Desalination and Water Treatment
www.deswater.com

12 (2009) 415–419

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doi: 10.5004/dwt.2009.1051

Porous ceramic membranes prepared from kaolin

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Received 25 August 2008; Accepted in revised form 22 November 2009

ABSTRACT

The prepared asymmetric kaolin microfiltration membranes have been investigated. The objectives of this work were to prepare the ceramic supports and membranes from clays. In this way, kaolin is one of the most popular starting materials for aluminosilicate-based ceramics, due to its common occurrence and good forming. Consequently, the usual starting materials (alumina, silica, cordierite, mullite, etc.) may be replaced by a local kaolin as raw material in order to reduce the cost of supports fabrication. These raw materials have been dictated by their natural abundance (low price) and their beneficial properties. The powders mixed with certain organic additives have been extruded to fabricate a porous tubular configuration with highly uniform porous structures. Subsequently, the influence of the sintering temperature on the total porosity, average pore size, pore size distribution and strength of supports was investigated. It was found that the average pore size of the membrane and its thickness were about 0.6 μm and 21 μm, respectively. Moreover, this membrane was tested with distilled water. The rejection for the membrane depends, in fact, on the nature and on the conformation of the polymer used for the filtration tests. The results obtained enable to conclude that a clay membrane may be used for tangential microfiltration.

Keywords: Supports; Membranes; Porosity; Microfiltration

1. Introduction

Ceramic membranes have a large potential over their polymer counterparts for applications at high temperatures, pressure and in aggressive environments [1–4]. Generally, porous ceramics supports are needed for membranes manufacturing.

The commercial supports and membranes are generally manufactured from compounds such as alumina (Al_2O_3), cordierite ($2MgO.2Al_2O_3.5SiO_2$), and mullite ($3Al_2O_3.2SiO_2$) [5–7], which have a relatively elevated cost. More recently, different processing routes for membrane supports preparation from kaolin have been proposed [1] in order to decrease this cost and to evaluate local natural resources [1,8]. In this way, both supports and membranes have been manufactured, in this work, from local kaolin as a raw material (Tamazert kaolin: TK).

In fact, the top layer (membrane) is closely related to its support [9]. In addition, the quality of the support is of crucial importance to the integrity of the membrane layers that are applied in the subsequent preparation steps. The surface roughness and homogeneity of the support will determine the integrity of these membrane layers, and,

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the surface roughness determines the minimal thickness of the membrane layer for complete surface coverage.

It should be noted that the chemical composition of this kaolin type (noted TK: Tamazert kaolin) is significantly different from that of the typical kaolinite (noted DDK: Djebel Debagh, Guelma region, Algeria). A preliminary study carried out on both types, under the same conditions showed that they behave differently.

Meanwhile, a recent study has been carried out on preparation and characterization of tubular membrane supports using centrifugal casting, but using TK as raw material [10]. The usual starting materials (Al_2O_3, ZrO_2, etc.) were also replaced by a local raw material (TK) in order to reduce the cost of supports fabrication. TK type was selected in that work on the basis of a preliminary study. It was found that the other kaolin types (DDK) did not behave similarly when they were used individually. This result might be due to their differences in chemical compositions and constituting phases. In fact, the main crystallized phases in DDK were mullite and cristoballite, whereas the main crystallized phases in TK were mullite and quartz. These 3 phases did not risk any dissociation when supports are used for water treatment.

However, these two kaolin types behave differently when they are used for acid filtration, such as hydrofluoric acid (HF). Therefore, because of the easy dissolution of cristoballite in HF, DDK cannot be applied for this application. By contrast, TK resists well because both mullite and quartz are indissoluble. This is why TK is selected in this work as an interesting raw material.

2. Experimental procedure

The chemical composition of the clays used in the present work given in weight percentages of oxides is: 50.56 wt% SiO_2; 34.15 wt% Al_2O_3; 1.15 wt% Fe_2O_3; 0.02 wt% CaO; 0.31 wt% MgO; 0.28 wt% TiO_2; 7.18 wt% K_2O; and a 6.35 wt% of solids lost by calcination. The two main preparation processes used in this work are described in Fig. 1. The tubular support was obtained by extrusion of the mixture of kaolin (80 wt%) and starch (20 wt%) as an organic additive. The flat configuration of the supports was obtained using a roll pressing technique and this configuration was used for mechanical tests.

The same powder used for support elaboration was crushed for 2 h with the assistance of a planetary crusher and calibrated at 50 μm by sieving. For preparing a microfiltration layer with kaolin powder, a deflocculated slip was obtained by mixing 10 wt% of kaolin, 20 wt% of PVA (12 wt% aqueous solution) and water (70 wt%). The deposition of the slip on the support was performed by the slip casting method [11]. After drying at room temperature for 24 h, the microfiltration layer was sintered at 1050°C for 1 h.

The tangential filtration experiments were performed using a home-made pilot plant at room temperature. The working pressure was obtained using a nitrogen gas source.

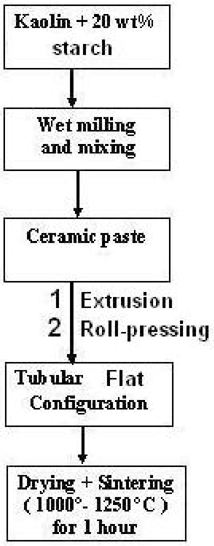

Fig. 1. A schematic diagram showing the main processes used for membrane supports preparation in this work.

The retention rate of the membranes was determined using solution containing dextran with a molecular weight equal to 580 kDa. The concentration of the solution was fixed at 0.5 g/l. All the experiments were carried out at room temperature (25°C). Moreover, the retention rates were estimated by the following simple relation:

$$R(\%) = 100\left(1 - C_p / C_f\right) \qquad (1)$$

where C_p and C_f are the solute concentration in the permeate and in the feed solution, respectively.

All the permeate concentrations were determined by chromatography technique.

The tests were carried out with a liquid chromatograph equipped with a Waters pump (M501), a manual U6K injector (Waters), a UV visible variable wavelength detector (Dionex) and a Varian 4400 integrator. 10 μl of a 20–60 ppm test solution (dextran, P.E.G.) was injected for chromatographic separation, the eluent flow being set at 1 ml/min. The eluent phase was composed of pure water.

The three-points bending test was performed in air at room temperature carried out on samples in the form of bars having rectangular sections.

Finally, the total porosity, average pore size and pore size distribution were determined by mercury intrusion porosimetry for supports sintered at different temperatures for 60 min.

3. Results and discussion

The porosity measurement and the average pore size were carried out for the supports sintered at different temperatures for 60 min. The results obtained are illus-

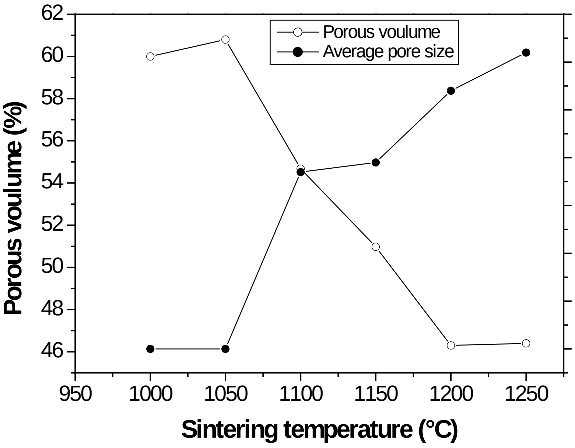

Fig. 2. Porous volume (%) and average pore size vs. sintering temperature.

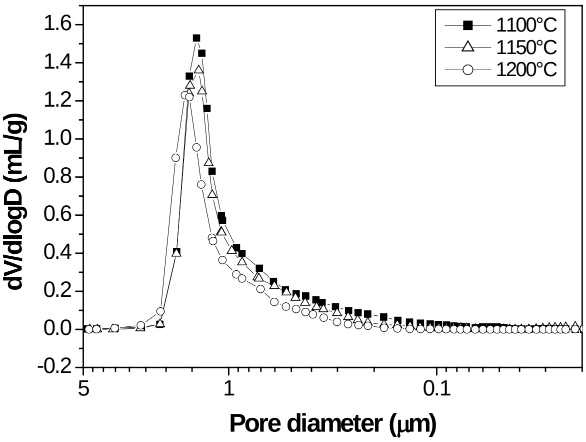

Fig. 3. Pore size distribution in samples sintered at 1100°C, 1150°C and 1200°C.

trated in Fig. 2. As would be expected, this figure shows, generally, that there is an increase in the average pore size and a decrease in the total porosity in samples when the sintering temperature is increased (Fig. 2). On the basis of the above results, it can be said that the increase in sintering temperature encourages the coalescence of pores which, in turn, leads to a larger average pore size. For example, the kaolin + 20 wt% starch (K + S) supports had a porosity ratio of ≈60% and an average pore size around 0.9 µm for samples sintered at 1050°C for 1 h, whereas the K+S supports had a porosity ratio of ≈46% and an average pore size around 1.4 µm for samples sintered at 1200°C for 1 h.

Consider Fig. 3 which presents a modal of pore size distribution for samples sintered at different temperatures for 1 h. It is almost single (mono) modal of pore size distribution (SMPSD) or homogenous pore distribution, as it has been mentioned elsewhere [1].

This single (mono) modal of pore size distribution is generally recommended by many manufacturers.

It should be noted that the pore size distribution were divided into 3 main modals. These consist of a single or Gaussian distribution, bimodal and multimodal pore size distributions. The single (mono) modal of pore size distribution is generally obtained for samples having a uniform pore size distribution. When the pore volume (%) is plotted against the pore size, the curve is characterised by a single peak. However, the bi-modal of pore size distribution (BMPSD) is characterised by two different or overlapping peaks. This means that there are two classes of pore size distribution. Finally, the multi modal of pore size distribution (MMPSD) is characterized by the presence of more than two distinct or overlapping peaks.

The flexural strength of porous ceramics (having different porosity ratios) was evaluated. The effect of sintering temperature on the flexural strength was also investigated. These porous kaolin samples have different microstructures in terms of porosity. Their mean pore diameters and porosities ranged from 0.9 to1.5 µm and from 60% to 46%, respectively. The flexural strength values of the porous kaolin samples are shown in Fig. 4. This figure shows that the flexural strength is closely related to the total porosity ratio which, in its turn, is sintering temperature-dependant.

For example, flexural strength was 4 MPa at a porosity of ≈60% and an average pore size around 0.9 µm, whereas flexural strength was about 24 MPa for K + S supports having a porosity ratio of ≈46% and an average pore size around 1.4 µm. These results are in good agreement with those reported elsewhere [12,13].

Fig. 5 shows a typical cross-section of a membrane consisting of a microfiltration layer coated on macroporous K + S support. The membrane structure shows a good homogeneity, which is an important property for potential MF applications. The thickness of the microfiltration layer may be controlled by the percentage of the mineral

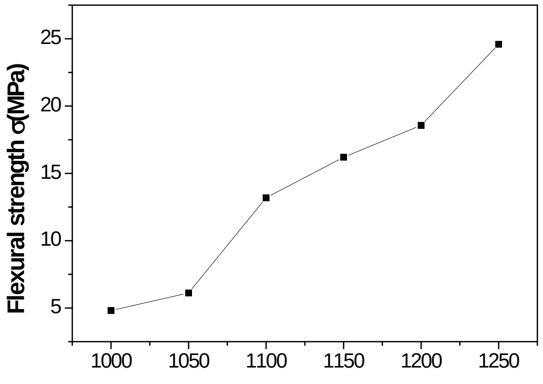

Fig. 4. Flexural strength as a function of sintering temperature.

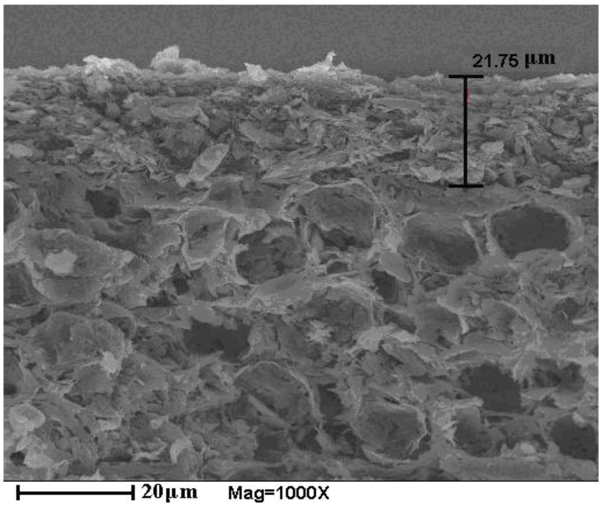

Fig. 5. SEM micrograph of the cross-section of both membrane and support.

powder added in to the suspension and the coating time. Under the used coating conditions, kaolin layer could be produced with an average thickness of about 21 µm and an average pore size around 0.6 µm.

The MF membrane was first characterized by its water permeability. Fig. 6 shows that the water flux through the membrane measured as a function of time depends on the applied pressure. A stable flux is obtained after a few minutes and the average permeability is about 140 l/h.m^2.bar. It should be noted that the membrane was conditioned by immersion in pure deionised water for 1 d before these measurements.

The rejection for the membrane depends, in fact, on the nature and on the conformation of the polymer used for the filtration tests. The rejection rate for the dextran molecules is equal to about 30%. The permeate fluxes measured in this test are plotted in Fig. 7.

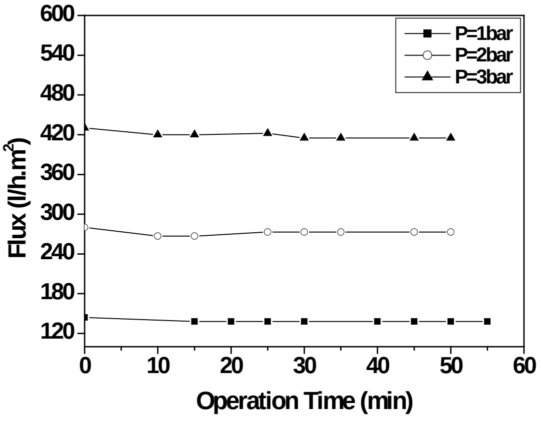

Fig. 6. Permeate flux vs. time at 3 working pressure values, using distilled water.

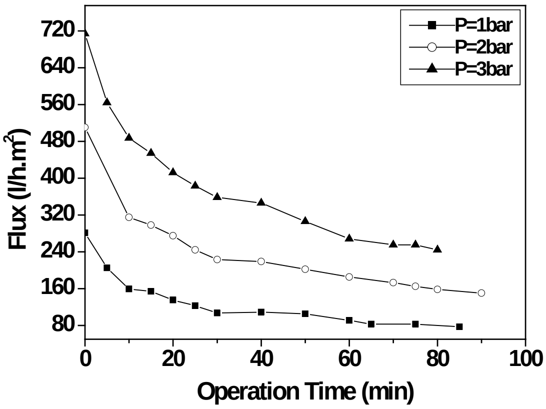

Fig. 7. Permeate flux vs. time at 3 working pressure values using distilled water containing 0.5 g/l dextran.

After a prolonged operation, the permeate flux, under operating conditions with organic additives decreased slightly and reached a constant value. However, the steady state flux when not using organic additives was found to be 2.5 times higher than that of organic additives. The final flux operated with no organic additive was about 140 l/h.m^2.bar, whereas the latter was about 60 l/h.m^2.bar. During the first 15 min of filtration the flux decreases rapidly. An explanation may be proposed: the membrane may probably capture some of small organic mater droplets within its structure leading to the rapid decline in the permeate flux.

4. Conclusions

In this work, the MF ceramic membrane was prepared by the slip casting method, whereas the supports were prepared by the extrusion method. Furthermore, the effect of temperature on porosity, flexural strength and average pore size of supports was investigated. It was found that the average pore size of the MF membrane was about 0.6 µm, while its thickness was about 21 µm. The results obtained enable to conclude that the clay membrane may be used for tangential microfiltration.

References

[1] F. Bouzerara, A. Harabi, S. Achour and A. Larbot, J. Eur. Ceram. Soc., 26 (2006) 1663–1671.
[2] H. Bissett, J. Zah and H.M. Krieg, Powder Technol., 181 (2008) 57–66.
[3] T.V. Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. Van der Bruggen and G. Maes, J. Membr. Sci., 207 (2002) 73–89.
[4] R.F.S. Lenza and W.L. Vasconcelos, J. Non-Cryst. Solids, 273 (2000) 164–169.
[5] S.H. Zhong, C.F. Li and X.F. Xiao, J. Membr. Sci., 199 (2002) 53–58.
[6] N. Saffaj, S.A. Younssi, A. Albizane, A. Messouadi, M. Bouhria,

M. Persin, M. Cretin and A. Larbot, Desalination, 168 (2004) 259–263.

[7] T. Mohammadi and A. Pak, Separ. Purif. Technol., 30 (2003) 241–249.

[8] J. Zhou, X. Zhang, Y. Wang, A. Larbot and X. Hu, J. Porous Mater., (2008) doi: 10.1007/s10934-008-9258-z.

[9] P.M. Biesheuvel, V. Breeveld, A. Higler and H. Verweij, Chem. Eng. Sci., 56 (2001) 3517–3525.

[10] A. Harabi, F. Bouzerara and S. Condom, Desal. Wat. Treat., 6 (2009) 222–226.

[11] S. Khemakhem, R. Ben Amar, R. Ben Hassen, A. Larbot, M. Medhioub, A. Ben Salah and L. Cot, Desalination, 167 (2004) 19–22.

[12] L. Palacio, Y. Bouzerdi, M. Ouammou, A. Albizane, J. Bennazha, A. Hernández and J.I. Calvo, Desalination, 245 (2009) 501–507.

[13] B.K. Nandi, R. Uppaluri and M.K. Purkait, Appl. Clay Sci., 42 (2008) 102–110.