Fabrication of kaolin hollow fibre membranes for bacteria removal

Flávia de Santana Magalhães¹, Eduardo de Paulo Ferreira¹, Lidiane Pereira Bessa¹, Camila Stéfanne Dias Costa¹, Melissa Gurgel Adeodato Vieira², Miria Hespanhol Miranda Reis¹,∗

¹School of Chemical Engineering, Federal University of Uberlândia, João Naves de Ávila Av. 2121, 38400-902, Uberlândia, Minas Gerais, Brazil
²School of Chemical Engineering, University of Campinas, Albert Einstein Av. 500, 13083-852, Campinas, São Paulo, Brazil

Received 22 March 2020; Received in revised form 5 August 2020; Accepted 23 September 2020

Abstract

This study examines the influence of the particle size, extrusion rate and sintering temperature on the characteristics of kaolin hollow fibre membranes. In addition, the produced membranes were applied for bacteria removal from an aqueous suspension. The milling process reduced the size of kaolin particles from 8.7 to 5.1 µm and greatly enhanced the morphology and mechanical resistance of the produced membranes. The increase in the sintering temperature up to 1250 °C caused crystallographic phase modifications in the crude kaolin, which were mainly assigned to transformations of quartz and kaolinite to mullite and cristobalite phases. The fibres sintered at 1250 °C have bending strength of 145 MPa, but this relatively high sintering temperature caused a substantial particle densification and drastic decrease of the membrane water permeability. The kaolin hollow fibre membranes enabled almost total removal of the Enterobacter bacteria from an aqueous suspension.

Keywords: ceramic membrane, kaolin, asymmetric hollow fibre, phase inversion, bacteria removal

I. Introduction

Membrane separation processes have been applied in several areas, including chemical, food and biotechnology industries [1]. Related to the material, ceramic membranes usually present greater resistance to harsh environment, microbiological degradation and high pressure conditions than polymeric membranes [2]. The phase inversion method is commonly applied for producing polymeric membranes and, since the beginning of the 21st century, this method has been modified and combined with a single sintering step in order to produce asymmetric ceramic membranes [3]. Fabrication of ceramic membranes involves the adjustment of several parameters, such as ceramic suspension and bore fluid compositions, extrusion flow rates and sintering temperatures [4]. The powder particle size also influences the membrane morphology, and materials with particle sizes smaller than 1 µm are usually used to produce ceramic membranes [5]. The choice of the ceramic powder is also crucial to develop a membrane with positive characteristics related to permeability, selectivity and cost. Actually, the cost of ceramic membranes, which is related to the material cost itself and the required sintering temperature, is a great obstacle for its widespread use [6].

Alumina (Al₂O₃) is the material most commonly used for producing ceramic membranes [7]. In addition to the relatively high cost of this high purity oxide, alumina membranes require sintering temperatures greater than 1500 °C in order to achieve suitable mechanical strength values. Thus, some studies have been carried out to evaluate low cost materials for membrane production [8]. The literature presents applications of several ceramic materials for producing membranes, such as kaolin [9], silica [10], dolomite [11], niobium pentoxide [12] and others. These mineral based materials are largely available and they usually require lower sintering temperatures than pure alumina.

Kaolin (Al₂Si₂O₅(OH)₄) is a clay mineral found in great abundance in many countries and it has been recently used as the starting material for producing ceramic membranes [13]. Zhou et al. [14] proposed the application of a ceramic mixture of kaolin and dolomite to produce low cost macroporous ceramic supports. Kaur et al. [15] produced kaolin based ceramic supports by

∗Corresponding author: tel: +55 34 3239 4284, e-mail: miria@ufu.br
using different amounts of calcium and sodium carbonates. Hubadillah et al. [13] applied the phase inversion method to produce a low cost kaolin-based ceramic hollow fibre membrane with asymmetric pore size distribution. Abdulhameed et al. [16] produced hollow fibre membranes from a powder mixture of alumina and kaolin. Chakraborty et al. [17] applied statistical tools to optimize the ceramic composition for producing kaolin membranes. Hubadillah et al. [9] modified kaolin membranes via grafting with fluoroalkylsilane in order to improve the membrane hydrophobicity. However, the relatively low mechanical resistance of the produced mineral membranes is still a drawback to be overcome. In general, the increase in the sintering temperature increases the mechanical properties. Nevertheless, mineral membranes are composed of mixture of oxide materials which are often converted into other phases during sintering. Thus, better understanding of the crystallographic transformations as function of the sintering process is crucial to produce ceramic membranes with reliable properties. Also, the applied extrusion conditions certainly dictate the characteristics of the produced membranes. Hubadillah et al. [18] suggested applying the phase inversion method to produce kaolin hollow fibres with enhanced mechanical strength and surface/volume ratio.

In this study, low cost asymmetric hollow fibre membranes were produced by using kaolin as the starting material. The influence of the powder particle size distribution, ceramic suspension composition, extrusion flow rate and sintering temperature on the membrane morphology, mechanical strength and water permeability was for the first time systematically investigated. Additionally, crystallographic transformations of the kaolin powder as a function of the sintering temperature were related to the membrane characteristics. Finally, the produced kaolin hollow fibre membranes were applied to remove the Enterobacter bacteria from an aqueous suspension.

II. Materials and methods

2.1. Materials

Kaolin powder was supplied by Kalamazon Estudos Geológicos LTDA (Brazil). Dimethyl sulfoxide (DMSO, Vetec, Brazil) and N-Methyl-2-pyrrolidone (NMP Vetec, Brazil) were used as solvents. PEG-30 Dipolyhydroxy stearate (Arlacel P135, Croda) and polyether sulfone (PES, Veradel 3000P, Solvay) were used as additive and polymer binder, respectively.

2.2. Preparation of kaolin hollow fibres

The kaolin powder was wet ball milled in order to reduce its particle size distribution. A porcelain vessel was filled with 1/3 of balls, 2/3 of distilled water and 125 g of kaolin powder. Porcelain balls of two different diameters (1.0 and 2.5 cm) were used to increase the milling efficiency. The wet ball-milling process was continuously carried out for 170 h without interruption. The powder material was removed from the liquid medium by decanting and evaporating at 105 °C. The milled and un-milled kaolin powders were then individually used to prepare the ceramic suspensions and NMP and DMSO were evaluated as solvents (Table 1). The ceramic suspension composition (0.37 wt.% additive, 55.17 wt.% solvent, 34.58 wt.% kaolin powder and 9.88 wt.% polymer) was based on the values suggested by Hubadillah et al. [19]. The additive (Arlacel) was firstly dissolved in the solvent (NMP or DMSO) followed by the addition of the kaolin powder and stirring in a ball mill for 48 h. Then, the polymer (PES) was added to the mixture and the final ceramic suspensions were stirred for another 48 h.

Hollow fibres were produced by the phase inversion/sintering technique following the methodology described by Kingsbury and Li [20]. After homogenization, the ceramic suspension was extruded through a tube orifice spinneret (outer and inner diameters of 3 and 1.2 mm, respectively). Two individual pumps (Harvard Apparatus, model XHF) were used to control ceramic suspension and internal coagulant flows. Distilled water was used as internal coagulant. The ceramic suspension and internal coagulant flow rates are presented in Table 1. The ceramic hollow as-prepared fibres were discarded into a water coagulation bath with an air gap of 5 cm and they were left in the coagulating bath for 48 h. Then, the as-prepared hollow fibres were washed with water to complete solvent removal. After that, the fibres were manually cut to the desired length, straighten and dried at room temperature (approximately 25 °C) for at least 48 h.

The fibres were sintered in a tubular furnace (Carbolite, model TZF 15) at different temperatures (1100, 1150, 1200 and 1250 °C) using a rate of 2 °C/min in the range from room temperature to 300 °C, a rate of 1 °C/min in the range from 300 to 600 °C with dwell

<table>
<thead>
<tr>
<th>Hollow fibre denomination</th>
<th>Kaolin powder</th>
<th>Solvent</th>
<th>Flow rates [ml/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ceramic suspension</td>
<td>Internal coagulant</td>
<td></td>
</tr>
<tr>
<td>K-NMP-7/15</td>
<td>Non-milled</td>
<td>NMP</td>
<td>7</td>
</tr>
<tr>
<td>MK-NMP-7/15</td>
<td>Milled</td>
<td>NMP</td>
<td>7</td>
</tr>
<tr>
<td>MK-NMP-15/25</td>
<td>Milled</td>
<td>NMP</td>
<td>15</td>
</tr>
<tr>
<td>MK-DMOSO-7/15</td>
<td>Milled</td>
<td>DMSO</td>
<td>7</td>
</tr>
<tr>
<td>MK-DMOSO-15/25</td>
<td>Milled</td>
<td>DMSO</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 1. Ceramic suspension and extrusion parameters for producing kaolin hollow fibre membranes
Figure 1. Scheme of the extrusion process

2.3. Characterizations

Particle size distributions of the kaolin powders before and after the wet ball-milling process were obtained using a laser particle size analyser (Mastersizer 2000, Malvern). Thermogravimetric analyses (TG-DTA) were performed in a thermobalance (Shimadzu, model DTG-60H) under a nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min from 30 to 1200 °C. Infrared absorption bands of the kaolin powders before and after sintering at 1100 and 1200 °C were verified using a Fourier transform infrared spectrophotometer (FTIR, Perkin Elmer, Spectrum two) coupled with attenuated total reflectance (ATR) at the frequency range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

Crystalline phases of the kaolin powders before and after sintering were characterized by X-ray diffraction (XRD) in a Shimadzu diffractometer (model XDR600) with an X-ray tube containing a copper anode (Cu-Ka wavelength) at a rate of 2 °/min. 2θ ranging from 10° to 80° with a step of 0.02°, a voltage of 40 kV and a current of 30 mA. The phases were identified using the ICDD Powder Diffraction File (PDF) database.

Morphological analyses of the powder samples and ceramic hollow fibres were performed using scanning electron microscopy (SEM, Carl Zeiss, model EVO MA10). The samples were first fixed in stubs with a double carbon tape and covered with a thin layer of gold in a metallizer equipment (Leica - EM SCD050). The pore structure and porosity of the kaolin hollow fibre MK-DMSO-15/25 sintered at 1150 °C were investigated by mercury intrusion porosimetry (MIP, Autopore IV 9500, Micrometrics) at a pressure range between 35 and 414000 kPa to ensure maximum mercury penetration into pores of diameters down to 0.003 μm.

The hollow fibres were also characterized in terms of mechanical strength and water permeability. The water permeability through the produced hollow fibres was measured at room temperature (approximately 25 °C) and at different transmembrane pressures. For these water flow measurements, the fibres were glued in a plastic tube and the lumen side of the fibre was kept open. The end of the fibre was closed with epoxy resin glue. The plastic tube was then connected to an automatic pumping system (Convergence Inspector Minus equipment, Netherlands) and Milli-Q® water was flowed through the fibres from lumen to shell side. Water flow was recorded at several transmembrane pressures (from 20 to 100 kPa) and the water flow permeability was calculated as the angular coefficient of the straight line which related water flux and transmembrane pressure according to the Darcy law [22]. For mechanical strength evaluations, the three-point bending test was performed using an Instron Model 9600 attached to a 5 kN cell and using hollow fibres with a length of 30 mm.

2.4. Filtrations of aqueous bacteria suspension

Dead-end filtrations experiments were carried out in order to sterilize a synthetic bacteria suspension. A bacteria suspension with the Enterobacter bacteria was prepared in a 0.9% NaCl solution at 4.0 × 10⁶ CFU/ml
(colony forming units per ml). The use of NaCl solution for bacteria suspensions allows the maintenance of bacteria size and viability over the filtration.

The prepared kaolin hollow fibres MK-DMSO-15/25 sintered at 1200 and 1250 °C were evaluated for this filtration. Three pieces of each fibre (filtration area of $1.7 \times 10^{-5}$ m$^2$) were glued in a plastic tube which was connected to a pressurized system and permeation was from lumen to shell side. Filtrations were carried out at room temperature (25 °C) and at transmembrane pressure of 20 kPa.

The permeate flow was recorded according to the filtration time. Experimental flux decay data were then adjusted to the mathematical model proposed by Hermia [23] (Eq. 1) in order to describe fouling mechanisms. The parameter $n$ in Eq. 1 dictates the fouling mechanism as follows: $n = 0$ for cake filtration; $n = 2$ for complete pore blocking; $n = 1$ for partial pore blocking and $n = 1.5$ for internal pore blocking:

$$\frac{-dJ}{dt} = K_n \cdot A^{2-n} \cdot J^{3-n} \quad (1)$$

where $J$ is the permeate flux, $t$ is the filtration time, $A$ is the membrane area and $K_n$ is an adjusted parameter.

Equation 1 was numerically adjusted to experimental data using the Levenberg-Marquardt method at an integration step of $10^{-3}$ with a precision of $10^{-8}$. The accuracy of Eq. 1 was evaluated according to the values of sum of square of the relative error (SSRE) between experimental and calculated flux data at each $n$ index [22].

Bacteria concentrations in permeate and feed solutions were determined by enumeration of CFU. The spread-plate method was used to determine the concentration of cells. A volume of 0.1 ml of the samples was pipetted aseptically on the different agar plates and overnight incubated at 37 °C [24].

III. Results and discussion

3.1. Kaolin powder characteristics

Figure 2 presents SEM images and the particle size distributions of the kaolin powders before and after the milling process. According to the SEM image (Fig. 2a) the kaolin powder presents particles with irregular shape and sizes. This wide particle size distribution was also verified by the laser particle size analysis (Fig. 2a), with $D_{50}$ of 8.7 µm and particles in the range of 0.37–34.2 µm ($D_{10}$–$D_{90}$). As it is evidenced by SEM images (Figs. 2a and 2b), the milling process reduced the kaolin particle size. The milled kaolin powder has $D_{50}$ of 5.1 µm with particles in the range of 0.51–23.4 µm ($D_{10}$–$D_{90}$).

The crystalline phases of the kaolin powder and sintered samples at different temperatures were evaluated by XRD (Fig. 3a). According to the ICDD Powder Diffraction File (PDF) database, the crude kaolin sample (before sintering) was associated with a mixture of quartz (SiO$_2$), PDF card No. 85-865 (unit-cell parameters: $a = 4.90$ Å and $c = 5.40$ Å) and kaolinite (Al$_2$SiO$_2$(OH)$_4$), PDF card No. 1-527 (unit-cell parameter $a = 5.14$ Å, $b = 8.93$ Å and $c = 7.37$ Å).

The sintering of the kaolin sample at 1100 °C caused the formation of a mullite phase (PDF card No. 89-2813, unit-cell parameter: $a = 16.35$ Å). According to Ptáček et al. [25], kaolinite is transformed into amor-
Figure 3. XRD patterns (a) and FT-IR spectra (b) of kaolin samples sintered at different temperatures

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} (2)

$$2(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \rightarrow 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 (\text{Al}–\text{Si}–\text{spinel}) + \text{SiO}_2 (\text{amorphous})$$  \hspace{1cm} (3)

$$3(2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2) (\text{Al}–\text{Si}–\text{spinel}) \rightarrow 2(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) (\text{mullite}) + 5\text{SiO}_2 (\text{amorphous})$$  \hspace{1cm} (4)

$$\text{SiO}_2 (\text{amorphous}) \rightarrow \text{SiO}_2 (\text{cristobalite})$$  \hspace{1cm} (5)

The TG curve of the kaolin powder (Fig. 4) showed that there was a mass loss of 5% in the temperature range of 400 to 600 °C. This mass loss was probably caused by a dehydroxylation reaction [28]. The thermal behaviour of the kaolin sample (Fig. 4) is similar to those reported by Fitos et al. [27] for kaolin samples of hydrothermal origin. The thermal stability of the kaolin powder is a positive aspect for the membrane production. The DTA curve showed that kaolin decomposition occurred at a temperature of approximately 200 °C due to the loss of physisorbed water, followed by the dehydroxylation of coordinated and structural water at approximately 400 °C and the condensation of hydroxyl groups at higher temperatures [29].

Figure 4. TG/DTA curves of kaolin powder sample

3.2. Characteristics of fibre membranes

Figure 5 presents SEM images of the as-prepared hollow fibres (before sintering), which were produced
at different extrusion rates and with different solvents (Table 1). The membrane produced with the un-milled kaolin powder (K-NMP-7/15) presented irregular cavities throughout the fibre. Relatively large particle size of the un-milled kaolin powder mitigated the formation of micro-voids during the phase inversion process, since the ceramic powder was surrounded by the coagulated polymer. The fibres produced with the milled kaolin powder presented finger like regions at the inner and outer surfaces of the fibre. The micro-voids at the finger like regions were formed due to the interfacial instabilities at the interfaces between the ceramic dispersion and the internal and external coagulant fluids. These instabilities were caused due to the density, viscosity and composition differences between the ceramic suspension and the internal and external coagulant fluids. Thus, there was a solvent mass transfer from the ceramic dispersion to the coagulant fluid (water), and the solvent output caused the polymer precipitation [30].

The micro-voids were formed on the shell and lumen sides of the fibre and a sponge like layer remained in the central region of the fibre. The observed asymmetric pore size distribution is similar to those reported by Terra et al. [22] for alumina hollow fibre membranes. However, the micro-void shapes observed in the kaolin hollow fibres were more irregular than those of the alumina hollow fibres, probably due to the larger particle size of the used kaolin powder. The inner surfaces of the fibres produced at the lowest evaluated extrusion rates (7 and 15 ml/min for the ceramic suspension and internal coagulant, respectively) were irregular. This irregular structure was probably formed because the internal coagulant flow rate at 15 ml/min was not enough to produce a hydrodynamic force against the ceramic suspension during the spinning process [31]. The increase in the internal coagulant flow rate to 25 ml/min resulted in a fibre with a regular internal contour, as observed in the SEM image of the MK-NMP-15/25 hollow fibre. However, the increase in the extrusion rates decreased the extent of the finger like regions, since it increased the phase inversion phenomenon. The use of DMSO as solvent produced long, straight, cylindrical and densely packed micro-voids. Lee et al. [32] evaluated different solvents for producing alumina hollow fibres and observed that cylindrical micro-channels were formed when DMSO was the solvent, while conical structures were formed when NMP was the solvent.

The fibres sintered at different temperatures showed slight modifications in their morphological characteristics, as it is shown in Fig. 6 for the MK-DMSO-15/25 fibre. The effect of the sintering temperature on the morphological characteristics was similar for all other produced hollow fibres.

Figure 6a shows that inner and outer surfaces of the as-prepared membranes were covered by the precipitated polymer, as a result of the phase inversion process during the extrusion. The relatively large particle size of the used kaolin powder compared to other conventionally used ceramic materials (alumina of 1 µm, for instance) promoted the polymer coagulation at the hollow fibre surface instead of inside the formed micro-voids structures. When the hollow fibre was sintered at 1150 °C (Fig. 6b), a porous structure was formed due to the complete elimination of the polymer. The increase in the sintering temperature from 1150 to 1200 °C caused the coalescence of kaolin particles (Fig. 6c). The particle coalescence is more evident on the outer and inner surfaces of the hollow fibre sintered at 1200 °C. However, a particle coalescence process was evidenced in the whole cross-section region of the fibre sintered at 1250 °C (Fig. 6d).

The pore structure of the kaolin hollow fibre MK-DMSO-15/25 sintered at 1200 °C was evaluated by the mercury intrusion technique, as shown in Fig. 7. The
Figure 6. SEM images (cross-section and inner and outer surfaces) of the hollow fibre MK-DMSO-15/25 as-prepared samples (a) and samples sintered at different temperatures: b) 1150 °C, c) 1200 °C and d) 1250 °C

Figure 7. Pore size distribution of the fibre MK-DMSO-15/25 sintered at 1150 °C

The last peak at 5.30 µm designates the pore size of the opened micro-channels. Lee et al. [7] reported that alumina hollow fibre membranes presented a sponge like-layer with pore sizes between 0.25 and 0.30 µm and micro-voids of 3.2 µm. Thus, the application of kaolin powder resulted in a loosely packed structure at the sponge-like layer region than conventional asymmetric alumina hollow fibres. However, the size of the micro-voids formed with kaolin is similar to those with alumina. The porosity of the MK-DMSO-15/25 fibre sintered at 1150 °C was evaluated to be 46% according to the mercury intrusion technique. Our previous study reported that pure alumina hollow fibres presented porosities of 64 and 54% when sintered at 1300 and 1400 °C, respectively. Obada et al. [34] reported a porosity of 62% for disk kaolin membrane sintered at 1150 °C, which was produced by the pressing method.

The porosity of the membrane critically influences its application and, in general, membranes with high porosity are suggested to be applied as a substrate for the deposition of a selective layer while denser membranes are used for proper separations. However, the mechanical
resistance of the membrane should not be negatively affected by its porosity. The pore distribution of the membrane and the sintering temperature are the main factors affecting the mechanical resistance of the membrane, as presented in Table 2.

Table 2. Bending strength values (MPa) of the kaolin hollow fibres sintered at different temperatures

<table>
<thead>
<tr>
<th>Hollow fibre membrane</th>
<th>Sintering temperature</th>
<th>1150 °C</th>
<th>1250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-NMP-7/15</td>
<td>-</td>
<td>20.74±1.90</td>
<td></td>
</tr>
<tr>
<td>MK-NMP-7/15</td>
<td>26.57±1.69</td>
<td>75.34±2.94</td>
<td></td>
</tr>
<tr>
<td>MK-NMP-15/25</td>
<td>30.70±3.68</td>
<td>81.99±3.62</td>
<td></td>
</tr>
<tr>
<td>MK-DMSO-7/15</td>
<td>31.60±2.85</td>
<td>81.09±5.86</td>
<td></td>
</tr>
<tr>
<td>MK-DMSO-15/25</td>
<td>41.98±2.61</td>
<td>145.64±9.88</td>
<td></td>
</tr>
</tbody>
</table>

**Mean values denoted by different letters at the same column are significantly different at p ≤ 0.05**

Due to the larger particle size of the un-milled kaolin powder, the hollow K-NMP-7/15 fibre sintered at 1150 °C was fragile and its mechanical resistance could not be evaluated. The mechanical resistance of the MK-NMP-7/15 fibre is 3.6 times greater than for the K-NMP-7/15 fibre, both sintered at 1250 °C. Thus, the milling of the kaolin powder was strictly necessary to produce hollow fibre membranes with reliable mechanical resistance. The change in the extrusion rates had no significant effect on the bending strength values of the fibres produced with NMP as solvent at both evaluated sintering temperatures (1150 and 1250 °C). However, the mechanical resistances of the fibres produced with DMSO increased with the increase in the extrusion rates. Actually, as presented in Fig. 5 for the fibres produced with DMSO as solvent, a larger sponge like layer was formed at higher extrusion rates, which contributed to the increase in the mechanical resistance of the fibre. The use of DMSO or NMP as solvent resulted in fibres with similar bending strength values if compared at the extrusion rates of 7 and 15 ml/min for ceramic suspension and bore fluid, respectively. However, at the highest extrusion rates of 15 and 25 ml/min for ceramic suspension and bore fluid, respectively, the mechanical resistance of the fibres produced with DMSO was higher than with NMP. The use of DMSO as solvent produced more organized micro-voids and, thus, the fibres produced with DMSO presented higher mechanical resistance. Chakraborty et al. [17] highlighted the importance of optimizing the conditions for producing kaolin membranes in order to have suitable mechanical resistances.

The increase in the sintering temperature from 1150 to 1250 °C increased the mechanical resistance of all the produced kaolin hollow fibres for approximately 3 times. The sample MK-DMSO-15/25 sintered at 1200 °C presented bending strength of 95.27±4.38 MPa. The increase in mechanical strength with the increase in the sintering temperature may be associated with the enhanced densification of the ceramic particles, as observed in the SEM images (Fig. 6). Hubadillah et al. [35] verified that the mechanical resistances of kaolin fibres were increased from almost 5 to 60 MPa when the sintering temperatures were increased from 1200 to 1500 °C. Terra et al. [36] reported that the increase in the sintering temperature of asymmetric alumina hollow fibres from 1300 to 1400 °C increased the bending strength of the fibres from 41.2 to 74.5 MPa. Thus, the fibres produced with kaolin as starting material and sintered at temperatures lower than 1250 °C presented suitable values of mechanical strength. Rekik et al. [37] related kaolin as reinforcing agent for polymeric membranes.

The water permeabilities of the MK-DMSO-15/25 fibres sintered at 1150, 1200 and 1250 °C were 23.38, 14.64 and 3.46 l/(h·m²·kPa), respectively. All other produced hollow fibres presented similar behaviour. The increase in the sintering temperature caused a pore densification which resulted in the increase in the mechanical resistance of the membrane, but also the decrease in its water permeability. The water permeability of the produced hollow fibres is quite similar to the values reported in the literature [13]. Sharma et al. [2] reported the use of a low cost kaolin-based membrane sintered at 950 °C for antibiotic removal from an aqueous solution, which presented water permeability of 12.96 l/(h·m²·kPa) and mechanical resistance of 28 MPa. Liu et al. [38] produced a layered kaolin membrane which was supported on a polymeric substrate and presented water permeability of 40.00 l/(h·m²·kPa).

3.3. Retention of bacteria by membrane filtration

The hollow MK-DMSO-15/25 fibres sintered at 1200 and 1250 °C presented suitable characteristics for filtration applications. The use of DMSO and extrusion rates of 15 and 25 ml/min resulted in a fibre with positive morphological characteristics: regular contours and asymmetric pore size distribution. The hollow MK-DMSO-15/25 fibres sintered at 1200 and 1250 °C presented suitable mechanical resistance. Figures 8a and 8b show the permeate flux of the bacteria solution through the hollow MK-DMSO-15/25 fibre sintered at 1200 and 1250 °C, respectively.

There was a pronounced flux decline during the first 15 min of filtration with both evaluated fibres. The permeate fluxes through the fibre sintered at 1200 °C were at least 3 times greater than through the fibre sintered at 1250 °C. Thus, the increase in the sintering temperature decreased the membrane porosity and reduced its permeability. The initial fluxes of the bacteria solution through both membranes were quite similar to the pure water flux at 20 kPa, but after 25 min of filtration, the initial fluxes through both membranes were decreased for approximately 3 times. This decrease was probably due to the membrane fouling occurrences during the filtration process.

The modelling of experimental data according to the differential equations proposed by Hermia [23] for
dead-end filtration showed that the main fouling occurrences were due to the partial and internal pore blocking mechanisms (Table 3). These mechanisms were probably more pronounced than total pore blocking and cake formation because the evaluated membranes presented larger pore sizes than the size of the filtered bacteria. According to the literature [39], Enterobacter is a rod-shaped bacterium that measures 0.6–1.0 µm wide by 1.2–3.0 µm long.

Notwithstanding, the hollow fibre membranes were quite efficient in removal of the Enterobacter bacteria from the feed solution. The bacteria retention values were 99.8% and 99.9% for the hollow fibres sintered at 1200 and 1250 ºC, respectively. Similarly, Kumar et al. [40] reported removal of 90% of Escherichia coli from an aqueous solution by using a ceramic membrane.

IV. Conclusions

The potential use of kaolin as the starting material for producing ceramic hollow fibre membranes was demonstrated. The milling of the ceramic powder was crucial to achieve the asymmetric pore size distribution in the membrane. The flow rate of the internal coagulant fluid (water) during the extrusion process was adjusted to 25 ml/min in order to produce enough hydrodynamic force against the ceramic suspension and, thus, produce a hollow fibre with regular internal contour. The fibres sintered at 1150 ºC presented a high porosity, but their mechanical resistance was not enough to guarantee its applicability in separation processes. The crystallographic transformations of the ceramic material at temperatures greater than 1100 ºC also caused modifications in the morphology of the produced hollow fibre membranes. The fibres sintered at 1200 and 1250 ºC facilitated a pore densification process which increased the mechanical resistance of the fibres. Moreover, they showed excellent potential for bacteria removal from water by demonstrating retention values of almost 100% of bacteria in water. The presented systematic analysis revealed proper conditions for producing kaolin-based hollow fibre membranes which can be extrapolated for using other mineral based ceramic materials.

Acknowledgments: We acknowledge financial support from FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

References


