Desalination and Water Treatment
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6 (2009) 222–226

Preparation and characterization of tubular membrane supports using centrifugal casting

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Received 15 September 2008; accepted 20 May 2009

ABSTRACT

In this paper, the manufacture of a tubular supports ceramics membrane is described. The main objective of this work consists of the preparation and characterization of adequate and less expensive membrane supports, using abundant local raw materials. A porous raw materials tube of 20 mm in diameters and 170 mm in length were successfully fabricated by centrifugal casting technique. Moreover, the obtained samples were characterized, using different techniques. The structure was analyzed by X-ray diffraction (XRD) and mercury porosimetry techniques. The pore size and the presence of possible defects in the supports were determined by Scanning Electron Microscopy (SEM). It has been found that tubular ceramic membrane supports had a highly homogeneous product and a smooth inside-surface. The influence of the sintering temperature on the total porosity, average pore size and pore size distribution of supports is taken into account. The obtained results enabled to conclude that clay supports can be used alone (without any additions), successfully, in tangential microfiltration or as a support for ultrafiltration membranes. Finally, this investigation demonstrates that centrifugal casting may be also considered as a promising technique in order to fabricate tubes for membrane application.

Keywords: Supports; Membranes; Centrifugation; Porosity

1. Introduction

Porous ceramics supports are, generally, needed for membranes manufacturing. For the development of high-quality supports, the following properties are of major importance: pore size distribution, total porosity ratio, surface quality with the absence of large defects or large pores, good mechanical properties and chemical stability [1]. In fact, the top layer is closely related to its support. 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 require thickness of the membrane is further limited by the smoothness of the support because the membrane material must cover all irregularities of the support to form a continuous, defects free layer [2].

The conventional method of preparing ceramic tubes is extrusion. Nevertheless, a problem of extruded ceramic tubes may be encountered such as low surface smoothness [3] and larger average pore sizes. Consequently, an alternative method for such a supports preparation has been proposed (centrifugal casting) [2-9]. Although this method is rather more expensive than extrusion, it is very suitable for manufacturing

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high-quality tubes [5]. A centrifuged tube when compared to an extruded tube shows an extremely good roundness, smooth inside surface and a narrow pore size distribution are obtained, which are essential for the quality of membranes that are, afterwards, deposited on this surface [3].

This is the main objective of this work which consists of the preparation of adequate and less expensive membrane supports using centrifugal casting process and to investigate the effect of organic content (such as starch) on porosity. For comparison, the raw materials with and without starch addition were prepared.

These Tubular supports, are destined to be used as supports of ultra-filtration or micro-filtration membranes. They permit to provide mechanical strength to a membrane top layer to withstand the stress induced by the pressure difference applied over the entire membrane and must simultaneously have a low resistance to the filtrate flow. The usual starting materials (Al_2O_3, ZrO_2...) are replaced in this work by a local raw material (Tamazert Kaolin: TK), in order to reduce the cost of supports fabrication.

It should be noticed that TK type has been selected in this work (to be used) on the basis of a preliminary study. In fact, the other kaolin types did not behave likely when they were used individually. This result might be due to their differences in chemical compositions and constituting phases.

2. Experimental procedure

2.1. Analysis of the raw materials

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 fine particles and the organic material present in the clay give plasticity to the green paste. The particle size distribution of this material was determined by the Dynamic Laser Beam Scattering (DLBS) technique. This method gives an average particle size around 4 μm.

2.2. Supports elaboration

The main preparation steps, used in this work, are as follow:

Firstly, 50 g (33.3 wt%) of the raw material powders were mixed with 100 ml (66.7 wt%) distilled water by magnetic stirring. Then, the prepared suspensions were ultrasonically treated during 10 min at 35 kHz to break down particle agglomerates. Afterwards, the obtained mixtures were poured into cylindrical metal moulds 20 mm in inner diameter and 170 mm in length. Then rotated rapidly around its central axis for 8 min at 6000 rpm and the remaining liquid was poured out of the moulds. The green tubes were vertically dried inside the moulds during 3 days at 22 °C and 50% relative humidity. After drying, the green tubes were removed out from the moulds and sintered horizontally at 1000, 1150, 1200 and 1250 °C during 1 h.

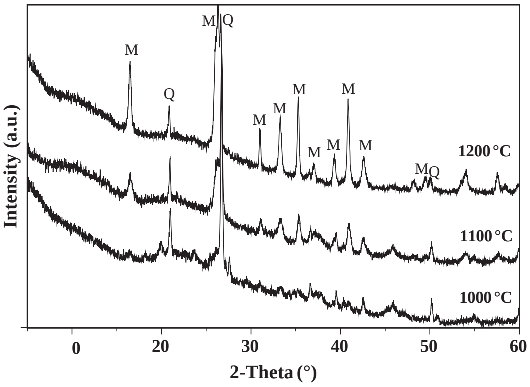

Fig. 1. XRD spectra of samples sintered at different temperatures during 1 h. M, mullite; Q, quartz.

In order to study the influence of the starch addition on the porosity and pore size distribution of the tubes, a series of different starch concentrations in the suspension have been prepared. In the stepwise method, the same procedure was repeated to form the next laminate. Suspensions, identified as S2 were prepared by adding the starch to raw materials.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the X-ray diffraction (XRD) spectra of samples sintered at 1000, 1100 and 1200 °C during 1 h. The main observed phases are: mullite ($3Al_2O_3{\cdot}2SiO_2$) and quartz. At 1000°C, the main dominant phase appearing at this temperature is quartz while at higher temperatures the main dominant phase is mullite. Mullite becomes more crystallized at 1100 °C (Fig. 1). Its content increased, thereafter, with increasing temperature. These identified phases are of great importance because of their promising physical and mechanical properties. For example, mullite is a useful refractory for high-temperature ceramics applications, because of its low thermal expansion and high creep resistance. In addition to this, it has a high load bearing capacity, abrasion and corrosion resistance.

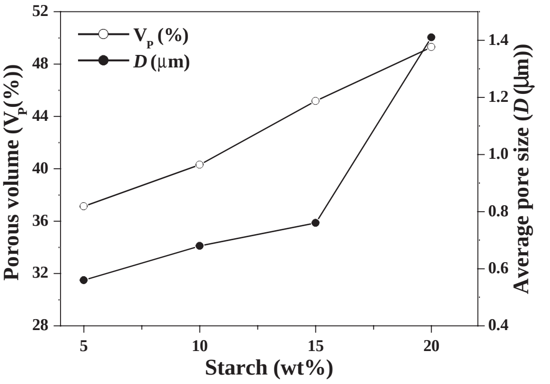

Fig. 2. Porous volume (%) and average pore size versus sintering temperature for kaolin with different wt% starch samples.

3.2. Pore characterization

For the development of high-quality supports, the following properties are of major importance: pore size distribution, total porosity ratio, surface quality with the absence of large defects or large pores, mechanical properties and chemical stability [1,10]. The pore size distributions of samples composed from the individual material and the binary mixtures were measured by mercury intrusion porosimetry (Micromeritics, Model Autopore 9220).

In order to select the appropriate starch amount that should be added into the studied kaolin, different percentages have been taken into account, as shown in Fig. 2. This figure shows clearly that both average pore size and porous volume (%) values increased with increasing starch percentages. For many applications, higher values of these 2 parameters were recommended; the 20 wt% starch addition has been selected.

The porosity measurement and the average pore size have been carried out for supports sintered at different temperatures during 60 min. The obtained results are illustrated in Figs. 3 and 4. As would be expected, these figures show, generally, that there is an increase in average pore size and a decrease in total porosity in the samples, when the sintering temperature is increased. On the basis of the above results, it can be said that the increase in sintering temperature encourages the coalescence of pores which, in turns, leads to a larger average pore size.

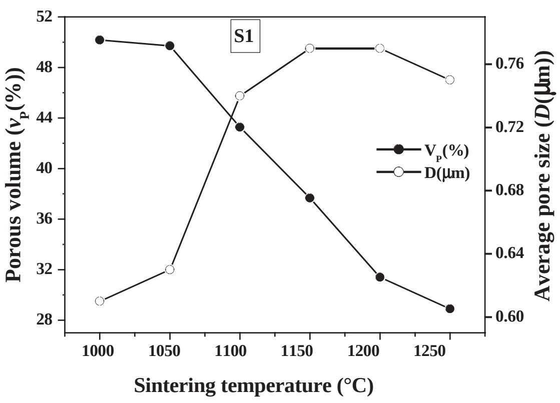

Fig. 3. Porous volume (%) and average pore size versus sintering temperature for kaolin samples.

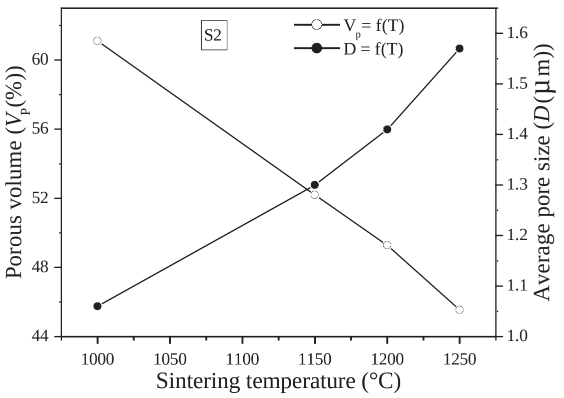

Fig. 4. Porous volume (%) and average pore size versus sintering temperature for kaolin with 20 wt% starch samples.

Moreover, it can be said that both the average pore size and porous volume are closely related to the preparation method. The obtained results show that the starch addition to raw materials has a positive effect on the porosity ratio of supports compared to those prepared from raw materials alone. For example, the raw materials supports had a porosity ratio around 31% and an average pore size around 0.77 μm, whereas the raw materials with 20 wt% starch supports had a porosity ratio around 49% and an average pore size around 1.41 μm, sintered under the same conditions (1200 C during 1 h).

Fig. 5 shows typical pore size distributions of samples (kaolin samples, S1 and kaolin with 20 wt% starch samples, S2) composed from raw materials and mixtures of 20 wt% starch. The mixtures of raw materials and starch samples have higher median pore diameters than the samples prepared from raw materials alone, proving the presence of larger pores in the mixtures. Apparently, the removed starch particles cause an increase in median pore diameter.

The pore size distribution modal may also be classified into 1 modal; single or Gaussian modal, The single modal of pore size distribution is generally obtained for samples having homogeneous pore size distribution. When pore volume (%) is plotted versus pore size, the curve is characterized by a single peak. Moreover centrifugal casting showed to be a very convenient way of preparing high quality tubular membrane supports.

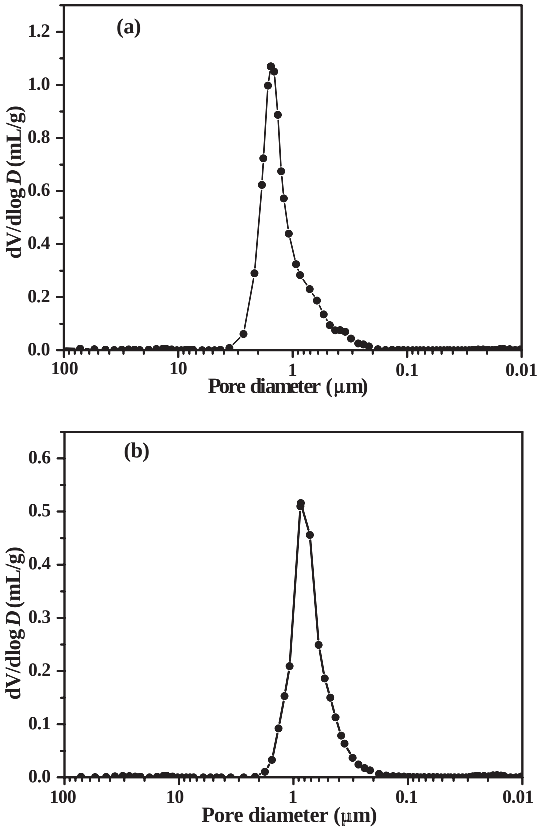

Fig. 5. Pore size distribution in samples sintered at 1200°C during 1 h. (a) Kaolin; (b) kaolin with 20 wt% starch samples.

These supports have smooth inside surface and a narrow pore size distribution. This is necessary for a good integrity of the membrane. The homogeneous pore size distribution is also confirmed by typical micrographs illustrated in Fig. 6. These micrographs indeed confirm the pores characteristics already obtained by pore size distribution curves.

Finally, tangential filtration experiments were performed on a typical prepared membranes support, using a home-made pilot plant at room temperature.

The working pressure was obtained using a nitrogen gas source. The prepared supports (S1) sintered at 1050 °C was characterized by theirs water permeability.

Fig. 7 shows that the water permeability through the support measured as a function of time depends on the applied pressure. A stable flux is obtained after few minutes. The relatively low water permeate flux value is as would be expected, because of its lower average pore size (0.6 μm) and its thickness (2 mm). Additionally, the effect of the applied pressure (bar) on water permeate flux has been taken into account. The flux increases linearly with the applied pressure and the average permeability is about 107 L/h m^2 bar

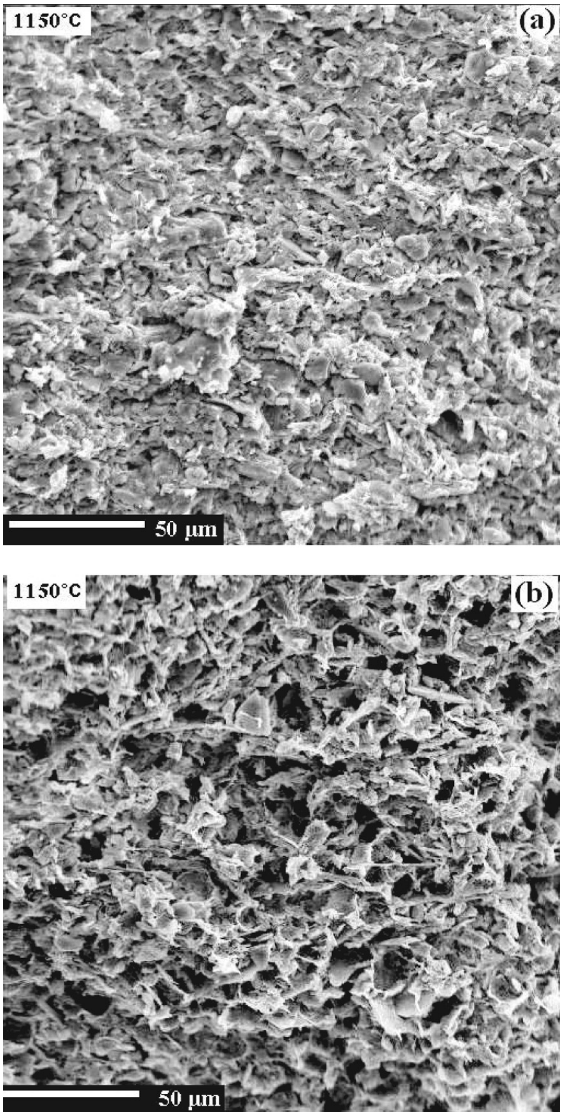

Fig. 6. SEM micrographs of samples sintered at 1150°C. (a) Kaolin; (b) kaolin with 20 wt% starch.

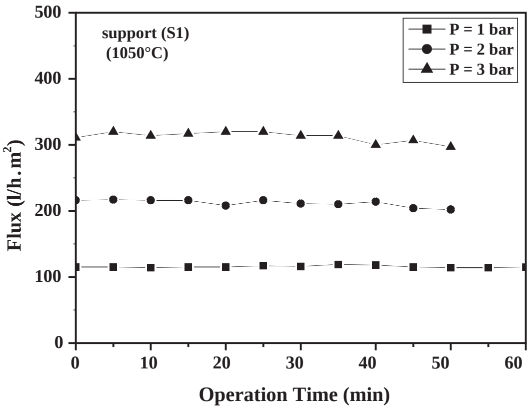

Fig. 7. Water permeability versus time, at 3 working pressure values.

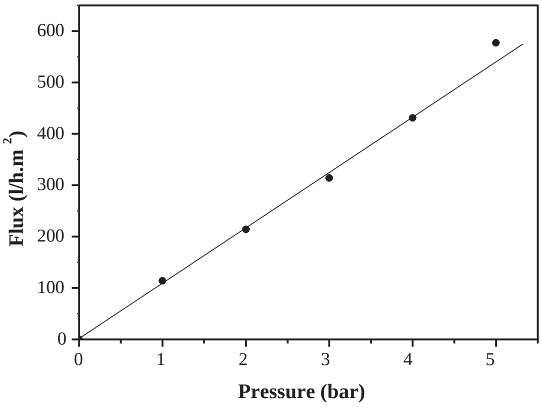

Fig. 8. Water permeability versus pressure.

as we can see in Fig. 8. This indicates that the pressure difference is the only driving force for permeation [11]. For transport driven only by convection, the volume flow rate is proportional to the pressure difference, following the Darcy law.

4. Conclusions

The present work allowed to fabricate aluminosilicate tubes for membrane applications using centrifugal casting technique. Obtained tubes were characterized in terms of porosity; these supports were extremely homogeneous as can be seen from the very sharp pore size distribution. Moreover, the raw materials employed were easily obtainable at low costs. Membrane supports manufactured from raw materials and starch mixtures presented features of porosity (porous volume and average pore size) more important than those elaborated from Tamazert kaolin; the manufactured membrane supports are mainly constituted of mullite and quartz phases. The presence of these phases may also extend further their use, even under severe atmosphere conditions.

References

[1] 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.
[2] P.M. Biesheuvel, V. Breeveld, A. Higler and H. Verweij, Chem. Eng. Sci., 56 (2001) 3517-3525.
[3] A. Nijmeijer, C. Huiskes, N.G.M. Sibelt, H. Kruidhof, H. Verweij, Am. Ceram. Soc. Bull., 77 (4) (1998) 95-98.
[4] C.H. Chen, K. Takita, S. Ishiguro, S. Honda, H. Awaji, J. Eur. Ceram. Soc., 25 (2005) 3257-3264.
[5] G.C. Steenkamp, K. Keizer, H.W.J.P. Neomagus and H.M. Krieg, J. Membr. Sci., 197 (2002) 147-156.
[6] C. Falamaki, J. Veysizadeh, Ceram. Int., 34 (2008) 1653-1659.
[7] G.C. Steenkamp, H.W.J.P. Neomagus, H.M. Krieg, K. Keizer, Sep. Purif. Technol., 25 (2001) 407-413.
[8] K.H. Kim, S.J. Choa, K.J. Yoon, J.J. Kim, J. Ha and D. Chun, J. Membr. Sci., 199 (2002) 69-74.
[9] R. Pinggen, I. Mikio, T. Takahiro and K. Isao, Ceram. Int., 29 (2003) 209-212.
[10] F. Bouzerara, A. Harabi, S. Achour and A. Larbot, J. Eur. Ceram. Soc., 26 (2006) 1663-1671.
[11] J. Sekulie, A. Magraso, J.E. Ten Elshof and D.H.A. Blank, Microp. Mesop. Mater., 72 (2004) 49-57.