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 (Gestel et al., 2002). 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 required 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 (Biesheuvel et al., 2001). The conventional method of preparing ceramic tubes is extrusion. Nevertheless, a problem of extruded ceramic tubes may be encountered such as low surface smoothness (Nijmeijer et al., 1998) and larger average pore sizes. Consequently, an alternative method for such a supports preparation has been proposed (centrifugal casting) [2-9] (Biesheuvel et al., 2001; Nijmeijer et al., 1998; Chen et al., 2005; Steenkamp et al., 2002; Steenkamp et al., 2002; Falamaki & Veysizadeh, 2008; Steenkamp et al., 2001; Kim et al., 2002; Pinggen et al., 2003). Although this method is rather more expensive than extrusion, it is very suitable for manufacturing high-quality tubes (Steenkamp et al., 2002). 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 (Nijmeijer et al., 1998).

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 Micro-Filtration (MF) or Ultra-Filtration (UF) 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 (Al₂O₃, Mullite, ZrO₂, …) are replaced in this work by a native raw material (Tamazert Kaolin: TK, Djebel Debbag kaolins: DD2 and DD3, dolomite, calcite), 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.

Because of their application in the treatment of big amounts of wastewaters (Benito et al., 2005), there is much current interest in the application of membranes in separation procedures. The use of ceramic membranes has many advantages such as high thermal and chemical stability, pressure resistance, long lifetime, and good defouling properties (Lee et al., 2002; Ding et al., 2006). MF and UF are often used to remove particles, microorganisms, and colloidal materials from suspensions (Gaucher et al., 2002). Asymmetric membrane usually consists of a thin top-layer responsible for separating components, and a porous ceramic support with single or multiple intermediate layers imparting the required mechanical strength to the membrane composite (Mori et al., 1998). In fact, the commercial support made of artificial material is an important part of the high price of the membranes, which is why some authors have focused their researches to develop the preparation of low coast supports made of natural raw materials such as clays (Saffaj et al., 2004). The industrial membrane production uses a limited choice of materials. As a consequence, ceramic membranes have a high price. A significant effort was then provided these last years in membrane technology field in order to find new porous ceramics materials at low price (Masmoudi et al., 2005; Rakib et al., 2000). In order to decrease this cost and to evaluate our natural resources, the supports have been manufactured (Elmoudden et al., 2001; Bouzerara et al., 2006), in this work, from kaolin (Al₂O₃·2SiO₂·2H₂O) and the calcium carbonates (CaCO₃) local raw materials. The choice of these materials has been dictated by their natural abundance (low price) and their thermal stability (Khemakhem et al., 2004).

In this chapter, the manufacture of a tubular supports ceramics membrane, using both centrifugal casting and extrusion methods, is described in more details. 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 UF membranes. Finally, this investigation demonstrates that centrifugal casting may be also considered as a promising technique in order to fabricate tubes for membrane application. Moreover, 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 TK; 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.
For comparison, other low cost raw materials (DD2 kaolin and CaCO\(_3\)) have been chosen in order to fabricate membrane supports but using extrusion technique. Finally, a correlation between microstructure and properties of all the prepared membrane supports was also taken into account. Since the ceramic filters are generally constituted of a thick support (2000 \(\mu\)m) and one or multi thin membranes (from 10 to 40 \(\mu\)m for each one). That is why this work or chapter is mainly focussed on ceramic supports rather than its deposed membranes. Therefore, replacing the more expensive starting materials, mentioned above, by other low cost raw materials for supports fabrication (which constitutes about 99% of the filter mass) is significantly important. So, what low cost raw materials does mean? It is incomparable; the alumina price is at least about 100 times more expensive than that of kaolin. Another important advantage is the substantial gain in energy by decreasing the sintering temperature from about 1600\(^\circ\)C (Harabi & DAVIS, 1995a) to about 1250\(^\circ\)C, when alumina supports were replaced by the proposed supports. Besides this, about 50% the prepared supports is pores (porosity) which may also be considered as a gain in its mass. The relatively lower theoretical density of the prepared supports (2.8 g/cm\(^3\)) when compared to that of alumina (3.98 g/cm\(^3\)) (Harabi & DAVIS, 1995a) is also a further exiting advantage. The authors ask readers to do calculation by themselves about the advantages mentioned above. One can claim that there is no need to do this calculation if these low price manufactured supports do not obey to the main internationally required support characteristics. Consequently, this chapter is devoted to go through these characteristics one by one in more details.

2. Important definitions

For reader whom not well familiarized with this kind of technology the definition of certain technology words such as inorganic membrane, extrusion and centrifugal methods is of great importance.

2.1 Inorganic membranes

A membrane is a physical barrier allowing selective transport of mass species, widely used for separation and purification in many industries. Membranes can be classified into organic, inorganic and hybrids of organic/inorganic systems. Inorganic membranes can be divided firstly into dense and porous structures, and for porous membranes into asymmetric and symmetric ones. Symmetric membranes exhibit homogeneous pore size throughout the membrane. Asymmetric membranes present a change of structure through the membrane. An inorganic membrane can be described as an asymmetric porous ceramic formed by a macroporous support with successive thin layers deposited on it. The support provides mechanical resistance to the medium. The successive layers are active in MF, UF or Nano-Filtration (NF), depending on their pore diameters. Most commercial ceramic membranes are in plate or tubular configuration in order to increase the surface area to volume ratio, which gives more separation area per unit volume of membrane element. The most common fabrication processes are extrusion, pressing, tape casting, slip casting, centrifugal casting, Sol-Gel process, dip and spin coating. From these, extrusion, pressing, slip casting, centrifugal casting and tape casting are used for support systems, tape casting and slip casting are used for microfiltration membranes, Sol-Gel process, dip and spin coating are used for UF and NF membranes.
2.2 Extrusion method
Extrusion is a process technology for the production of ceramic tubes. In extrusion: a stiff paste is compacted and shaped by forcing it through a nozzle. In general the manufacturing process of tubular ceramic supports using extrusion method includes the following steps:
- Steps of mixing various materials, including raw material, organic additive, and other extrusion-aid materials to form a paste.
- Passing the paste through an extruder to form a cylindrical, tubular supports.
- Placing the tubular supports on rotating rollers to cause the support to rotate and to dry.
- Firing the tubular ceramic support. The firing will remove all organic binders and chemicals utilized in the ceramic manufacturing process, such as the starch, amijel and methocel. It will also remove any residual water not removed.

2.3 Centrifugal method
Centrifugal casting is a new process technology for the production of ceramic tubes. In centrifugal casting a cylindrical mold is filled with suspension and rotated rapidly around its axis. This results in the movement of the particulate phase towards the cylinder wall and the formation of a tubular cast.

3. Experimental procedure
3.1 Analysis of the raw materials
The chemical compositions of the 3 clays (KT, DD2 and DD3) used in the present work given in weight percentages of oxides are given in table 1.

| Clay | SiO₂ | Al₂O₃ | TiO₂ | Fe₂O₃ | K₂O | Na₂O | CaO | MgO | MnO | I. L. at 1100°C |
|------|------|-------|------|-------|-----|------|-----|-----|-----|----------------|
| KT   | 50.56| 34.15 | 0.28 | 1.15  | 7.18| -    | 0.31| 0.28| -   | 06.4           |
| DD2  | 45.29| 38.36 | 0.44 | 0.09  | 0.33| 0.07 | 0.23| 0.03| 0.19| 15.8           |
| DD3  | 45.90| 37.49 | 0.44 | 0.40  | 0.41| 0.07 | 0.41| 0.01| 1.52| 16.5           |

Table 1. Chemical composition of the three clay types expressed as wt% of equivalent oxides, used in this chapter.

When extrusion technique is used, the supports were prepared from domestic kaolin (DD2) and calcium carbonates derived from Guelma and Constantine regions (Algeria), respectively. The purity of CaO obtained from calcined calcite was about 99.7%. The other starting raw materials were domestic kaolin (DD3) and dolomite derived from Guelma and Batna regions (Algeria), respectively. The chemical composition of this kaolin is given in table 1, where the main impurities are CaO, MnO and Fe₂O₃. The doloma (CaO.MgO) has been obtained from dolomite after calcination at 950°C for 4 hours. The purity of the added doloma is about 99,6 wt%. It contains, mainly, 0.27 wt% Fe₂O₃, 0.07 wt% Al₂O₃ and 0.02 wt% Na₂O as impurities.

3.2 Characterization techniques
The structure was analyzed by X-ray diffraction (XRD) and Hg-porosimetry techniques. The presence of possible defects in the prepared supports was checked by using Scanning Electron Microscopy (SEM). The tensile strength testing of sintered samples at room temperature was carried out using the diametral compression test, at a constant displacement rate of 0.2 mm/min., using hard metal plattens. Generally, three samples of each composition sintered under the same conditions were tested and an average value was taken. Following previous
strength testing procedures, packing strips (Manilla office file) of 0.30 mm thickness were used. This technique is well detailed elsewhere (Harabi & DAVIS, 1995b).

3.3 Supports preparation
There are three different procedures (1, 2 and 3) which were followed in this chapter for supports preparation (1 by centrifugation and 2 by extrusion).
Firstly, the main preparation steps, used in the first one, are shown in Fig. 1.

Fig. 1. Steps order of membrane supports fabrication using centrifugal casting technique.
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 minutes 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 minutes 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 hour. 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 has 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.

Fig. 2. A schematic diagram showing the main processes (1, 2, 3 and 4), used for membrane supports preparation, in this work.

Secondly, the kaolin (DD2) is properly crushed, then calcinated at 540°C for 1 hour to be later on sieved at 150 μm. After that, a quantity of 28 wt% of calcium carbonate powder is
added. In order to improve the properties that facilitate the forming, some organic materials, such as 3 wt% methocel, as a plasticizer and 3 wt% amijel, as a binder have been added. This mixture should be continuously mixed up with water so as to get the plastic paste. For a good diffusion of the water in the paste, this latter should be properly covered in a plastic case for at least 12 hours. After that, extrusion technique takes place to make some tubular samples. For a good drying of these tubular samples, they should be placed at room temperature on rotating aluminum roll. In order to eliminate organic materials added and avoid the microcrackes in the samples, the rate of sintering chosen is 2°C/min.

Thirdly, the main steps of the 4 processing routes (noted 1, 2, 3 and 4) for samples preparation, used in this work, are described in Fig. 2. One of the main differences between these processes is the shape of the product. The flat configuration is obtained when processes 1, 2 and 4 were applied while a tubular one was achieved when process 3 was used. Another important difference is the doloma addition (process 4) and doloma coupled with methocel and amijel additions (processes 2 and 3). After doloma addition to kaolin, the mixture loses its plastic properties. To improve these properties and facilitate the shaping of products, organic materials have been added (processes 2 and 3). The organic additions used are: 4 wt% of methocel, derived from methylcellulose (The Dow Chemical Company) as a plasticizer and 4 wt% of amijel, derived from starch (Cplus 12072, Cerestar), as a binder.

3.4 Membranes preparation
Due to the chemical and thermal properties of zirconium oxide, it is widely used for membranes preparation. This powder has a specific surface area which is about 43.5 m²/g and average particle size of about 0.22 μm. This material has been prepared by Cezus Chimie campany.

For preparing a microfiltration layer with zirconia powder, a deflocculated slip was obtained by mixing 10 wt% zirconia powder, 25 wt% PVA (12 wt% aqueous solution) and water (65 wt%). The deposition of the slip on the support was performed by the slip casting method (Khemakhem et al., 2004). In this case of the tubular membranes, the tube was closed at one end and filled with the solution. The coating was carried out by capillary suction. The thin layer thickness was determined by the capillary pressure and is depended on the support porosity, on the coating time and on the suspension viscosity (Masmoudi et al., 2005). The deposition time was between 5 and 10 min. After drying at room temperature for 24 hours, the microfiltration layer was sintered at 1150°C for 2 hours. A temperature plate at 250°C for 15 minutes is necessary in order to eliminate completely the PVA, which is in great quantities in the slip. A relatively slow temperature rate (2°C/min) was needed in order to avoid the formation of cracks on the layer (Masmoudi et al., 2006). The distribution of the pore diameters of the membrane was determined by mercury porosimetry.

4. Results and discussion

4.1 Phases identification
Phases identification is of great importance before any supports and membranes manufactures. Because of the presence of certain phases may limit their application for water filtration only, rather than acids filtration or gases separation.
For example, Fig. 3 shows the X-ray diffraction (XRD) spectra of samples sintered at 1000°, 1100° and 1200°C during 1 hour. The main observed phases are: mullite (3Al$_2$O$_3$.2SiO$_2$) and quartz (Harabi et al., 2009). 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. 3).

![XRD spectra](image)

Fig. 3. XRD spectra of samples sintered at different temperatures during 1 hour. M: Mullite; Q: quartz.

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. Moreover, in the case of supports prepared by extrusion method from kaolin DD2 type (Al$_2$O$_3$.2SiO$_2$.2H$_2$O) and the calcium carbonates (CaCO$_3$) local raw materials the main observed phases are: mullite and anorthite (Boudaira et al., 2009). By contrast, when supports were prepared only from kaolin DD3 type the main observed phases are: mullite and cristoballite ((Bouzerara et al., 2009). Apart from cristoballite all the above formed phases are chemically stable in acids. In order to transform this undesirable phase into another stable phase, about 37 wt% of ZO$_2$ was added into kaolin. It has been found that the main formed phases were mullite and zicon (ZrSiO$_4$) (Mecif et al., 2010).

### 4.2 Pore characterization of supports prepared by extrusion technique

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. Structural characteristics of the final membrane supports, prepared from kaolin and kaolin + doloma, according to the four different processing routes are summarized in Table 2.
| Used processes | Sintering temperature (°C) | Total Porosity (%) | A.P.S. (µm) | PSD modal | Tensile Strength (MPa) |
|----------------|---------------------------|--------------------|-------------|-----------|------------------------|
| Process 1      | 1000                      | 37.26              | 0.02        | BMPSD     |                        |
|                 | 1200                      | 15.68              | 3.49        | MMPSD     |                        |
|                 | 1250                      | 13.50              | 3.32        | SMPSD     |                        |
|                 | 1300                      | 15.94              | 4.28        | SMPSD     |                        |
| Process 2      | 1000                      | 56                 | 7.68        | MMPSD     |                        |
|                 | 1200                      | 53.31              | 12.72       | MMPSD     |                        |
|                 | 1250                      | 51.23              | 22.31       | SMPSD     |                        |
|                 | 1300                      | 51.9               | 39.40       | SMPSD     |                        |
| Process 3      | 1150                      | 39.89              | 1.65        | MMPSD     |                        |
|                 | 1200                      | 38.29              | 2.89        | BMPSD     |                        |
|                 | 1250                      | 43.18              | 27.72       | SMPSD     |                        |
|                 | 1300                      | 40.53              | 48.93       | SMPSD     |                        |
| Process 4      | 1000                      | 41.94              | 0.69        | MMPSD     | 6                      |
|                 | 1100                      | -                  | -           | -         | 9                      |
|                 | 1200                      | 40.99              | 3.77        | SMPSD     | 15                     |
|                 | 1250                      | 40.81              | 11.09       | BMPSD     | 15                     |
|                 | 1300                      | 37.63              | 23.48       | SMPSD     | 9                      |

Table 2. Some properties of samples prepared from kaolin and kaolin + doloma according to the four different processes.

The total porosity, average pore size and pore size distribution have been determined by mercury intrusion porosimetry (Micromeritics, Model Autopore 9220) for supports sintered at different temperatures for 60 min. The obtained results are illustrated in Fig. 4. As would be expected, this figure shows, generally that there is an increase in average pore size and a decrease in total porosity in samples, when the sintering temperature is increased. Moreover, it can be said that both the average pore size and porous volume are closely related to the preparation method. The obtained results (Table 2 and Fig. 4) show that the doloma addition to kaolin has a positive effect on the porosity ratio of supports compared to those prepared from kaolin alone. For example, the kaolin support (process 1) had a porosity ratio of ≈13% and an average pore size around 3 µm, whereas the kaolin–doloma supports (process 2) had a porosity ratio of ≈ 51% and an average pore size around 22 µm, sintered under the same conditions (1250°C for 1 hour).
The pores characterisation may be divided into three main features (categories). These consist of total porosity, average pore size and the modal distribution of pore size. The pore size distribution modal may also be classified into three distinct modals; single or Gaussian distribution, bi-modal and multi-modal pore size distributions. The Single (mono) Modal of Pore Size Distribution (SMPSD) is generally obtained for samples having a uniform pore size distribution. When pore volume (%) is plotted against pore size, the curve is characterised by a single peak (Fig. 5a).

Fig. 4. Porous volume (%) and average pore size versus sintering temperature for kaolin samples, using process 1(a) and for kaolin + 15 wt% doloma samples, using processes 2(b), 3(c), 4(d).

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 (Fig. 5b). Finally, the Multi Modal of Pore Size Distribution (MMPSD) is characterized by the presence of more than two distinct (Fig. 5c) or overlapping peaks (Fig. 5d). The BMPSD observed in Fig. 5b, using process 1, consists of two different pore origins, existing at this lower sintering temperature (1000°C). The origin of finer pore sizes may be attributed to the H₂O escaping, while the coarser ones are due to the voids existing between kaolin starting particles. When the sintering temperature is increased (1300°C), the coalescence of finer pores leads to the disappearance of the second peak (Table 2) and a SMPSD is obtained, within an average pore size of about 4 µm. The BMPSD (mentioned above) becomes MMPSD (Figs. 5c and 6a) when
further starting materials have been added such as Mg(OH)$_2$, Ca(OH)$_2$, amijel and methocel, for samples sintered at a lower temperature (1000°C).

Fig. 5c is a good example for that it illustrates well that the number of peaks is about five which corresponds to the number of starting materials (kaolin, Mg(OH)$_2$, Ca(OH)$_2$, amijel and methocel). A uniform pore size distribution (SMPSD) is also obtained when samples were sintered at higher temperature (1300°C), as shown in Figs. 5a and 6c. Therefore it can be said that these modal distributions are closely related to the processing routes used in this work. Moreover, the compacting pressure is a major factor controlling the modal distribution of pore size. For example, a uniform pore size distribution is already obtained for samples sintered at 1200°C (Fig. 6b), using process 4 (75 MPa), while the appearance of this modal is delayed to 1300°C, using process 2 (hand roll pressing). It should be mentioned that the pore size distribution is almost uniform for samples sintered at 1250°C for 1 h, using process 4 (Fig. 6c).

Fig. 5. Pore size distribution in kaolin using process 2 (a) and in kaolin + 15 wt% doloma samples using processes 1 (b), 2(c) and 3(d).
Fig. 6 displays the modal distributions of pore size, for samples sintered at different temperatures for 1 h, using process 4. It is clear that the pore size distribution modal is temperature dependent. It is almost mono-modal distribution (uniform distribution) in compacts sintered at 1200°C (Fig. 6b) and 1300°C (Fig. 6d), whereas the bi-modal and multi-modal pore size distributions were obtained in those sintered at 1250°C (Fig. 6c) and 1000°C (Fig. 6a), respectively. It should be mentioned that even though the modal of pore size distribution is the same (homogeneous) for samples sintered at 1200 and 1300°C, they may behave differently. In fact, the large interval of pore size distribution (0.1–10 µm) in samples sintered at 1200°C is shifted towards a narrow interval of pore size distribution (8–50 µm). 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 (Table 2). These kinds of pore size distribution curves do not tell us more information about both cumulative porous volume (%) and average pore size (µm). Consequently, curves of cumulative porous volume (%) versus pore diameter were replotted in Figs. 7a–d, using four different processing routes. It should be mentioned that the average pore size is directly given by mercury intrusion porosimetry. Moreover, these values are in good agreement with those determined also from the pore size corresponding to 50% of cumulative volume (Figs. 7a–d).

Fig. 6. Pore size distribution in kaolin + 15 wt% doloma samples, using process 4 sintered at different temperatures for 1 hour.
These figures show mainly that the average pore size is shifted towards higher values when sintering temperature is increased. For example, the average pore size values in samples sintered at 1150, 1200, 1250 and 1300°C, using process 3 were 2, 3, 27 and 50 μm, respectively. These values correspond to a cumulative porous volume = 50% (in Fig. 7c). Furthermore, these curves may inform us about the percentage (%) of any pore size interval, at a given sintering temperature and processing route. In some applications this information is required. All in all, it can be said that each processing route has its advantages and potential uses.

One can notice that a uniform pore size distribution is already obtained for samples sintered at 1200°C for 1 h (Fig. 6b), using process 4 (75 MPa). Its average pore size value is about 4 μm within a cumulative porous volume = 41%. These characteristics may be considered (amongst others) as a candidate support for MF and UF membranes. A careful exam of this paragraph and table 2 may allow without any hesitation that these parameters or characteristics of these proposed supports are under control.

Fig. 7. Cumulative porous volume (%) as a function of pore size for kaolin using process 1 (a) and in kaolin + 15 wt% doloma samples using processes 2 (b), 3(c) and 4(d).
4.3 Pore characterization of supports prepared by centrifugation technique

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. 8. 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 minutes. The obtained results are illustrated in Fig. 9. 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.

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 hour).

Fig. 10 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.

Fig. 10. Pore size distribution in samples sintered at 1200°C during 1 hour. (a) kaolin and (b) kaolin with 20 wt% starch samples.

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. These supports have smooth inside surface and a narrow pore size distribution. This is necessary for a good integrity of the membrane.

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 their water permeability.

Fig. 11a 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.m².bar as we can see in Fig. 11b. This indicates that the pressure difference is the only driving force for permeation (Sekulie et al., 2004). For transport driven only by convection, the volume flow rate is proportional to the pressure difference, following the Darcy law.

It should be mentioned that when the average pore size is around 0.77 or 1.41 µm, this support may be directly used for UF membranes deposition without any intermediate MF membranes.
4.4 Tensile strength
After their preparation and pore characterization, the supports should mechanically be tested, before any membranes deposition. For example, the effect of sintering temperature on tensile strength of supports (using extrusion technique) is illustrated in Fig. 12a. This figure shows that there are three different stages. A state of constant tensile strength is reached for supports sintered in the range (1150 and 1200°C) and this is due to stability in the pore size and porosity ratio. However, in the range (1200 and 1250°C) the tensile strength increased rapidly, the mechanical properties have been improved, this improvement is due to the effect of sintering in samples where materials grains have been densified; and this is well shown in Fig. 12a (samples sintered at 1250°C). Afterwards, in the range (1250 and 1300°C) there is a sharp decrease in tensile strength which is due to the considerable increase in pores volume. A maximum equivalent flexural strength of about 40 MPa for samples sintered at 1250°C for 1 h.

Fig. 11. Water permeability versus time, at 3 working pressure values (on the left) and water permeability versus pressure (on the right).

Fig. 12. Tensile strength as a function of sintering temperature (a) (Bouzerara et al., 2006) and (b) (Boudaira et al. 2009).
The same behavior was observed for other supports but with enhanced values (Fig. 12b). In fact, this improvement is well justified by the SEM micrographs shown in Fig. 13. Moreover, the reader may readily notice the significant effect of both process and starting materials on flexural strength. Indeed, the flexural strength value (65 MPa) was nearly doubled (within the error bars) for samples sintered under the same conditions, as shown in Fig. 12.

Fig. 13. SEM micrographs of cross-section, left, and the surface, right, of support, sintered at 1250°C for 2 h

4.5 Microfiltration membrane characterization

After their preparation and characterisation these low price supports, they should be used for membranes deposition in order to check out their adherence. Fig. 14 is a good example. The average pore diameters and the porous volume of the active layer are around 0.35 μm (Fig. 14) and 52%, respectively. It is known that the particle size distribution (PSD) has an influence on the pore size distribution, as a narrow PSD results in a narrow pore size distribution, while a wide PSD would result in a wider pore size distribution (Bissett et al., 2008). The pore size indicates that this kind of membranes can be utilized in the microfiltration range (Masmoudi et al., 2005). SEM images of the prepared membranes are shown in Fig. 15. This figure gives information on the texture of the elaborated membrane surface (Khemakhem et al., 2006). It is noticed that there is no cracks and the pore distribution of the membrane is uniform.

The thickness of the microfiltration layer is about 24 μm (Fig. 15), it can be controlled by the percentage of the mineral powder added in the suspension and the period of the deposited time. Tangential filtration tests were carried out at room temperature. The membrane is immersed in distilled water for 24 hours. The water flux through the membrane was measured as a function of time at different transmembrane pressure values, where the flux are stables after period of 15-40 min of filtration depending on the working pressure (Fig. 16).
The permeability was determined from the different flux values for each working pressure. The obtained curve is a straight line with a slope equal to around 1440 l/h.m².bar. It is amongst the best permeability values when compared to those reported by other authors [11] (Khemakhem et al., 2004). Moreover, these ceramics supports were also used for other MF membranes such as ZnO, anorthite, within a good adherence. More recently, UF membranes were successfully deposited on this low price fabricated supports (Harabi et al., 2010). Since the average pore size ranges of these deposited MF and/or UF membranes were situated between 350-500 nm and 30-50 nm respectively, a huge number of applications are expected. It is well known that these MF and/or UF membrane domains may be used from used water purification to water sterilization. This work is in progress for the deposition of NF membranes on these proposed low price supports for further applications.
On the basis of the whole chapter body from phase identification to the membranes deposition step, the following remarks and/or conclusions may be drawn and commented.

- All the supports were mainly constituted of one or more of mullite, cistoballite, anorthite and quartz phases. Apart from cristoballite, all the manufactured supports containing these phases may be used even for acids filtration. Besides this, there are no signs that these phases or raw materials may be considered as against environment.

- As far as pore characterization of manufactured supports, using both centrifugal casting and extrusion methods, it can be said that homogeneous pore distributions (Gaussian distribution) were successfully obtained for all followed procedures (under given conditions of sintering). Moreover, the average pore size was also under control, within a volume pore size generally ranging between 42 and 50%.

- The measured flexural strength (ranged between 40 and 65 MPa) is significantly acceptable for highly porous supports (about 50%).

- The selected supports (according to international standards) were afterwards used for different MF and NF membranes deposition. The adherence between these membranes and their supports as well as absence of large defects were carefully visually checked and observed by SEM.

Consequently, it can be said that these characteristics may modestly confirm that the commercial alumina supports may be replaced by these low expansive supports when commercialized.

5. Conclusions

As far as centrifugal casting technique is concerned, this chapter allowed fabricating aluminosilicate tubes for membrane applications using this technique (procedure 1). 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 TK kaolin alone; 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.
Even though, these interesting characteristics of the manufactured supports encounter some difficulties such as their shaping limitations and their limited production at the commercial scale.

However, when the extrusion technique was used 2 procedures (2 and 3) have been followed. The attractiveness in the present work (using procedure 2) is the development of membrane supports manufactured from native kaolin and doloma (obtained from dolomite) mixtures, available in our country. This kind of supports presents features of porosity (porous volume and average pore size) more important than those elaborated from kaolin as a raw material. They can be used as supports of membranes of MF and UF. Moreover, these supports are characterised by a reduced manufacture cost since the used raw materials are very abundant (in Algeria) and their mechanical properties seem to be acceptable. The manufactured membrane supports are mainly constituted of mullite, cordierite and anorthite phases. The presence of these phases may also extend further their use, even under severe atmosphere conditions. Finally, it has been found that the pore structures (modal distributions of pore size, total porosity and average pore size) may be controlled by the sintering temperature, additions and processing routes. For examples, a uniform pore size distribution within a total porosity ratio of 43% and 28 μm as an average pore size, were obtained, for samples prepared according to process 3 and sintered at 1250°C for 1 hour. However, a relatively higher porosity ratio (51%) was reached when process 2 was applied, under the same sintering conditions.

Using procedure 3, other kind of membrane supports was manufactured from local kaolin (DD2) and Calcium carbonate mixtures, available in our country. The ceramic support was formed by extrusion of a ceramic paste from kaolin and calcium carbonats mixtures. The microfiltration layer, deposited on the supports, was obtained by the slip casting technique using suspensions of zirconia powder. This membrane can be used for MF and also used as supports for UF.

Since the ceramic filters are generally constituted of a thick support (2000 μm) and one or multi thin membranes (from 10 to 40 μm for each one). That is why this work or chapter is mainly focussed on ceramic supports rather than its deposed membranes. Therefore, replacing the more expansive starting materials, mentioned above, by other low cost raw materials for supports fabrication (which constitutes about 99% of the filter mass) is significantly important. So, what low cost raw materials does mean? It is incomparable; the alumina price is at least about 100 times more expensive than that of kaolin.

Another important advantage is the substantial gain in energy by decreasing the sintering temperature from about 1600°C to about 1250°C, when alumina supports were replaced by the proposed supports. Besides this, about 50% the prepared supports is pores (porosity) which may also be considered as a gain in its mass. The relatively lower theoretical density of the prepared supports (2.8 g/cm³) when compared to that of alumina (3.98 g/cm³) is also a further exiting advantage.

Finally, this work is in progress for the deposition of NF membranes on these proposed low price supports for further applications.

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For this book, the term "desalination" is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to "Desalination, Trends and Technologies", INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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