Synthesis and characterization of low-cost ceramic membranes using red mud from the eastern Amazon as waste from the Bayer process

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ABSTRACT

This research presents the development and characterization of ceramic membranes from a mixture of Red Mud and Clay. Characterized as for the Apparent Porosity (AP), Water Absorption (WA), Linear Retraction (LR), Apparent Density (AD), Pore Distribution, Hydraulic Permeability and Rejection to a solute of interest. XRD, SEM / EDS, and Rietveld Technique were used to characterize the raw materials. The composition *L35A65* shows the best results, with WA = 29.55 ± 0.2, AP = 44.72 ± 0.62, AD = 1.5 ± 0.01, LR =1.67 ± 0.0, mean diameter of pores equal to 0.418µm and hydraulic permeability, Lp = 721.4 Lh/m^2.bar. The rejection for yeasts was 99.9% and for starch was 96.8%.
Keywords: Inorganic Membranes, Microfiltration, Material Characterization, Red Mud.

RESUMO

Este trabalho apresenta o desenvolvimento e caracterização de membranas cerâmicas a partir da mistura de Lama Vermelha e argila. As mesmas foram caracterizadas quanto a Porosidade Aparente (PA), Absorção de Água (AA), Retração Linear (RL), Densidade Aparente (DA), Distribuição de Poros, Permeabilidade Hidráulica e Rejeição a soluto de interesse. Para caracterização das matérias-primas primas foram utilizadas DRX, MEV/EDS, e Técnica de Rietveld. A composição L35A65 apresentou os melhores resultados, sendo AA=29,55±0,2, PA=44,72±0,62, DA=1,5±0,01, RL=1,67±0,0, diâmetro médio de poros igual a 0,418µm e Permeabilidade Hidráulica, Lp=721,4 L.h/m^2.bar. A rejeição para as leveduras foi 99,9% e para o amido foi de 96,8%.
Palavras-chave: Membranas Inorgânicas, Microfiltração, Caracterização de Materiais, Lama Vermelha.

INTRODUCTION

In several process, membranes act like a selective barrier, allowing or restricting components that permute based on affinity from molecules with the material from the membrane or the difference between the pores from the membrane e the molecules. In this way, membranes can be fabricated from different materials organics and inorganics to have a characteristic that is need for given separation[1].

Ceramics materials are also known as inorganics membranes, that are formed by one layer or multiple layers from ceramics materials in the pattern.

The main materials include contain alumina (Al2O3), zirconia (ZrO2), titanium oxide (TiO2), Silicon oxide (SiO2)[2], etc. Besides that, presents major advantages regarding other materials, about bigger quality of life, easiness to clean, chemical and biological stability and resistance to high temperatures and pressures. However, the high price from fabrication it is still a dilemma for large utilization and fabrications for those membranes with the possibility for application in various branches of industry[3-5].

In this way, becomes evident the increase of a search for alternative and viable sources from raw materials for membrane preparation. For over the years, low-cost membranes have been developed from a variety of raw materials, such as Sugarcane Bagasse[6], Mullite[7], Tunisian Clay[8], Algerian kaolin[9].

In this sense, this research aims the development of a low-cost membrane, using as raw material red mud, waste from the aluminum processing industry, generated from the refining of bauxite to produce alumina (Al2O3) through Bayer process[10]. In addition, also have been use clay from the river Paracurí localized in the edge of Icoaraci, Belém/PA, natural raw material, easy to obtain and abundant.

METHODS

The membranes were synthesized from a mixture of red mud (RV), provided by Hydro Alunorte (Barcarena/PA) and Clay (C) from the fair of Paracurí (Icoaraci - Belém/PA). The raw materials were first dry in furnace at 105 °C for 24h for further sieving, being choose for material utilization between 0,15-0,3 mm, for both. The test pieces were manufactured in the form of circular discs with of 9 cm diameter and 2 mm of thickness, using a mold made with steel VC 131, according to the Figure 1. The composition of the membranes can change according to the following proportions RM/C (%, m/m): 20/80, 35/65, 50/50, 65/35 e 80/20, respectively.

Figure 1 – Mold prepared with VC 131 steel.

After being pressed by a hydraulic press MARCON-MPH-10, as shown in Figure 2, the specimens were

dried by natural convection at room temperature for 48h, then in an furnace at 105 °C for 24 hours. Posteriorly, the samples were calcinated at a rate of 10 °C/min until reaching 900 °C and kept constant for one hour. The cooling was made by natural convection, after the oven shutdown.

Figure 2 – Hydraulic Press (MARCON-MPH-10).

RM and C were characterized by X-Ray Diffraction (Bruker/D8 Advance) and quantified using the Rietveld method. The membranes obtained were characterized by Apparent Porosity (AP), Water Absorption (WA), Linear Retraction (LR), Apparent Density (AD), using the ASTM C20 (2000) standard; Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS) (Hitachi/TM-3000). The apparatus shown in Figure 3 was prepared in the laboratory for the analysis of Water Absorption, Apparent Density and Apparent Porosity.

The membranes were further analyzed for Hydraulic Permeability, rejection of the solute of interest and permeate flux. The studied solutes were yeast *Saccharomyces cerevisiae* (Eagle) and commercial corn starch. The quantification of yeasts in the permeate and concentrated phases was performed by the counting method in an optical microscope (Biofocus/B1600TA-L) using a Neubauer chamber. The determination of starch content in both phases was carried out via acid hydrolysis[11], followed by the Somogyi-Nelson method.

Figure 3 – Apparatus used to determine the physical properties of membranes: Absorption in Water (WA), Apparent Density (AD) and Apparent Porosity (AP).

After preparation, the solutions containing the solutes of interest were

processed individually, in a bench microfiltration (MF) system (PAM Membranes) (Figure 4), using the manufactured membranes, each for a period of 60 min, with constants measurements of permeate flux for each tested solute.

Figure 4 - Microfiltration (MF) system used to test confectioned membranes.

RESULTS AND DISCUSSION

Figures 5 and 6 has shown the analysis results of XRD (Bruker/D8 Advance) from red mud and clay in nature, respectively.

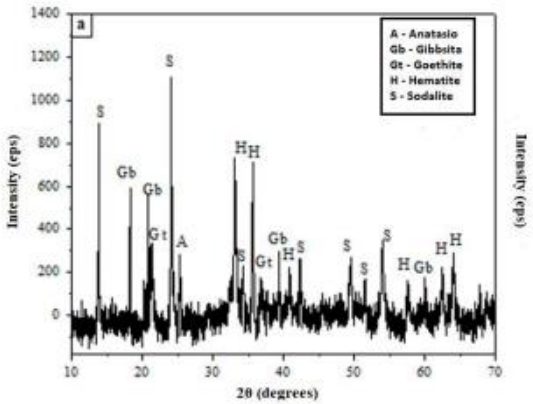

Figure 5 - X-ray diffraction from the Red Mud.

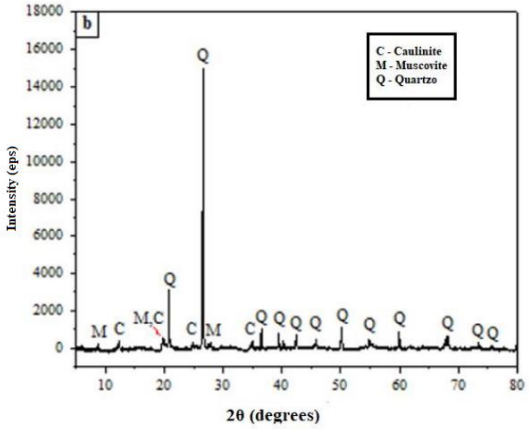

Figure 6- X-ray diffraction from the Clay.

The diffractogram presented in Figure 5 show the presence of Hematite (41%), Sodalite (29,6%), Gibbsite (17%) Goethite (7,8%) e Anatase (4,6%), characteristic of minerals from RM[10,12]. Furthermore, the XRD of Clay material from the Paracuri-PA region (Figure 6) indicates majority peaks from Quartz (67%), Muscovite (21%) e Kaolinite (12%), compatible with the results found in the literature[7, 13, 14]. The composition for both raw materials was quantified using the Rietveld Technique[15-17].

The manufactured circular ceramics membranes are shown in the Figure 7, after the sintering process.

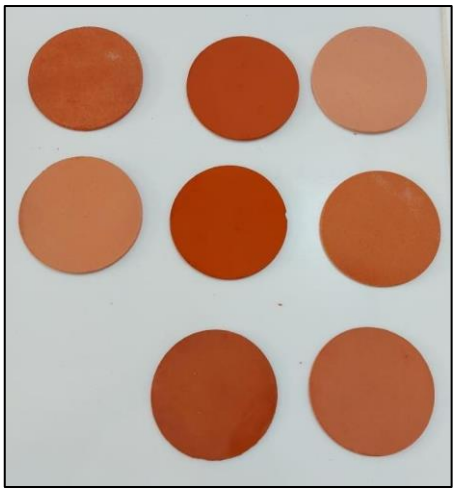

Figure 7- Different compositions of ceramics membranes after sintering.

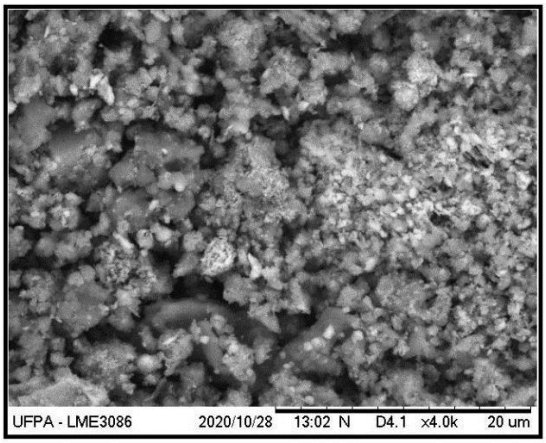

Figure 8 - Electron Micrograph from the longitudinal section of L35A65 ceramic membrane with 4000x magnification.

As seen Figure 7, fabricated membranes in circular shape are presented with integrity and no cracks, which is the evidence in electronic micrographs of the L35A65 membrane (RM=35%; C=65%), down below in the Figures 8 and 9, since the regions observed, transversion and longitudinal, were showed integrate, with the presence of fissures. Predominantly, it can ensure the presence of particles of irregular size and shape inferior and porous agglomerates in the form of larger flakes (>2,0 μm). It is possible to assure that solid particles belong to the group of iron minerals and/or minerals presented in bauxite that did not suffer modifications during process (hematite, quartz), while very thin particles from the smaller size in form of flakes or porous agglomerate belong to aluminosilicates known as desilicon products (DP)[12,18].

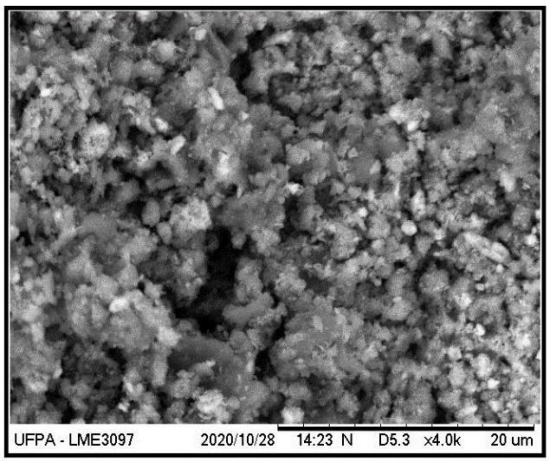

Figure 9 - Electron micrograph of the transversal section of the L35A65 ceramic membrane at 4000x magnification.

Tables 1 and 2 shown the mineral composition of the raw material, red mud, and clay, quantify by Rietveld Technique[15-17]. Besides, the Table 3 shows the semi-quantitative chemical composition of the L35A65 ceramic membrane, performed by Energy Dispersive X-Ray Spectroscopy (EDS) (Hitachi/TM-3000).

Table 1 - Mineral composition of Clay.

Mineral	Comp. (%)
Quartz	67
Muscovite	21
Kaolinite	12

Table 2 - Mineral composition of the Red Mud.

Mineral	Comp. (%)
Hematite	41
Sodalite	29,6
Gibbsite	17
Goethite	7,8
Anatase	4,6

Table 3 - Chemical composition of the membrane (L35A65).

Element	Comp. (%)
Fe	39,788
O	35,120
Al	9,658
Si	8,324
Na	5,455
Ti	1,654

Physical properties of the membrane are also characterized by sintering temperature influence in each composition variation. These data are obtained by Water Absorption, Apparent Porosity, Apparent Density and Linear Shrinkage. These parameters are graphically presented in Figures 10 and 11 below.

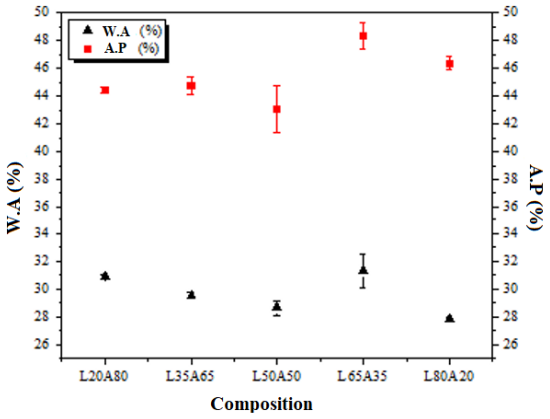

Figure 10 - Physical properties of membranes: Water absorption (%) and Apparent Porosity (%).

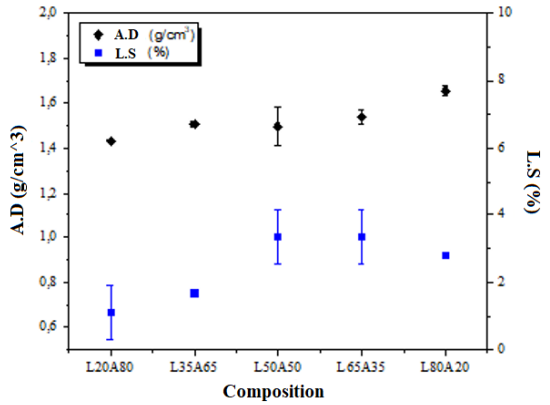

Figure 11 - Physical properties of membranes: Apparent Density (g/cm3) and Linear Shrinkage (%).

In the Figure 10, it is observed a variation with a downward trend, however small, for the Water Absorption (WA) in the membranes as the concentration of RM and its composition increases. It is also noticed that Apparent Porosity (AP) follows the WA growth/decay profile for the different membranes, which is the expected

behavior, since these properties are directly proportional.

Figure 11, it is noticed a small increase of the linear retraction in view of the red mud content incorporated in the ceramic aggregate. This behavior more evident in higher temperatures, above 1000 °C, due the greater formation of the vitreous phase, for the composition of the fluxing oxides that compose the RM, main responsible for the liquid phase formation, reacting with SiO2 providing material densification that also explains Apparent Density (AD) behavior with the rise of the RM content in the membrane[10,19].

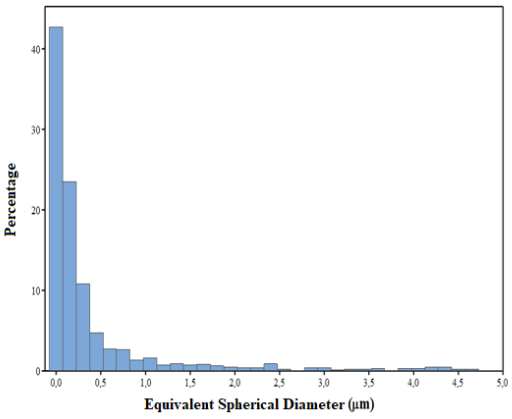

Figure 12 - Pore distribution of the L35A65 membrane.

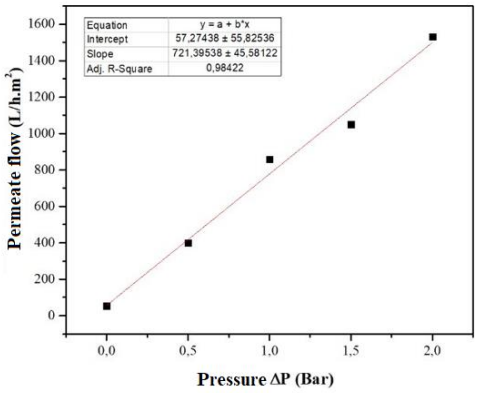

Figure 13 - Hydraulic permeability of the L35A65 membrane.

The Figure 12 shows pore distribution of the L35A65 membrane, from the treatment of images of the external surface of the membranes obtained in the SEM, using the ImageJ v.1.53e software. The average equivalent spherical diameter of the pore it is equal to 0,418 µm, varying between 0,01-4,725 µm, being able to be classified as microfiltration membrane[20].

For the hydraulic permeability and solute rejection tests, were presenting the results of the L35A65 membrane (RM=35%, C=65%) because its produce better performance in relation to the others. Figure 13 exhibits permeability (Lp) results using distilled water as pure solvent, being equals to 721,4 L.h/m^2.bar.

Rejection solute test could be discussed by the permeated flow behavior during time break with different solutions prepared with starch

and yeast *Saccharomyces cerevisiae* (Eagle), described in the graphic in Figure 14 below.

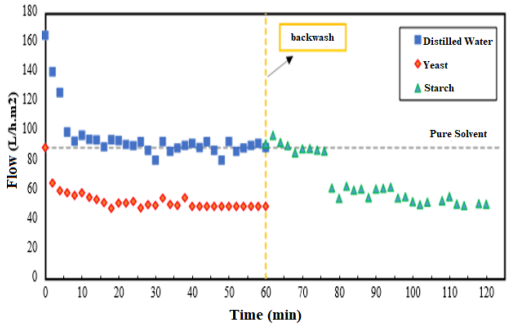

Figure 14 - Permeate flow for distilled water, yeast, and starch solution.

Still regarding the rejection solute test, it is possible visually observe in Figure 15 the overt difference between the process solutions of MF, concentrate and permeated.

Figure 15 - Samples of starch solution from concentrate (left) and permeate (right).

The Figure 14 shows the permeate flow result for pure solvent and two solutes studied, yeast *Saccharomyces cerevisiae* (Eagle) and commercial corn starch, where the flow for pure solvent stabilized at approximately 89 L/h.m^2, while the solutes of interest stabilized in 49,2 e 50,789 L/h.m^2 for yeast and starch, respectively. In the permeate flux profile for yeasts, the contribution of the effects of concentration polarization and fouling in the flow decrease can be clearly seen, while for the permeate flux using starch, better fouling effect is observed. Operation time for each solute was 60 min, where the flow stabilization for both tests occurred. Between one and another, was accomplished the cleaning of the system and a backwash with distilled water. The efficiency of the backwash is noted, where a flow returns to its initial condition. The rejection for yeast was 99.9% and for starch it was 96.8%. This last result is attested by Figure 15, where the permeate solution or passing through the membrane has a clear difference in turbidity compared to the concentrate solution.

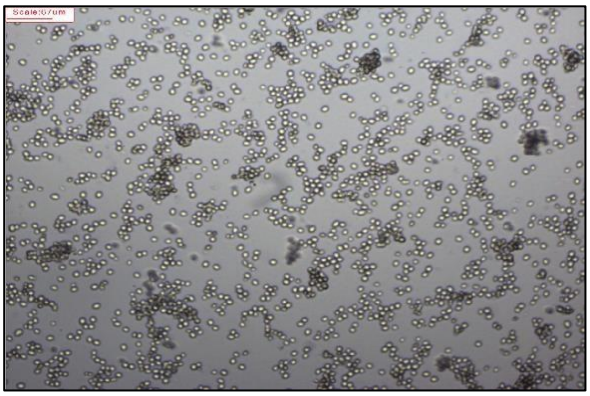

Figure 16 - Microscopy of the yeast solution used in the MF process.

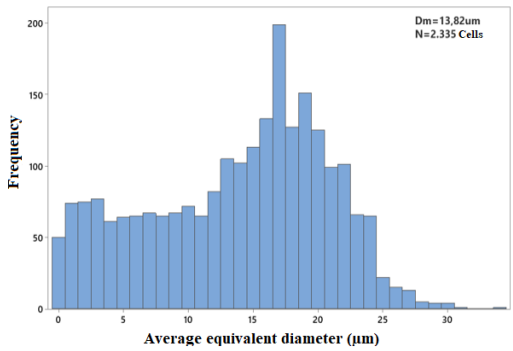

Figure 17 - Yeast equivalent mean diameter count and distribution.

Figure 16 shows the concentrate yeast solution applied in microfiltration (MF) tests, analyzed under a polarized light optical microscope. The mean equivalent diameter of these yeasts is seen in Figure 16. After processing the image obtained in microscopy, the value of 13.82 µm is obtained, reinforcing the high membrane rejection, with an average pore diameter of 0.418 µm, in relation to this solute used in the microfiltration (MF) process. The analyzes of the starch solutions without and with heating are shown below in figures 18 and 19, and in Figures 20 and 21, respectively. Optical microscopy and image treatment analyzes were performed to obtain the mean equivalent diameter of the two different preparation modes.

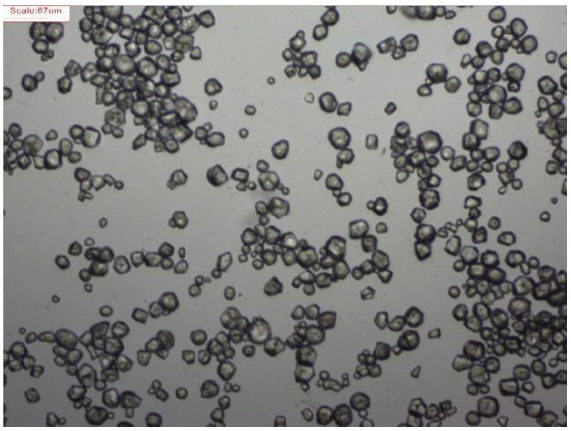

Figure 18 - Microscopy of the unheated starch solution.

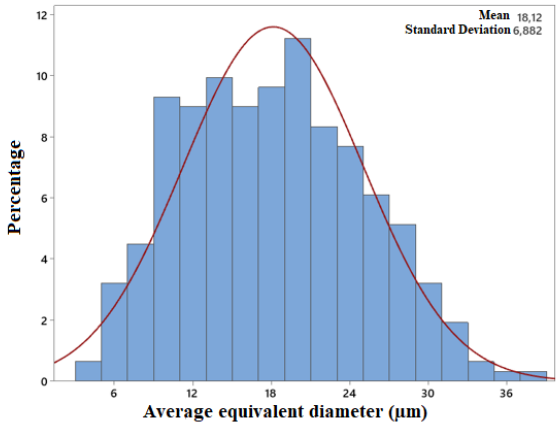

Figure 19 - Count and distribution of the mean equivalent diameter of the unheated starch solution.

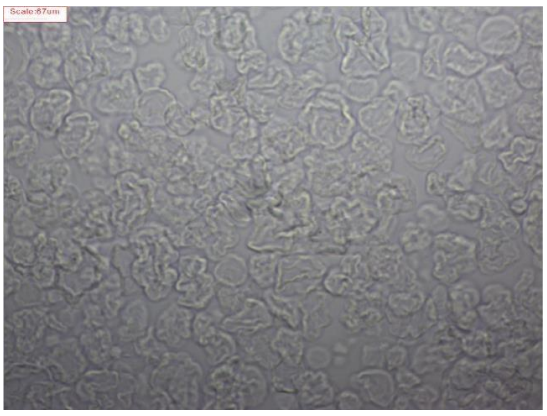

Figure 20 - Microscopy of the starch solution after heating used in the MF process.

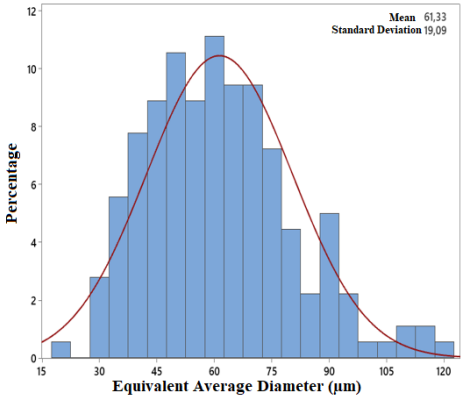

Figure 21 - Count and distribution of the mean equivalent diameter of the starch solution after heating.

As can be observed in the figures above, heating the starch solution interferes in the particles size. The granules of natural starch when observed under a polarized light microscope (Figure 18), present the birefringence and the typical "malta cross" that provide evidence of the different degrees of crystallinity of the starch structure by refraction of the crystalline regions. When subjected to the gelatinization process (Figure 20), the granules suffer a loss of birefringence, loss of malt cross and swelling, having much larger diameters than granules that did not undergo gelatinization [21-23]. Thus, it is observed in Figures 19 and 21 that the natural starch solution has granules with a mean equivalent diameter of 18.12 µm, while the heated starch solution has 61.33 µm.

CONCLUSION

The use of red mud has shown auspicious in the synthesis of ceramic membranes. The use of this low-cost raw material had good efficiency in its results and presents itself as an effective alternative in separation processes, since it uses viable and abundant sources. The membranes were classified as microfiltration membranes, with physical properties compatibles with the ones described in the literature, own good stability and high rejection of the studied solutes.

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