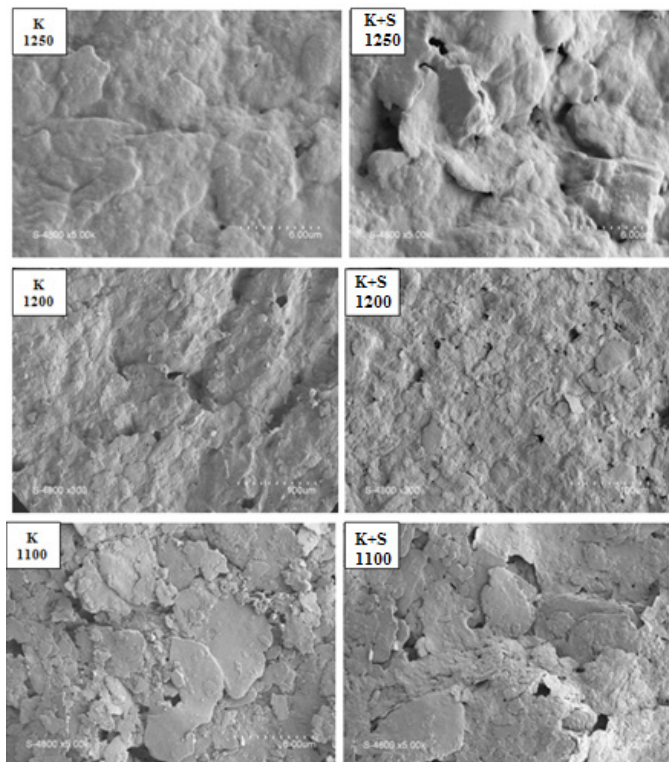


Fig. 7 SEM micrographs of kaolin and kaolin + 10 wt% starch samples

3.2.2 Mercury porosimetry

The evolution of the membrane characteristics as a function of the sintering temperature is shown in Fig. 8. The evolution of the average pore diameter and the porosity reveals that the porosity decreases from 44 to 27% between 1150°C and 1250°C, while the pore diameter increased from 0.41 to 0.73 μm. This behavior corresponds to an opening of the pores in the same time as a material densification occurring when the temperature increases [24, 28, 41, 42].

Moreover, it can be said that both the mean average pore size and the porous volume are closely related to the preparation method. The obtained results show that the starch addition to kaolin has a positive effect on the porosity ratio of membranes compared to those prepared from kaolin alone. For example, the kaolin membrane had a porosity ratio of 27% and an average pore size of about 0.73 μm, whereas the kaolin + 10 wt% starch (K+S) membrane had a porosity ratio of 36% and an average pore size of about 1.41 μm, for samples sintered under the same conditions (at 1250°C for 1 hour). As the corn starch burn out during sintering process, it will leave a pore in the sintered body which contributed to apparent porosity.

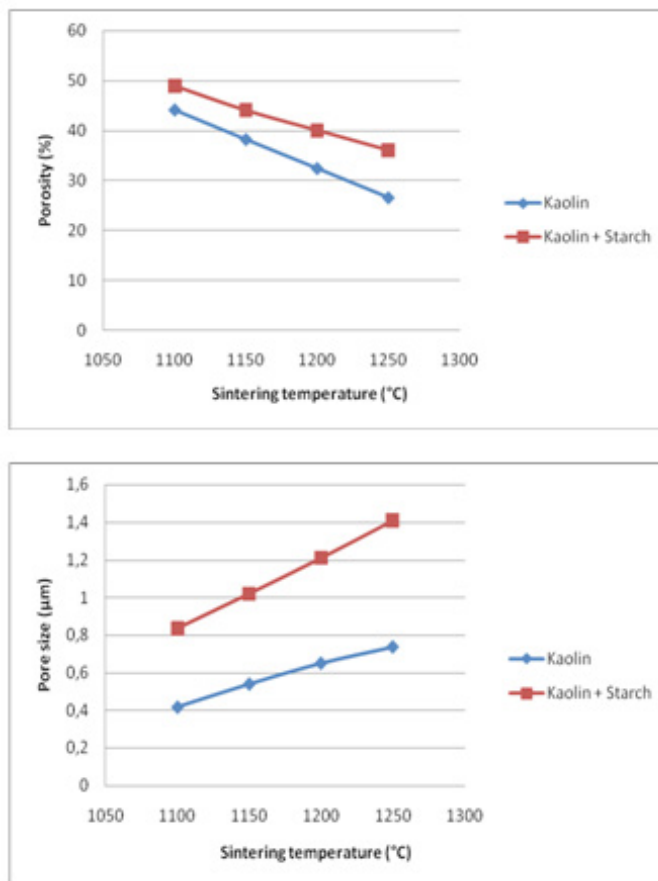


Fig. 8 Effect of sintering temperature on average pore size and porosity of samples prepared from kaolin (K) and kaolin + starch (K+S)

The pore size distribution curves of specimens sintered at 1250°C, for kaolin (K) and kaolin + 10% starch (K+S), are illustrated in Fig. 9. As it can be deduced from this figure, the pore size distribution of the membrane is a single (mono modal) distribution. This is a clear indication that the samples have a uniform pore size distribution.

The average pore diameters of membranes are determined to be 0.4, 0.70, 0.8 and 1.41 μm for membranes (Kaolin and Kaolin+ Starch) sintered at 1100 °C, 1250 °C respectively corresponding to the micro-filtration range.

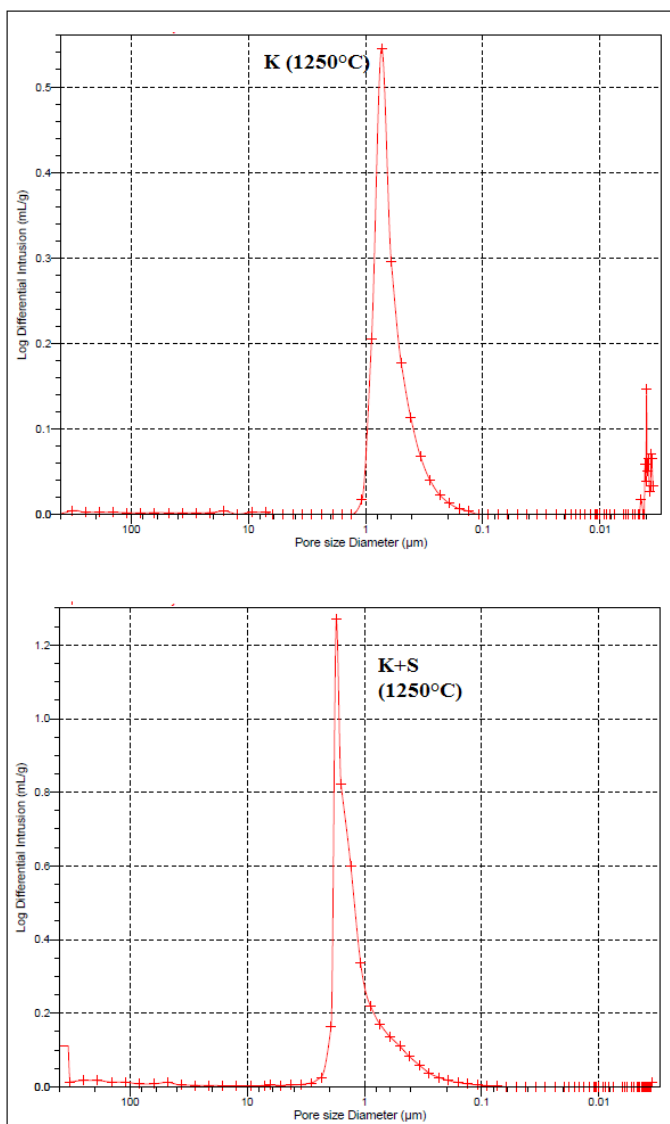


Fig. 9 Pore size distribution of samples prepared from kaolin and kaolin + starch sintered at 1250°C for 1 hour

3.2.3 Mechanical resistance

Fig. 10 shows the variation of tensile strength with sintering temperatures. In accordance with the SEM pictures and the porosity values, the increase of the sintering temperature is accompanied with a densification phenomenon and consequently an increase in the tensile strength from 4 MPa at 1000 °C to 28 MPa at 1250°C for membranes prepared from kaolin.

As shown in Fig. 10, the flexural strength values of the porous kaolin samples without pore former addition were higher than those of porous kaolin + organic additive samples. This figure shows that the flexural strength is closely related to the total porosity ratio which is in turn sintering temperature-dependent. For example, flexural strength was 28.41 MPa at a porosity of 27% and an average pore size of 0.73 μm, whereas flexural strength was about 21 MPa for k+S membranes having a porosity ratio of 36% and an average pore size of 1.41 μm. Both K and K+S supports were sintered at 1250°C for 1 hour.

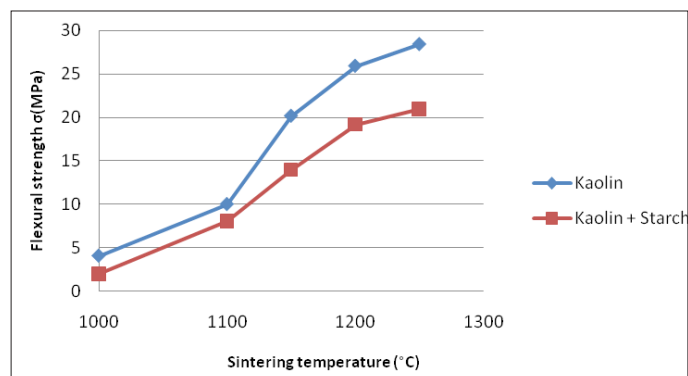


Fig. 10 Flexural strength as a function of sintering temperature for kaolin (k) and kaolin + 10 wt% starch (k+S) samples

3.2.4 Choice of the membrane

The prepared membranes sintered at 1250°C offer a better mechanical strength (28 MPa). Such resistance is high enough to achieve filtration. Thus, membrane prepared from kaolin alone and sintered at 1250°C for 1 hour (average pore diameter of 0.73 μm and 27 % of porosity) was retained for corrosion tests and filtration study.

3.2.5 Chemical resistance

The weight loss due to the corrosion by acids and alkali is shown in Fig. 11. It can be seen that the membrane shows a better acid corrosion resistance, since its mass loss is much lower than those of membranes after alkali corrosion. Therefore, the observed results in weight loss during corrosion tests suggest that the prepared membrane possesses a good chemical corrosion resistance and it is suitable for applications involving acidic and basic media [42].

3.2.6 Determination of membrane permeability

The membrane was initially characterized by the determination of water permeability. It can be seen that the pure water flux increases linearly with increasing the applied pressure (Fig. 12). Pure water permeability was determined from the slope of the linear variation of flux (l/h.m²) versus the applied pressure. The membrane permeability was found to be equal to 20 l/h.m² .bar.

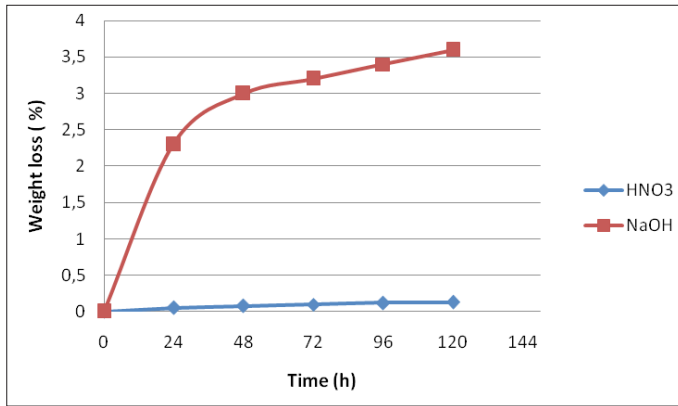


Fig. 11 Weight loss of membranes in nitric acid (45°C) and soda solutions (80°C) as a function of time

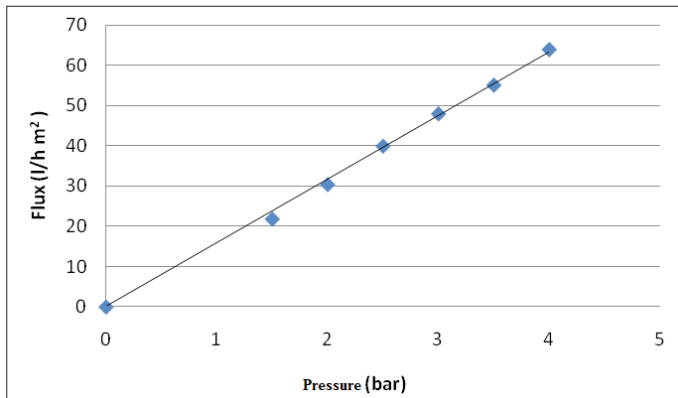


Fig. 12 Pure water flux versus operating pressure

3.3 Application to the treatment of the cuttlefish effluents

The elaborated membranes have been applied to the cuttlefish effluents treatment. Fig. 13 gives the variation of permeate flux with transmembrane pressure after 2 hours of filtration at 25°C. Permeate flux increased linearly with transmembrane pressure until 4 bar and then became pressure independent. This behaviour can be explained by the formation of a concentrated polarization layer. Beyond 4 bar, the flux value is about 25 l/h.m².

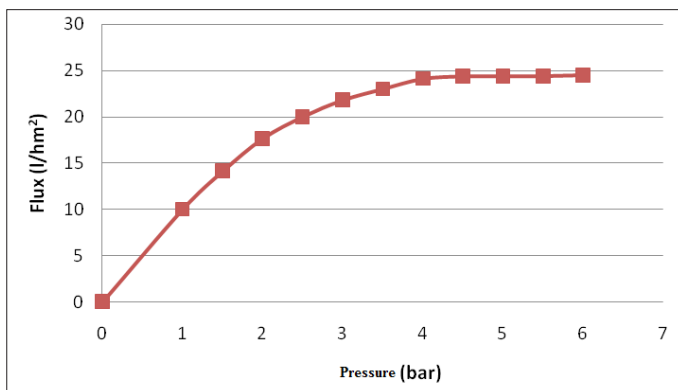


Fig. 13 Variation of the permeate flux vs transmembrane pressure

On the other hand, the variation of the permeate flux with time at different transmembrane pressures (TMP) from 2 to 4 bar shown in Fig. 14 provides information of how the membrane works. The flux decreases slightly from 43 to 20 l/h.m² during 60 min when operated at 3 bar TMP. Then it levels off at a constant value over time. The flux evolution corresponds to a decline of about 54%.

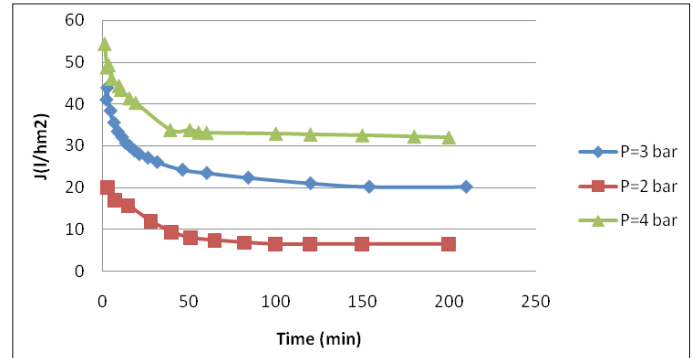


Fig. 14 Variation of the permeate flux with time of filtration

A similar behavior has been reported in literature for the same application [3, 39, 43]. The filtration flux evolution can be divided into two stages: first a sharp decrease followed by a stabilization phase. At the beginning of the filtration, it was assumed that a partial pore size reduction and the deposit of a loose particle layer at the surface take place by interaction of the melanin particles with the membrane material entailing the rapid decrease of the permeation flux. When this stage is completed, the filtration flux reaches a plateau that is only dependent on the TMP. It is also interesting to note that the constant permeate rate is reached more quickly when the pressure is high.

3.3.1 Microfiltration performances

Table 2 shows the main characteristics of the raw and treated effluents. The COD values of raw effluents from the production process ranged between 2000 and 3000 mgL⁻¹ with an average concentration of 2615 mgL⁻¹. The turbidity measured for the raw effluent presents a very high value which is about 335 NTU. As seen in the Table 2, a strong decrease of COD was obtained by filtration using kaolin membranes since the turbidity of the microfiltered sample was as low as 0.86, 1.10 and 2 NTU respectively for filtration at 2, 3 and 4 bar. On the other hand, the COD reduction was between 75 and 67% (from 699.5 to 862.6 mg L⁻¹ with TMP from 2 to 4 bar). By contrast, the conductivity in permeate was in the range of 150-170mS.cm⁻¹ showing a slight decrease (25-35%) indicating the contribution of the charged species retained by the membrane.

Table 2 Characteristics of the effluent before and after filtration on kaolin membranes.

	Pressure (bar)	Turbidity (NTU)	COD (mg.L ⁻¹)	Conductivity (mS.cm ⁻¹)
Raw effluents		335	2615	204
	2	0.86	699.5	150
Filtrate	3	1.10	777.8	166
	4	2	862.6	170
TR (%)	3	99	70	20

TR : percentage reduction

Fig. 15 shows the noticeable discoloration of permeates compared to the feed. This observation is consistent with the strong decrease of turbidity since the black color of the feed solution is related to the presence of suspended melanin particles.

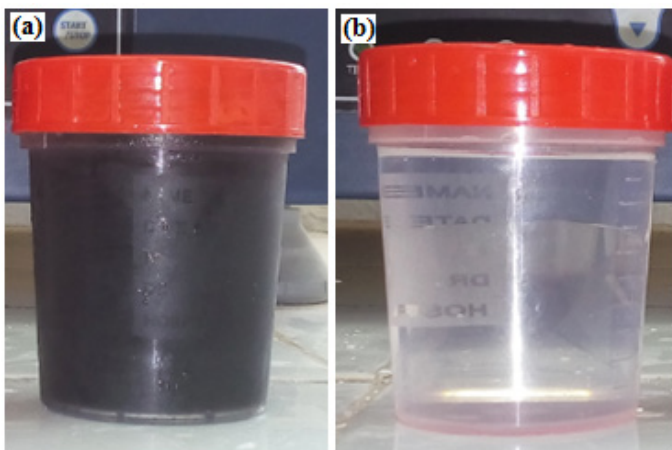


Fig. 15 Picture of the cuttlefish effluent: (a) before MF treatment and (b) after MF treatment.

Turbidity of permeate was found to get reduced by 99% when MF was carried out at a TMP of 3 bar, whereas COD was reduced by 70% and conductivity by almost 30%. In fact, turbidity reductions were found to be more than the corresponding COD reduction on percentage basis. It can then be concluded that the kaolin MF membrane mainly retained the suspended matter (melanin) while the soluble fraction consisting of organic (macro) molecules and salts pass through the membrane. Such results are in agreement with the values given in the literature for inorganic MF membranes in similar applications (waste water treatment) [18, 29, 39, 43].

All studied parameters (turbidity, COD and conductivity) were found to increase by raising the TMP, which was attributed to a higher rejection at lower TMP. Melanin particles are smaller than the mean pore radius as mentioned above [18,39] and they are retained by a partial pore blockage. It is then assumed that a pressure increase enables a very small amount of melanin particles to cross the membrane leading to a decrease of the membrane performance.

It appears from these results that the kaolin membranes can afford a highly satisfactory MF stage regarding the rejection of the suspended matter particularly as melanin particles is a valuable by-product that can be recovered.

3.3.2 Evaluations of resistances

The intrinsic membrane resistance, cake layer resistance and fouling resistance deduced from Eqs. (3), (4) and (5) for kaolin membrane are presented in Table 3.

The polarised layer resistance (R_p) was lower than the irreversible fouling resistance (R_f) and the major part of the total resistance was due to fouling ($(R_p+R_f) / R_t = 66.67\%$). The reason for the high resistance, caused by the irreversible fouling, is that kaolin membrane presented large pores. Thus most particles are adsorbed on or plugged into the membrane pores ($R_f > R_p$).

Table 3 Resistance values for kaolin membrane.

$R_t(10^{12})$ (m ⁻¹)	$R_m(10^{12})$ (m ⁻¹)	$R_p(10^{12})$ (m ⁻¹)	$R_f(10^{12})$ (m ⁻¹)	R_m/R_t (%)	R_p/R_t (%)	R_f/R_t (%)
54	18	5	31	33.33	9.27	57.4

4 Conclusions

In this work, a comprehensive study on the fabrication and characterization of ceramic membrane from kaolin and starch mixtures were performed. The membranes were prepared by the extrusion procedure.

Ceramic membrane manufactured from kaolin and starch mixtures presented features of porosity (porous volume and average pore size) with values significantly higher than those elaborated from kaolin alone. It has also been found that the pore structure may be controlled by the sintering temperature.

The prepared membranes sintered at 1250°C offer a better mechanical strength (28 MPa compression strength), chemical stability (<5% weight loss in acidic media and negligible weight loss in acidic media), good porosity (27%) and a higher average pore size (0.73 μm).

The application of this membrane to the treatment of washing cuttlefish waters shows good performances in term of permeate flux and suspended matter (mainly melanin particles) rejection leading to a strong discoloration of the deep black feed.

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