Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2015, Article ID 371697, 7 pages
http://dx.doi.org/10.1155/2015/371697

Research Article

Effect of Sintering Temperature on Membranes Manufactured with Clays for Textile Effluent Treatment

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Received 5 September 2014; Accepted 25 November 2014

Academic Editor: Guocheng Lv

The aim of this work is to use cheap raw materials, such as kaolin and ball clay, for the manufacture of ceramic membranes for application in effluent treatment from textile industry and to evaluate the influence of sintering temperature in the structural and morphological characteristics of those membranes. The ceramic mass was characterized by X-ray diffraction and thermal analysis. The membranes were characterized by scanning electron microscopy, Hg porosimetry, and water permeability with desalinated water. The variation in the sintering temperature directly affected the structural and morphological characteristics of the membranes. The increase in sintering temperature of the membranes has raised the average pores diameter from 0.116 to 0.179 μm but decreased the porosity of the membrane, from 40.30 to 25.16% for temperatures from 900 to 1100°C, respectively. The reduction in porosity of the membrane affected the water permeated flux and decrease from 35.82 Kg/h·m^2 (at 1000°C) to 15.68 Kg/h·m^2 (at 1100°C). All the membranes have been applied with success in the effluent treatment from textile industry, resulting in the decrease in turbidity and discoloration, reaching approximately 100% of rejection of solid particles.

1. Introduction

Despite all the advantages that the processes involving ceramic membranes exhibit the search for making these articles with the minimum possible cost is still under consideration. The clays are natural materials that have grown in importance and have interested the scientists in this area. These materials are abundant in nature and require low temperatures during sintering process, when compared, for example, with metal oxides.

The first researches on the preparation of ceramic membranes used α-Al_2O_3 as a precursor and then γ-Al_2O_3, zirconia, silica, and titania, valuable materials, when compared to those used in recent work where some researchers began working with natural raw materials and residues, such as apatite, ash powder, and kaolin, to reduce the cost of the membrane [1].

Among some recent works reported in the literature that refer to the use of natural raw materials for the manufacture of membranes, can be cited, for example, the study done by Fakhfakh et al. [2] who dedicated their work to the study of ceramic membranes prepared from mineral oxides for use on tubular support of clay.

Jana et al. [1] prepared ceramic membranes for microfiltration using clay. They prepared two different membranes; the first was done with pure clay and the second with clay and small amounts of sodium carbonate, boric acid, and sodium metasilicate. In its results the authors showed membranes with potential for use in the treatment of effluents containing heavy metals. Recently Zulhairun et al. [3] used clay for the preparation of membranes to be used in gas permeation processes, and the results showed that the gas permeation rate increased with increasing clay content in the mass composition used to prepare the membranes. Khemakhem

and Amar [4] developed a membrane for microfiltration with clay from Tunisia and the rejection rates results were superior to 99% of salt. From the various applications for which the use of membrane technology is intended, the treatment of effluents is distinguished by excellent results presented. A large amount of these effluents is from industries that make the disposal of these products without a proper pretreatment.

Textile industry, which generally uses large volumes of water and hence long sequence of wet processing stages, consumes many resource inputs and produces quantities of wastewater. The main sources of wastewater are rinsing waters from fiber preparation and continuous dyeing, alkaline waste from preparation, and batch dyeing waste containing large amounts of salts, acid, or alkali chemicals [5]. In this way, the interest in applied membrane for reuse of waste water from textile processes is increasing thanks to technological innovations which make them reliable and viable compared to other systems [6]. Membrane technology is today the dominant technique in the treatment of several types of wastewater: wastewater from some industries, such as electronic [7], petrochemical [8], treatment of radioactive waste [9], effluents containing natural organic matter [10], heavy metals [11], and aqueous samples containing pesticides and herbicides [12] industries.

According to this context, the aim of this work is to obtain microfiltration membranes from raw materials of low cost and simple processing, such as kaolin and ball clay, evaluate the effect of different sintering temperatures (900, 1000, and 1100°C), in structural and morphological characteristics of these membranes, and apply these membranes to the textile industry effluent treatment.

2. Materials and Methods

The composition used for preparation of ceramic mass to obtain membranes was composed of ball clay (44% w/w) and clay (56% w/w) from the state of Paraíba (Brazil).

To obtain the ceramic mass, the kaolin and ball clay were passed in a sieve with aperture of 0.074 mm, according to ABNT standard, and homogenized in a blender manufactured by METVISA Company, for a period of 6 hours. After that, water (20% w/w) and lubricant (diesel oil, 3% w/w) were added to the mass, to acquire the proper texture for extrusion.

The ceramic mass processing was conducted in a vacuum of extruder from Verdés, 051 model, in tubular format with internal and external diameters of 7.0 and 10.0 mm, respectively. After that, the extruded parts were dried in two stages, at room temperature for a period of 7 days and at 100°C for a period of 24 hours.

The membranes were sintered on electric oven, model LF0914, from Jung Industry, with the following temperature program during the firing process: from room temperature to 400°C with heating rate of 2°C/min, from 400 to 700°C with a heating rate of 1°C/min, and from 700 to maximum temperature at a heating rate of 3°C/min, staying at this maximum temperature for period of 1 hour. Maximum temperatures were 900, 1000, and 1100°C.

The ceramic mass was characterized by thermal analysis performed in a thermal analyzer, model RB-3000-20, manufactured by the BP Company, with heating rate of 12.5°C/min, in nitrogen atmosphere, using a platinum crucible and range from room temperature to a maximum temperature of 1000°C. The ceramic mass was also submitted to an X-ray diffractometer XRD-6000 model Shimadzu, with kα radiation from copper with scanning of 2θ from 2 to 80°.

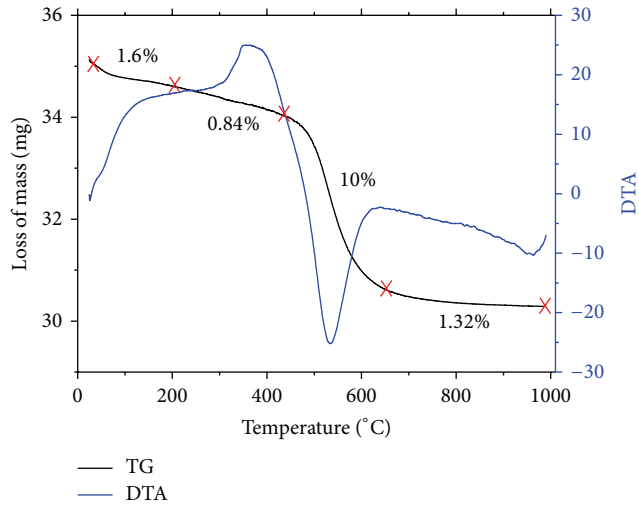

Figure 1: Thermogravimetric and differential thermal analysis of the mass before the sintering.

The membranes were characterized by scanning electron microscopy using model SSX-550, from Shimadzu and mercury porosimetry through an Analyzer Autopore model IV, from Micromeritics, and permeated flow tests were conducted with distilled water, with tangential flow at 25°C.

The membranes have been applied to the treatment of effluent from the dyeing step of a textile industry from Fortaleza city, Brazil.

3. Results and Discussion

3.1. Characterization of Massiness Ceramics. Figure 1 shows the graph for the thermal analysis of the ceramic mass before the sintering stage.

According to the thermogravimetric curve a first event which begins from 25°C up to 200°C was observed showing a loss in mass of 1.6% of the adsorbed water that is eliminated from the surface of the mass. From 200 to 435°C there is a discrete mass loss equivalent to 0.84%, due to elimination of organic matter, confirmed by differential thermal curve that shows an exothermic peak at the same interval of temperature, indicating the combustion of organic matter. At 435°C starts the third and biggest event that follows up to 625°C, showing a 10% mass loss due to elimination of hydroxyls groups of the clay fraction. From 630°C until the end of the analysis there is a slight loss of 1.32% mass, caused by decomposition and loss of carbonates and hydroxides. The last endothermic peak appears in differential thermal curve at 960°C and is due to nucleation of mullite. In total the mass loss has reached a value of 13.8%.

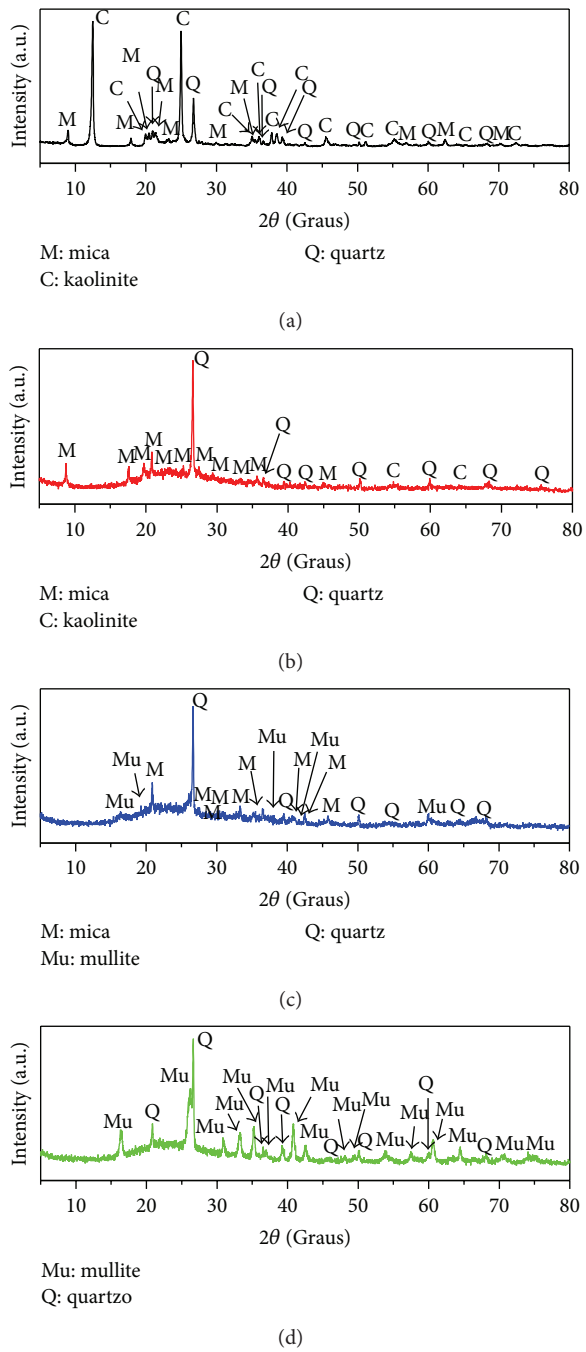

Figure 2: X-ray patterns of (a) ceramic mass before the sintering and sintered mass at (b) 900°C, (c) 1000°C, and (d) 1100°C.

Figure 2 shows the X-ray curves of the ceramic mass before and after the sintering stage at temperatures of 900, 1000, and 1100°C.

It is observed through Figure 2 that, for the first sintering temperature, at 900°C, the peaks presented in curves were the same crystalline phases presented to the mass before the sintering, with the presence of quartz and mica. The kaolinite was present in just a few traces due to its transformation into a metakaolinite. The increase in temperature in sintering process causes a reaction between silica (SiO_2) and alumina (Al_2O_3) present in the raw materials forming mullite ($3Al_2O_3{\cdot}2SiO_2$) (standard sheet JCPDF 15-0776) as shown in the curve for sintered mass at 1000°C. As for the curve of sintered mass at 1100°C, there is also the presence of the quartz and mullite, differentiating from the curve of sintered mass at 1000°C, by presenting more intense and defined peaks and the absence of mica, due to probably the destruction of its structure and/or its contribution to formation of mullite.

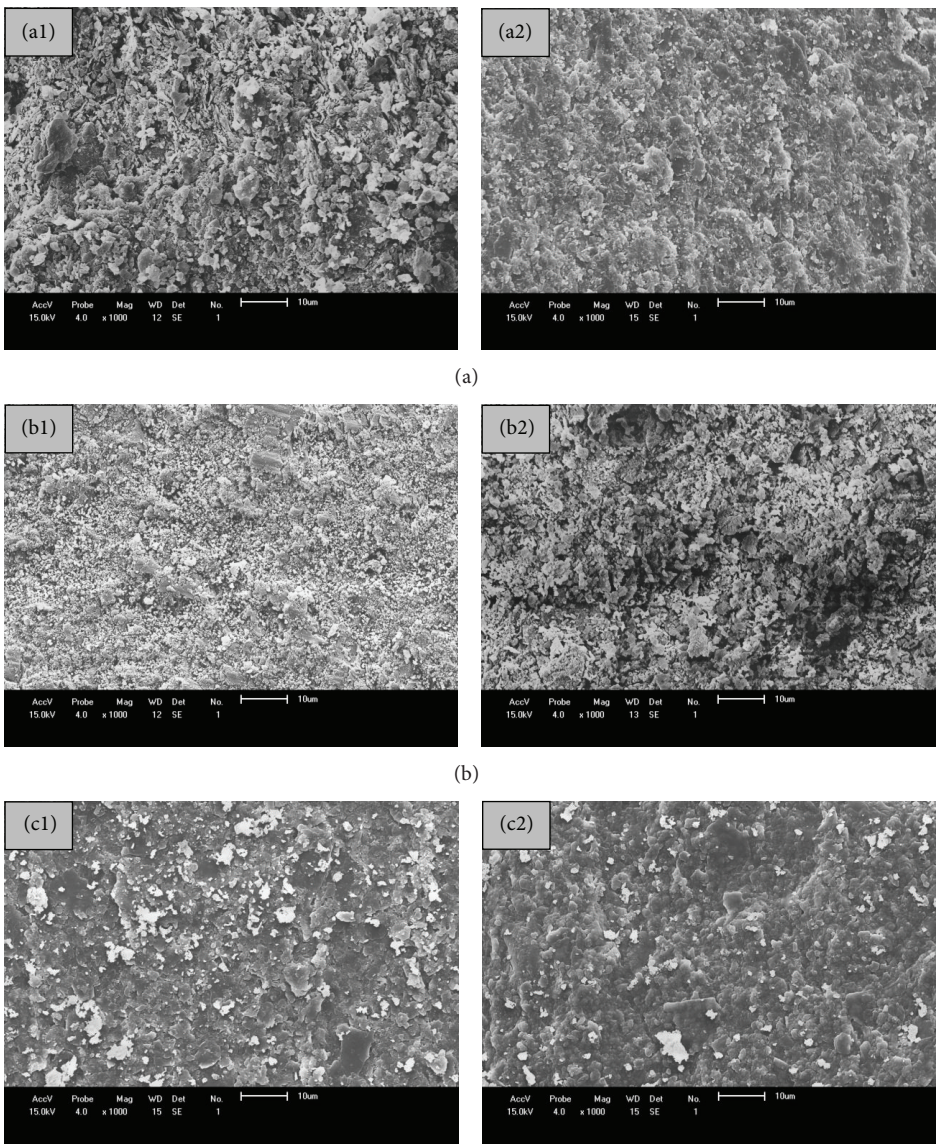

Figure 3: SEM images of longitudinal (1) and transversal (2) sections of the sintered ceramic membranes at 900 (a), 1000 (b), and 1100°C (c).

3.2. Characterization of Ceramic Membrane. Figure 3 shows the SEM images of the cross-sectional and longitudinal sections of the membranes sintered at 900, 1000, and 1100°C.

The image illustrated in Figure 3 allows the indication of the porous structure of the membrane, with the presence of grains with irregular plates formats, randomly distributed, with sizes larger than 2 μm.

From Figure 3(a) it is realized that the sintering temperature was not enough to promote good sintering, since it is possible to show isolated grains, also in the form of irregular plates. Despite the structure being porous, the micrographs do not allow estimating with accuracy the pore size and the degree of porosity of the membranes. It can be evaluated from Figure 3(b) that the increase in 100°C in the sintering temperature has caused the increase of grain size, but there is still the presence of some grains with distinct geometries, different sizes, distributed along the membrane. These images when compared with the images from Figure 3(a) make possible the observation that the rise in the sintering temperature provided a better visualization of pores present in the membrane. The images allow the evaluation that the increase in sintering temperature caused a difference in the superficial aspect of the membranes. Despite the presence of grains well sintered, it is still possible to note a few isolated and scattered grains along the membrane. The grains are spread in a more homogeneous way when compared with the images of the sintered membranes at 900 and 1100°C.

Figure 4 presents the variation of pores diameter of ceramic membranes as a function of the accumulated intrusion volume of mercury.

In Figure 4 the three curves corresponding to three sintering temperatures show that the vast majority of pores

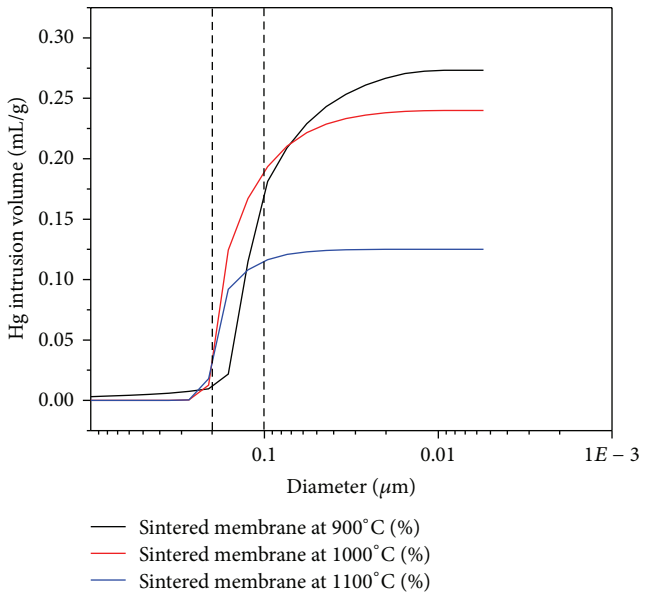

Figure 4: Variation of pore diameter versus mercury intrusion volume of the membranes sintered at 900, 1000, and 1100°C.

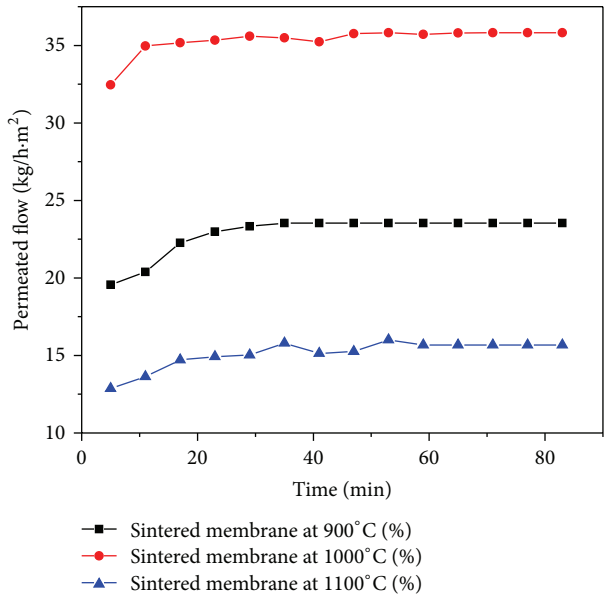

Figure 5: Distilled water permeated flows to the ceramic membranes sintered at 900, 1000, and 1100°C.

Table 1: Values of the average pore diameter and porosity of sintered ceramic membranes at 900, 1000, and 1100°C.

Sintering temperature (°C)	Average pore diameter (μm)	Porosity (%)
900	0.116	40.30
1000	0.164	38.75
1100	0.179	25.16

have sizes ranging from 0.1 to 0.2 μm, which characterizes membranes for microfiltration processes. Table 1 presents the values of the average pore diameter and porosity of ceramic membranes in relation to sintering temperature.

It can be observed that the increase in temperature of sintering from 900 to 1100°C led to a small increase in the average pore diameter from 0.116 to 0.179 μm. But as regards the porosity, the difference between sintered membranes from 900 and 1100°C reached 15.14%.

The increasing temperature increases the amount of liquid phase formed during the sintering process, which by capillarity effect penetrates the pores of smaller diameter leading to the reduction or even the disappearance of them. According to Nandi et al. [13] the capillary strains cause the liquid to redistribute itself between the particles and into the small pores, leading to further rearrangement and enlargement of the size of big pores. According to Germman [14] the formation of liquid phase can also lead to the growth of grain. In this way, there has been an increase in the values of the size of the average pore diameter and the decrease in the values of porosity.

Figure 5 illustrates the flow curves of distilled water permeated through the membrane as a function of time.

The membrane that obtained greater water permeated flow was sintered membrane at 1000°C, showing stabilized

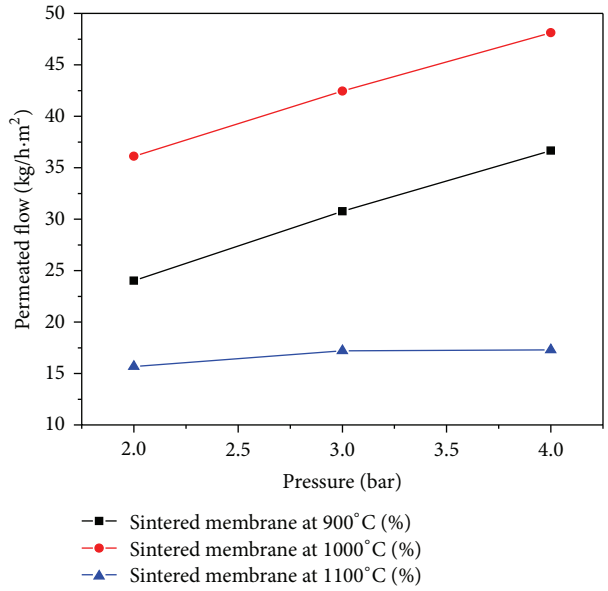

Figure 6: Water permeated flow versus applied pressure for the membrane sintered at 900, 1000, and 1100°C.

value of 35.82 kg/h·m^2 after 30 min, followed by the membrane sintered at 900°C with 23.54 kg/h·m^2 and 1100°C with 15.68 kg/h·m^2. Obviously, for same pressure and very close pore sizes, the porosity features greater influence in the permeated flow with distilled water through the membrane.

Figure 6 shows the water permeated flow versus applied pressure for the membranes sintered at 900, 1000, and 1100°C.

From Figure 6 the water permeated flow increases with the increase in transmembrane pressure. The values obtained for the permeability of ceramic membranes were 6.32, 6.00, and 0.81 Kg/h·m^2·bar for sintered membranes at 900, 1000,

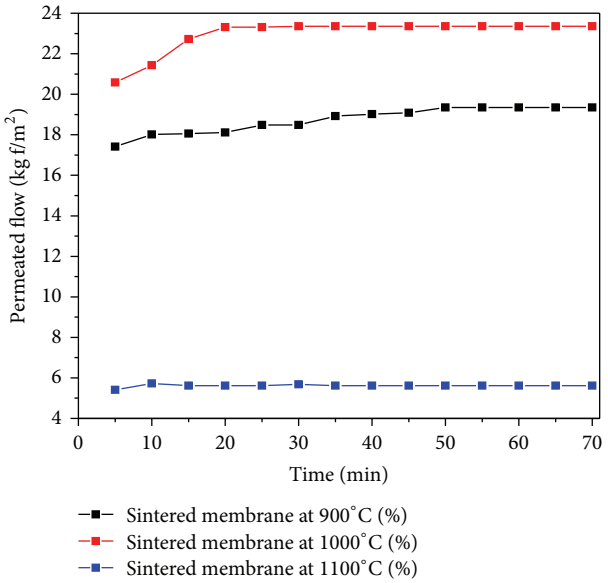

Figure 7: Textile effluent permeated flow of the ceramic membranes sintered at 900, 1000, and 1100°C.

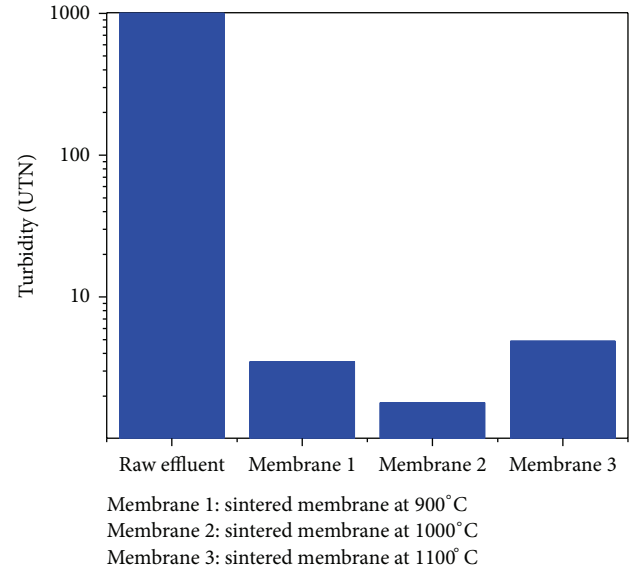

Figure 8: Turbidity of textile effluent before and after permeation through the sintered ceramic membranes at 900, 1000, and 1100°C.

Table 2: Comparative values between the permeated flows from distilled water and industrial effluent.

Sintered temperature (°C)	Permeated flow (kg/h·m^2)	
	Distilled water	Effluent from textile industry
900	23.54	19.35
1000	35.82	23.62
1100	15.68	5.62

and 1100°C, respectively. According to Vasconcelos [15] the permeability of porous materials is a function of the volumetric fraction of pores, as well as the average pore diameter. The greater permeability was achieved by sintered membrane at 1000°C, due to higher product value between average pore diameter and porosity reached at this temperature. The lowest permeability presented by the membrane sintered at 1100°C is due to the lower porosity caused by shrinkage when compared with membranes sintered at 900 and 1000°C.

3.3. Application of Membrane. The results of the behavior of the permeated flow of textile effluent by ceramic membranes using a pressure of 2 Bar are presented in Figure 7.

According to Figure 7 it was verified that the permeated flows stabilized in values of 19.35, 23.62, and 5.62 Kg/h·m^2 for the sintered membranes at 900, 1000, and 1100°C, respectively, and the largest permeated flow was achieved by the membrane sintered at 1000°C.

Table 2 presents the average values of the permeated flows of the ceramic membranes using distilled water by comparing them with the values of permeated flows using the industrial effluent.

It is observed that the industrial effluent permeated flows decreased when compared with distilled water permeated flows, this decrease being more pronounced for sintered membrane at 1100°C, and this occurs due to clogging of the pores of the membrane with suspended particulates from the effluent. The particles size distribution of the effluent showed average diameter of 2.22 μm and 10% of the particles have sizes smaller than 0.26 μm. These values are close to those of membrane pore diameters sintered at 1100°C (0.179 μm), which can penetrate the pores, causing an obstruction.

Figure 8 presents the results of turbidity for the industrial raw effluent and after permeation through membranes sintered at 900, 1000, and 1100°C.

The results obtained of turbidity for the effluent after passing through the ceramic membranes showed that the separation was efficient, retaining solid particles present in the effluent. The values after permeation were 3.49, 1.79, and 4.85 UTN for sintered membranes at 900, 1000, and 1100°C, respectively. Fersi and Dhahbi [16] studied two treatments with membrane, the first with ultrafiltration and the second with nanofiltration, and reached retention of textile effluent color with approximately 95%. This confirms the potential of the membranes obtained through this research, which significantly reduced the turbidity.

Figure 9 presents the images of textile effluent before and after permeation by ceramic membranes.

Through visual analysis of Figure 9 the difference found for the industrial effluent before and after permeation through membranes is clear. It is possible to observe the high turbidity of raw effluent and the removal of solid particles of permeated.

4. Conclusions

The preparation of ceramic membranes with kaolin and ball clay is a viable alternative, with excellent results for the treatment of effluent from textile industry. The sintered

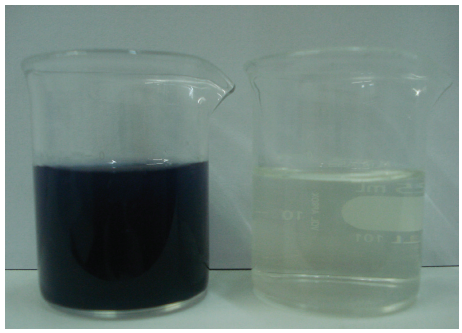

Figure 9: Images of the textile effluent before and after permeation through ceramic membranes.

ceramic membranes at three temperatures, 900, 1000, and 1100°C, presented in the pore diameter for use in microfiltration processes, showing efficiency in treating effluent from textile industry, reaching solid rejection rate close to 100%. The increase in sintering temperature of the membranes has raised the average pores diameter from 0.116, 0.164 to 0.179 μm but decreased the porosity of the membrane, from 40.30 to 25.16% for temperatures from 900 to 1100°C, respectively. The reduction in porosity of the membrane with the increase in sintering temperature affected the water permeated flux and decrease from 35.82 Kg/h·m^2 (at 1000°C) to 15.68 Kg/h·m^2 (at 1100°C). All the membranes have been applied with success in the effluent treatment from textile industry, resulting in the decrease in turbidity and discoloration, reaching approximately 100% of rejection of solid particles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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