Preparation and characterization of ZnO microfiltration membrane and its support using kaolin (DD3) and $CaCO_3$

(Preparação e caracterização de membrana de microfiltração de ZnO e seu substrato usando caulim (DD3) e $CaCO_3$)

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Abstract

The objective of the present paper was to prepare a ceramic support with membrane. Tubular ceramic supports prepared from kaolin (DD3) and calcium carbonate with 6 and 10 mm inner and outer diameters, respectively, were extruded and sintered at 1200 °C. It has been found that sintered supports had interesting characteristics: average pore size of about 5 µm, porosity of about 50%, and monomodal pore size distribution. This support was used to be substrate for a membrane layer of microfiltration. This membrane layer was elaborated from zinc oxide, using slip casting technique. The specimens were subsequently sintered at 1000 °C. The microstructure and porosity as well as the permeability have also been studied. It has been found that the average pore size was about 1.2 µm, the layer thickness was ~33 µm, and the water permeability measured was about 880 $L.h^{-1}.m^{-2}.bar^{-1}$.

Keywords: kaolin (DD3), calcite, supports, membranes, microfiltration, extrusion, slip casting.

Resumo

O objetivo deste trabalho foi preparar um suporte cerâmico com membrana. Suportes cerâmicos tubulares preparados com caulim (DD3) e carbonato de cálcio com 6 e 10 mm de diâmetros interno e externo, respectivamente, foram extrudados e sinterizados a 1200 °C. Foi observado que os suportes sinterizados apresentaram características interessantes: tamanho médio de poro de cerca de 5 µm, porosidade de cerca de 50% e distribuição de tamanho de poro monomodal. Este suporte foi usado como substrato para uma camada de membrana de microfiltração. Esta camada de membrana foi elaborada com óxido de zinco, usando a técnica de colagem. Na sequência, as amostras foram sinterizadas a 1000 °C. A microestrutura e porosidade, assim como a permeabilidade, foram também investigadas. Observou-se que o tamanho médio de poro foi cerca de 1,2 µm, a espessura da camada foi de ~33 µm e a permeabilidade à água medida foi de cerca de 880 $L.h^{-1}.m^{-2}.bar^{-1}$.

***Palavras-chave**: caulim (DD3), calcita, suportes, membranas, microfiltração, extrusão, colagem.*

INTRODUCTION

Ceramic membranes are used in the cross flow filtration mode because they allow maintaining a high filtration rate if compared with the direct flow filtration mode used in conventional filtration processes. Microfiltration (MF) and ultrafiltration (UF) are often used to remove particles, microorganisms, and colloidal materials from suspensions [1]. The use of ceramic membranes has many advantages such as high thermal and chemical stability [2]. 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 [3]. There are many countries in the world that have abundant raw materials, such as calcite ($CaCO_3$), dolomite ($CaCO_3$. $MgCO_3$), bones (natural derived hydroxyapatite (NHA): $Ca_{10}(PO_4)_6(OH)_2$), kaolin, feldspar and quartz. Many works have already been published for valorizing these native raw materials, mainly referring to advanced ceramics [4-7], ceramic membranes [8-11] and bioceramics [12-15]. In this way, a particular MF ceramics membrane, made of a thinner active layer laid on a porous support has been prepared. It should be mentioned here that all these publications are closely related to this work and clearly highlight their possible multifunctional applications. As far as ceramic membranes publications are concerned [16-19], a lot of low price materials were also fabricated using the abundantly available raw materials as mentioned above. Recently, many studies were carried out on porous anorthite based ceramics using kaolin and limestone native raw materials [20-23]. One can notice the importance of these prepared porous products when are used as membrane supports [24-27]. Besides this, the relatively higher porosity ratios (42 to 52%) of these porous bioceramics may also be qualified as membrane supports. Moreover, these supports were applied for elaboration of low cost ceramics microfiltration membranes [28-31] applied to the sterilization of plant tissue culture media [30].

MF is often used to remove particles, microorganisms and colloidal materials from suspensions [32]. Among various commercial and research applications of membrane technology, ceramic membranes have been substantially investigated [33]. Due to their unique properties and practical use in industrial separation, ceramic membranes have drawn great interests since their appearance [34]. At present, they potentials have many interesting applications, such as filtration, dye particles separation [35], bacterial and virus removal as well as biotechnological and environmental applications [36]. Several recent studies have shown that membrane filtration is a viable option for removing contaminants from aqueous solutions. The range of applications includes removal of oil from water [34], removal of toxic heavy metal ions [37], salts rejection [38], and waste-water treatment [39]. Besides, an interesting application may be sterile filtration. In various industrial fields, such as food, medical industries and biology, it is becoming very important to sterilize the solutions media [40] aiming at reducing the risks of contamination. In this work, the study is related to the development of a ceramic support using Algerian natural materials (kaolin DD3 type) and natural calcium carbonate ($CaCO_3$), whereas the top layer was made from zinc oxide (ZnO).

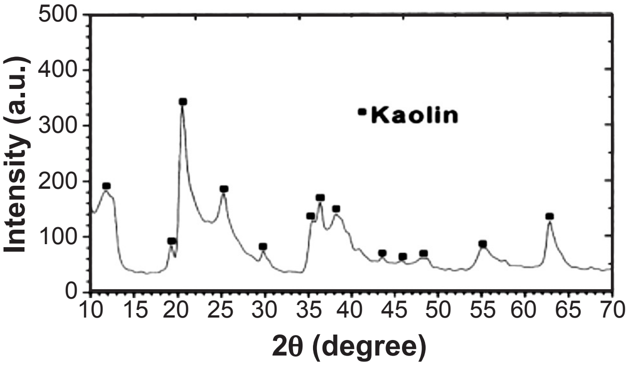

Figure 1: X-ray diffraction pattern of the as received Algerian halloysite powder (DD3 kaolin).
[Figura 1: Difratograma de raios X do pó como recebido de haloisita argelino (caulim DD3).]

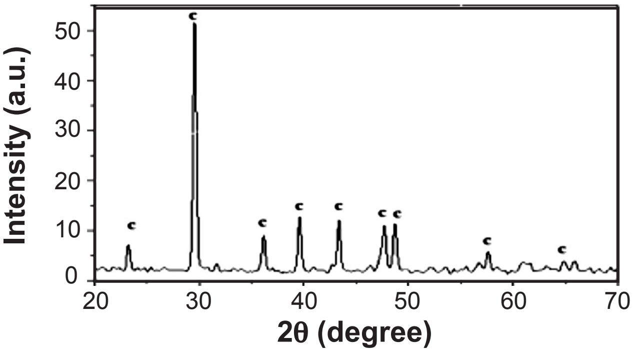

Figure 2: X-ray diffraction pattern of the as received Algerian calcite ($CaCO_3$) powder.
[Figura 2: Difratograma de raios X do pó como recebido de calcita argelino ($CaCO_3$).]

ANALYSIS OF THE RAW MATERIALS

In this study, the support was prepared from domestic kaolin DD3 and calcite ($CaCO_3$) from Guelma and Constantine regions (Algeria), respectively. The chemical composition of the kaolin DD3 is given in Table I. The majority of the used powder (81 wt%) consists of SiO_2 and Al_2O_3, whereas the main impurities are CaO, MnO and Fe_2O_3. The particle size distribution of this material was determined by the dynamic laser beam scattering (DLBS) technique [8-10]. This method gave an average particle size in the order of 0.8 μm [8]. The kaolin powder, obtained by calcination of the finely ground mineral at 540 °C, showed an average particle size smaller than 1.2 μm [9].

Fig. 1 shows XRD pattern of kaolin DD3 powder which confirms that its structure is halloysite type. The purity of CaO obtained from calcined calcite was about 99.7%, using X-ray fluorescence (XRF) analysis. It mainly contains 0.15 wt% Fe_2O_3, 0.05 wt% Al_2O_3 and 0.03 wt% Na_2O as impurities. As reported by [41], this raw material may be classified as a high-purity calcium oxide (CaO $\geq$ 99.0%). The particle size distribution of calcite was determined by DLBS, which gave an average particle size in the order of 4.8 μm [10]. Moreover, it has been confirmed by XRD pattern of calcium carbonate powder that only calcite phase was detected. This pattern shows also that the calcite powder is well crystallized (Fig. 2).

Because the starting kaolin and calcite powders undergo structural evolution and weight loss during their heating, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been judged useful before any other characterization techniques. TGA curves recorded during heating compacts (Fig. 3) permit the following remark: a

Table I - Chemical composition of the used Algerian kaolin halloysite type (in wt%), from XRF analysis [6].
[Tabela I - Composição química do caulim argelino tipo haloisita (% em massa), obtido de análise de FRX [6].]

Clay	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	K_2O	Na_2O	CaO	MgO	MnO	I.L.*
DD3	45.90	37.49	0.44	0.40	0.41	0.07	0.41	0.01	1.52	16.5

* *Ignition loss.*

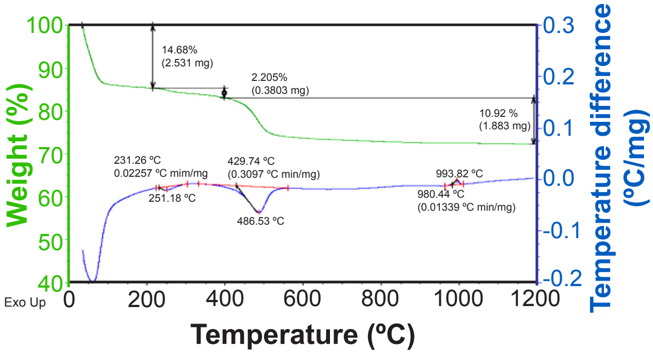

Figure 3: DSC and TGA curves for kaolin powder.
[Figura 3: Curvas de DSC e TGA para o pó de caulim.]

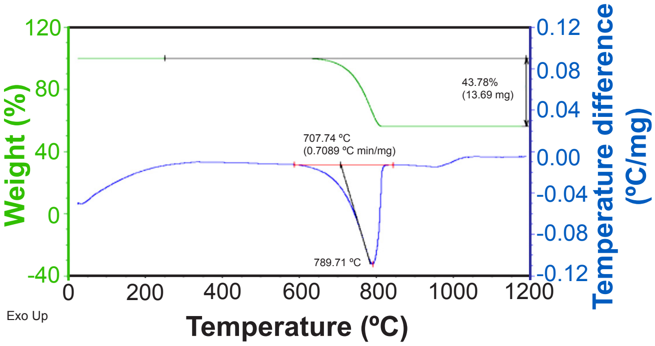

Figure 4: DSC and TGA curves for calcite powder.
[Figura 4: Curvas de DSC e TGA para o pó de calcita.]

total weight loss ratio (WLR) of about 27.80% for kaolin compact is measured. In fact, this weight loss consists of three main distinct stages. The first one is attributed to the humidity (water added into the starting mixtures and typical H_2O of hydration for halloysite kaolin type) whereas the second is related to the combustion of organic materials. However, the third stage may be attributed to water loss (by vaporization) in the kaolin chemical composition itself. The WLR of the last stage is more pronounced (Fig. 3). The three endothermic phenomena, appearing at 60, 231 and 430 °C, correspond respectively to the first, second and third stages of WLR. A fourth stage, which is characterized by an exothermic reaction, appeared at about 994 °C (Fig. 3). The origin of this reaction is not understood yet. Some works attribute this reaction to spinel formation while others attribute it to mullite nucleation [42]. Fig. 4 shows that there is only an endothermic peak (mass loss of 43.73%) in the range 650 to 800 °C which may be due to the thermal decomposition of $CaCO_3$ into CaO and CO_2. This reaction is also confirmed by XRD analysis [10, 43].

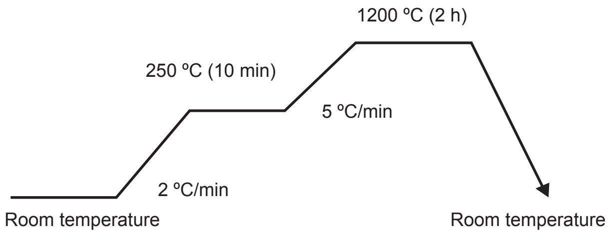

Figure 5: Scheme of the thermal treatment for support.
[Figura 5: Esquema do tratamento térmico do suporte.]

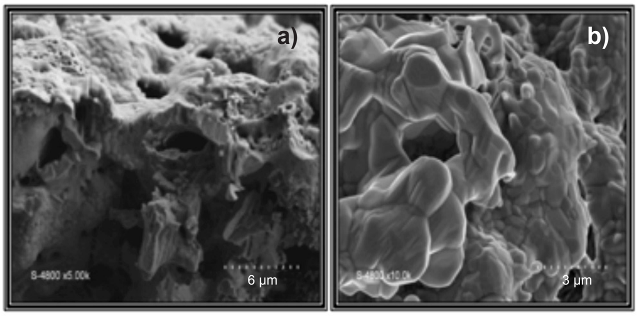

Figure 6: SEM micrographs of cross-section (a) and the surface (b) of support sintered at 1200 °C for 2 h.
[Figura 6: Micrografias obtidas por microscopia eletrônica de varredura da seção transversal (a) e da superfície (b) do suporte sinterizado a 1200 °C por 2 h.]

SUPPORT ELABORATION AND CHARACTERIZATION

The kaolin (DD3) is properly crushed, then calcined at 540 °C for 1 h to be later on sieved at 150 µm. After that, a quantity of 15 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 h. 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 rolls. These dried tubular samples were sintered at 1200 °C for 2 h. A temperature plateau at 250 °C for 10 min during the heating stage was applied in order to eliminate the added organic materials and to avoid the microcracks in the samples. The choosing sintering rate was 2 °C/min [10] (Fig. 5). The supports fired at 1200 °C and characterized by mercury porosimetry showed pore diameter centered near 5 µm and 50% of porosity. Fig. 6 confirms the relatively good sinterability of samples sintered at 1200 °C (strong necks or bridges formation). These characteristics [25] are of great importance because of their promising physical and mechanical properties.

MEMBRANE ELABORATION AND CHARACTERIZATION

The used ZnO powder (Cheminova International S.A. Co.) has an average particle diameter of about 2.3 µm. For preparing a microfiltration (MF) layer with zinc oxide powder, a deflocculated slip was obtained by mixing 10 wt% ZnO powder, 30 wt% PVA (12 wt% aqueous solution) and water (60 wt%). The deposition of the slip on the support was performed by the slip casting method. In this case of the tubular membranes, the tube (6 and 10 mm of inner

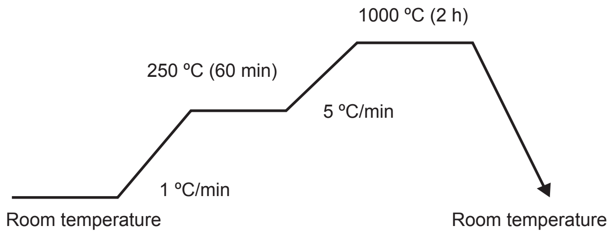

Figure 7: Scheme of the thermal treatment for membrane on support.
[Figura 7: Esquema do tratamento térmico da membrana sobre o suporte.]

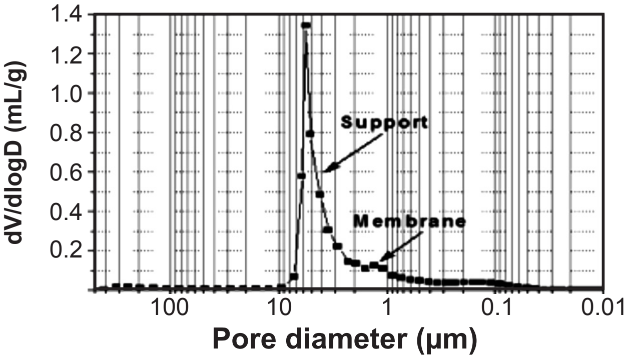

Figure 8: Pore size distribution of support with membrane.
[Figura 8: Distribuição de tamanho de poros do suporte com membrana.]

and outer diameters) was closed at one end and filed with the suspension. 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 [44]. The deposition time was between 5 and 10 min. After drying at room temperature for 24 h, the MF layer was sintered at 1000 °C for 1 h (Fig. 7). A temperature plateau at 250 °C for 60 min is necessary in order to eliminate completely the PVA, which is in high quantity in the slip. A relatively slow temperature rate (1 °C/min) was needed in order to avoid the formation of cracks in the layer [45]. The distribution of pore diameters of the membrane was determined by mercury porosimetry. The average pore diameters and the porous volume of the active layer are around 1.2 µm (Fig. 8) and 52%, respectively.

SEM images of the prepared MF membrane are shown in Fig. 9. This figure gives information on the texture of the elaborated membrane surface [46]. It is noticed that there are no cracks and the pore distribution of the membrane is uniform. The thickness of the MF layer is about 33 µm (Fig. 9): it can be controlled by the percentage of the mineral powder added into the suspension and the period of deposited time. Tangential filtration tests were carried out at room temperature. The membrane is immersed in distilled water for 24 h. 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 0–60 min of filtration depending on the working pressure (Fig. 10). 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 about 880 $L.h^{-1}.m^{-2}.bar^{-1}$. It is amongst the best permeability values when compared to those reported by other authors [47]. Finally, this membrane support may be used for MF.

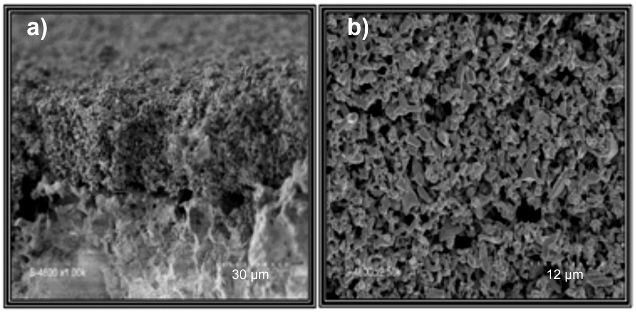

Figure 9: SEM micrographs of cross-section (a) and the surface (b) of membrane sintered at 1000 °C for 2 h.
[Figura 9: Micrografias obtidas por microscopia eletrônica de varredura da seção transversal (a) e da superfície (b) da membrana sinterizada a 1000 °C por 2 h.]

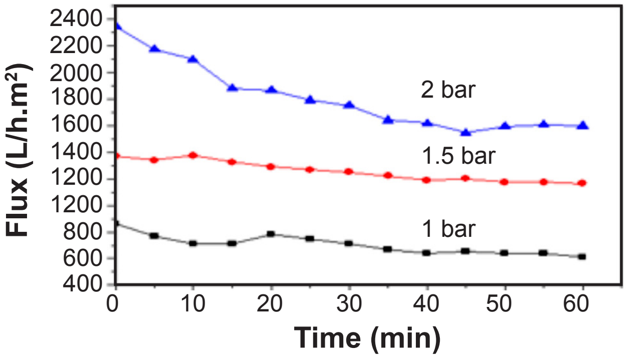

Figure 10: Water flux as a function of time for three working pressure values.
[Figura 10: Fluxo de água em função do tempo para três valores de pressão de trabalho.]

CONCLUSIONS

The attractiveness in the present work is the development of membrane supports manufactured from kaolin (DD3) and calcium carbonates mixtures, available in many countries. The ceramic support was formed by extrusion of a ceramic paste from kaolin and calcium carbonate mixture. The microfiltration layer, deposited on the supports, was obtained by the slip casting technique using suspensions of zinc oxide powder.

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(Rec. 22/08/2015, Rev. 10/12/2015, Ac. 28/12/2015)