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Characterization of Mullite Ceramic Membranes and their Application in the Removal *Escherichia Coli*

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This paper aims the morphological and structural characterization of ceramic membranes of mullite and their application in the removal of *Escherichia coli.* A complex irregular structure presented by the pores of the membrane was verified by scanning electron microscopy (SEM). The average pore size and distribution were determined by mercury intrusion porosimetry. The average pore size of the material presented was 0,39 μm. Microfiltration tests resulted in a protein retention of 46, 76 and 89% for trypsin (TR), egg albumin (EA) and bovine serum albumin (BSA), proving the efficiency of the membrane microfiltration tests for molecular weight of 69 kDa. The application of the membranes on the retention of gram-negative bacterium *E. coli* resulted in a 66% efficiency at a pressure of 200 kPa and a 98% efficiency when applied a pressure of 50 kPa. Therefore, the use of mullite membranes show limited efficiency towards bacteria retention. Nevertheless, they present fluxes similar to other materials proposed in the literature.

Keywords: *Characterization, Ceramic membranes, Microfiltration, Retention.*

1. Introduction

The search for technologies that provide better quality and greater ease in treatment processes becomes one of the main subjects studied today. The process of separation by membrane (PSM) is a technology that has gained prominence because of its advantages compared to conventional separation procedures [1,2]. However, a major problem presented by the membranes is the decrease in permeability over its use due to fouling caused by organic matter contained in the raw water and microorganisms that adhere to the microporous wall or inside the pores [3,4].

Many studies described in literature proved that the use of ceramic membranes offer several advantages over the polymer ones, especially with respect to durability, resistance to high temperatures and pressures, easy clean condition, biological stability and chemical inertness [5,6]. The main drawback presented by ceramic membranes is their high cost, due to the used raw materials that are imported and synthetic [7,8]. Compared to traditional methods such as distillation and centrifugation, the use of ceramic membranes in water treatment processes have low power consumption and occupy less physical space [9,10]. Many ceramic materials have been used in the manufacture of membranes, among which stand out alumina, silicon oxide, zirconia, titania, mullite and cordierite [11-13].

The mineral mullite is the only crystalline phase stable intermediate in the binary system Al_2O_3-SiO_2 in the range 70.5 to 74.0% by weight Al_2O_3.SiO_2 at atmospheric pressure. In recent years, mullite has had increasing applications in the field of advanced, structural and functional ceramic, in response to its excellent physical properties such as low thermal expansion (4.5 to 5.6 x 10^{-6} $°C^{-1}$), low thermal conductivity (0.06 $W \cdot cm^{-1} \cdot K^{-1}$), high melting point (> 1800 °C) and low density (3.16 - 3.22 $g \cdot cm^{-3}$)[14].

In this study tubular and microporous ceramic membranes of mullite were characterized and implemented in separation processes in order to retain the bacteria *Escherichia coli*. The control of microorganisms is a major concern in the production of drinking water for human consumption and in the medical field. The World Health Organization (WHO) recommends that all water intended for human consumption should contain zero CFU (Colony Forming Units) of *Escherichia coli* per 100 mL of sample. Numerous chemical and physical processes are proposed such as the use of free chlorine and ozone, ultraviolet radiation and filtration. However, some of these processes can bring about undesired effects to humans. Given this context, there is an alternative PSM, which uses the microporous membrane retaining microorganisms [15-17].

2. Experimental

2.1 Materials

The mullite tubular ceramic membranes (Figure 1) were provided by Tecnicer-Cetebra, São Carlos, São Paulo, Brazil. The sintering temperature was 1150°C. The effective membrane area of 52 cm² corresponds to a length of 210 mm, inner diameter of 8 mm and 2 mm of thickness with an average pore size of 0,39 μm.

The proteins used for microfiltration tests were trypsin, egg albumin and bovine serum albumin, which have molecular weights of 20, 45 and 69 kDa, respectively. The purpose

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of this was to obtain the molecular weight cut-off of the ceramic membranes evaluated. Table 1 shows the physical characteristics of the studied proteins.

2.2 Characterization of the membranes

2.2.1 Morphology and composition of the membranes

The analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of the surface and cross section of the composite membrane were performed using scanning electron microscope (Scanning Electron Microscopy) ZEISS SEM-LEICA/400 coupled to an detector EDS. The membranes were fractured and metallized by sputtering with a thin gold layer prior to their characterization.

2.2.2 Porosimetry by mercury intrusion

The pore size and distribution were determined by mercury intrusion porosimetry. The analysis was performed on a porosimeter brand Quantacrhome, model PM-60-17 at the Institute of Ceramic Materials (ICM) of the University of Caxias do Sul (UCS).

2.2.3 Permeate flux with pure water

All microfiltration tests were performed in a bench system (Figure 1). The system comprises a 3-liter feed tank, a pumping system with a diaphragm pump with three chambers with positive displacement and an engine of Permanent Magnet P/N 11-155-05. The flux rate used was 0.93 L·min $^{-1}$ corresponding to a Reynolds number of 2630.

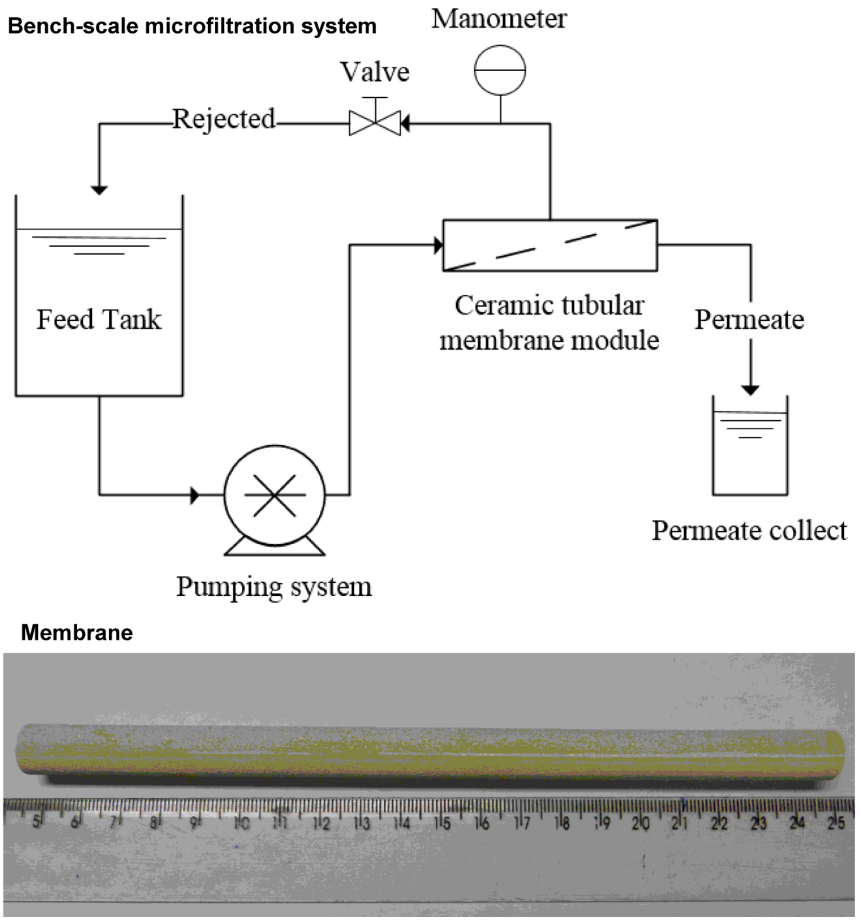

Figure 1. Microfiltration system and mullite ceramic membrane.

Table 1 - Permeate flux presented by membranes for the different proteins used in this study**.** The fluxes were measured at transmembrane pressure of 100 kPa.

Proteins	Molecular weight (kDa)	Average solute radius (nm)	Average flux ($L \cdot m^{-2} \cdot h^{-1}$)
TR	20	2.15	80.2 ± 5.2
EA	45	3.30	34.9 ± 2.1
BSA	69	4.50	28.6 ± 4.3

The tubular ceramic membrane was characterized by distilled water permeation flux behavior at a pressure of 100 kPa, calculated according to Equation 1. The experiment time was 60 min. Protein retention study was performed using protein solutions of different molecular weights, trypsin (TR) (20 kDa), egg albumin (EA) (45 kDa) and bovine serum albumin (BSA) (69 kDa). The protein solutions were individually prepared at a concentration of 100 ppm.

Firstly, tests were performed with distilled water and then with proteins in the following order: TR, EA and BSA. For each test performed was used a new membrane. Experiments were performed in triplicate to the tests with distilled water and protein solutions. At the end of experiments with proteins was performed chemical cleaning of the membranes (sodium hypochlorite 3% (v/v)) and posteriorly were performed tests with distilled water in order to check the recovery of the water flux.

During the tests, the flux rates from single protein solutions were measured at a constant pressure of 100 kPa. Samples of feed and permeate were collected every 20 min for measurements of membrane retention efficiency. Protein concentrations were measured from the absorbance readings at a wavelength of 280 nm using a UV spectrophotometer - Genesys 10UV, Termo Spectronic (UV-Visible). The absorbance was converted to concentration by the use of a standard absorbance curve versus protein concentration. The retention of protein (% R) was calculated by Equation 2.

$$J_w = \frac{V}{A \cdot \Delta t} \quad (1)$$

$$\%R = \left(1 - \frac{C_p}{C_f}\right) x100 \quad (2)$$

where J_w is the water flux ($L \cdot m^{-2} \cdot h^{-1}$), V is the permeated volume (L), A is the permeating area of the membrane (m^2), Δt is the permeation time considered (h), %R is the retention percentage, C_p is the protein concentration in the permeate solution and C_f is the protein concentration in the feed solution.

2.3 Microbiological experiments

2.3.1 Microbiological culture medium

Before starting the crossflow microfiltration experiments to evaluate the retention of ceramic membranes a survey of the growth curve of the bacteria *E. coli* was performed to standardize the bacterial contamination in solution. The growth curve was performed by counting bacteria in Petri dishes and in parallel, for spectrophotometric analysis of the optical density (turbidity analysis) with a reading wavelength of 600 nm. The used *Escherichia coli* suspensions in water have a concentration of ~10^5 CFU·mL^{-1}.

Nutrient Broth (Merck) was used in the preparation of a liquid culture medium for growth of E. coli bacteria at concentration of 8 g·L^{-1}. Cells of *E. coli* bacteria were inoculated in 50 mL of solution containing nutrient broth and incubated at 35°C for 24 h. After, 10 mL this solution spiked with *E. coli* bacteria was added in 1 L of sterile distilled water, providing a quantity of ~ 10^5 CFU·mL. Were necessary dilutions up to 10^{-5} para realizar a contagem das CFU.

2.3.2 Application of ceramic membranes in retaining *Escherichia coli*

The permeability and selectivity of the solution containing the gram-negative bacterium *Escherichia coli* were calculated according to Equations 1 and 2, respectively. The tests were performed under pressures of 50, 100, 150 and 200 kPa. The experiment time was 60 min. Each test was performed in triplicate. For each test in triplicate was used a new membrane. Samples of feed and permeate were collected every 20 min for measurements of membrane retention efficiency. Was performed plating of feed and permeate streams. Then the plates were incubated at 35 ° C for 24 h.

3. Results and discussion

3.1. Characterization of tubular ceramic membranes - pore diameter and morphology

The morphology of tubular ceramic membranes, evaluated by SEM, can be seen in Figure 2. It is observed that the membrane structure is characterized by irregularly distributed pores with a relatively complex shape. This feature is a peculiarity promoted by the process of getting this

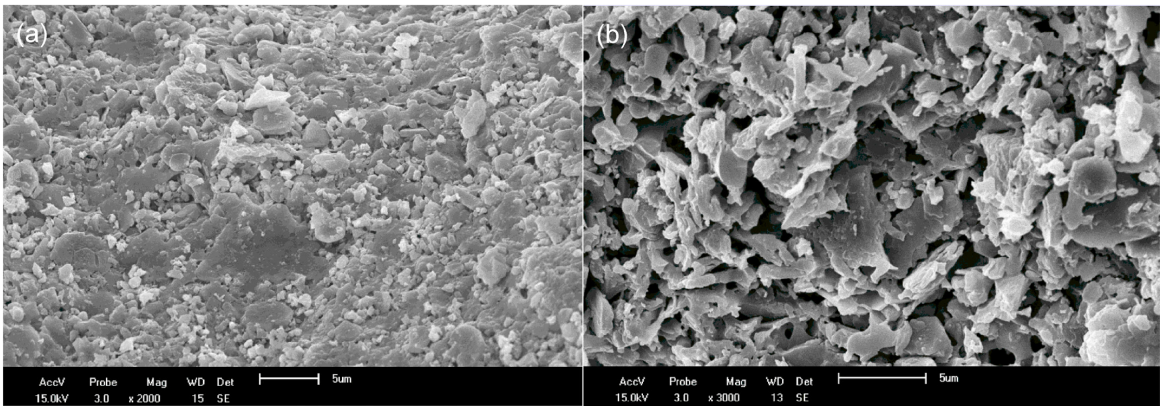

Figure 2. Scanning electron microscopy (SEM) of the tubular ceramic membrane (a) surface and (b) cross section.

material and its own characteristic structural arrangement. This confirms the highly porous structure with a homogeneous pore distribution. The pores are randomly shaped. At the same time, we notice the absence of macro-defects such as cracks. These features are important for the fabrication of quality supports. The surface quality of the support is important for the efficiency of microfiltration [18-20].

Figure 3 shows the result of the composition by energy dispersive spectroscopy of the tubular ceramic membrane. It can be seen peaks relating to aluminium, oxygen and silicon demonstrating that the ceramic membrane tube consists of alumina and silicon oxide. According to the manufacturer, this material has 65% alumina (Al_2O_3) and 35% silica (SiO_2). The presence gold occurred due to coating of a thin layer of the same sample for analysis by SEM.

The pore size distribution for the mullite ceramic membrane can be seen in Figure 4a. This shows the plot of the derivative of the cumulative curves, dV/d, versus the pore diameter of the studied ceramic membrane. The dV/d function is widely used for determination of diameter which occurs in the penetration of the maximal mercury.

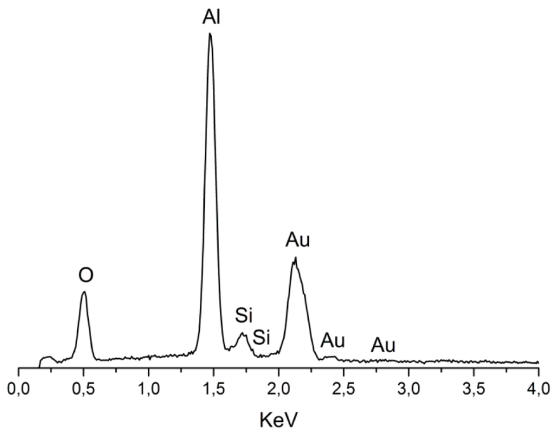

Figure 3. Energy dispersive spectroscopy (EDS) of the tubular ceramic membrane.

Analyzing the profile presented by ceramic membranes illustrated in Figure 4a, there is a predominant presence of pores with diameters of 0.13 to 2.21 μm, indicated by the appearance of a broad peak in this pore diameter range. The quantification of the distribution of pore size can be obtained from the volume distribution as a function of the diameter, Dv (d), which presents the change in the volume of mercury intruded per interval unit of the pore diameter.

Figure 4b shows the mercury intrusion curve as a function of pore size for mullite ceramic membrane. Initially there was a intense increase in the mercury intrusion volume, and subsequently a constant region of intrusion. According Lowell and Shields, this behavior is characteristic of powder samples and depends on the size, shape and geometry of the particle packing[21]. The initial intrusion observed in the samples studied occurred at very low pressures, due to the penetration of mercury in interparticle spaces of the sample. This behavior is characteristic of powder samples and depends on the size, shape and geometry of the particle packing [22]. Thus, the interparticle voids of various dimensions will be filled progressively with increasing pressure. The average volume of mercury intruded in mullite ceramic membranes was 0.08 $cm^3 \cdot g^1$.

The cumulative specific surface area of the studied ceramic membranes, calculated from the porosimetry data, was 0.215 $m^2 \cdot g^{-1}$. This value is considered to be relatively low when compared to the specific surface area of some inorganic materials such as catalysts [22,23]. However, this value has the same order of magnitude as those found for other ceramic membranes of the same pore size measured by mercury porosimetry [22]. The low surface area values found for the ceramic membranes can be attributed to the predominance of macropores ($\phi > 50$ nm), since small pores are responsible for high specific surface area values[21]. The contribution of large pores (macropores) is not very significant in determining the specific surface area.

Figure 5 shows the permeate flux results for the mullite tubular ceramic membrane. The tests were conducted with distilled water and protein solutions.

Ceramic membranes averaging initial permeate flux of $1.9x10^2$ $L \cdot m^{-2} \cdot h^{-1}$ to microfiltration distilled water in a time of 60 min. It can be seen that the molecular weight

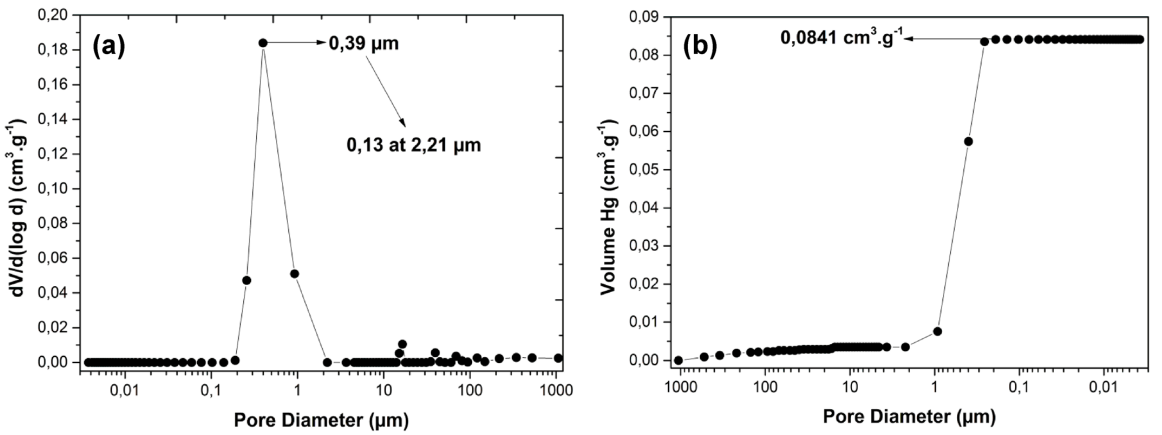

Figure 4. Pore size distribution by mercury intrusion porosimetry of tubular ceramic membrane of mullite.

of proteins directly influence the permeate flux. As can be seen in Table 1, the molecular weight and the average radius size of the proteins influence on permeated flux of the membrane. The decrease in permeate flux occurred with increasing molecular weight and the molecular radius of the proteins studied. The decrease in average flux observed with the filtration of a protein solution with a higher weight can be interpreted based on total blockage of some pores or due to an increase of a molecular layer of adsorbed protein on the inner surface of pores of membranes.

Figure 6 shows the result of protein retention for the ceramic membrane. A decline of the permeate flux occurred with the increase in molecular weight and thus an increase in the efficiency of membrane separation of solute (protein) of distilled water. The ceramic membrane showed retention of 46, 76 and 89% for TR, EA and BSA, respectively. This result leads us to make a reference to the adequate treatment of wastewaters with contaminant of molecular weight above 69 kDa by microfiltration with this ceramic membrane. As shown in Figure 6, it shows high retention capacity.

3.2. Application of ceramic membranes in the retention of the E. coli bacteria

Figure 7 shows the permeate flux results for the mullite ceramic membrane with distilled water containing *E. coli* and sterile distilled water. Firstly, were performed tests with sterile distilled water, followed of tests with distilled water containing *E. coli* bacteria and after sterilization and chemical cleaning of the membrane were performed tests with sterile distilled water again. The increased pressure directly influenced the increase of permeate flux, however one can observe the presence of the microorganism reduces the permeate flux [14]. After chemical cleaning with sodium hypochlorite solution (3% v/v) 89% of the initial flux was recovered in the permeate stream.

Figure 8 shows the retention results of the filtration of *E. coli* suspensions at different transmembrane pressures, from experiments reported in Figure 7. With increasing pressure there was a decrease in retention, yet the *E. coli* retention efficiency of the membrane at different pressures was low (66% under 200 kPa and 98% under 50 kPa), demonstrating the membrane mullite proposal can be an interesting alternative to be used in bacteria-retaining processes, however the presence of bacteria demonstrates a need for improvement in the proposed material.

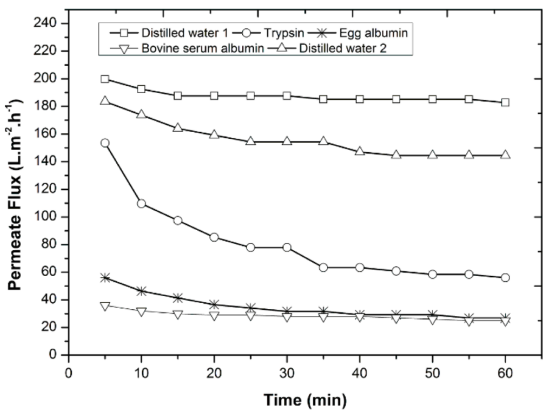

Figure 5. Permeate flux to distilled water and different proteins.

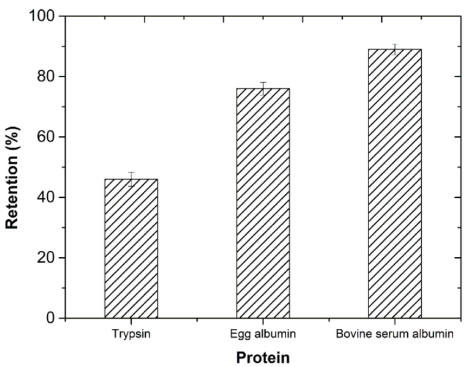

Figure 6. Retention of ceramic tubular membranes for different proteins.

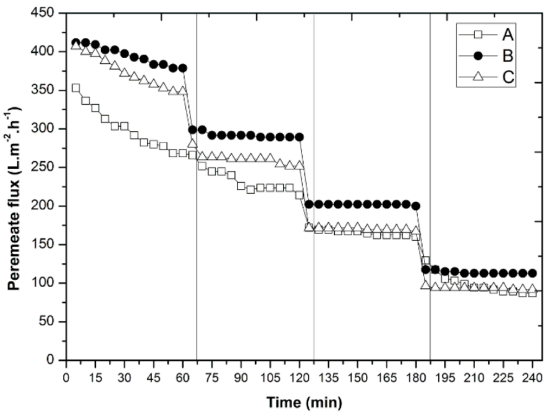

Figure 7. Permeate flux to the mullite tubular membrane tested at different pressures. Where A is distilled water containing *Escherichia coli*, B the initial test with distilled water and C the test with distilled water after the test A after membrane cleaning with sodium hypochlorite 3% (v/v).

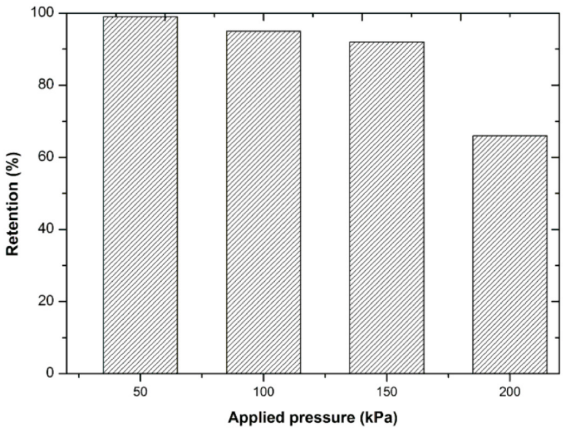

Figure 8. Retention of *Escherichia coli* bacteria at different pressures applied to the mullite tubular ceramic membrane (alumina and silica).

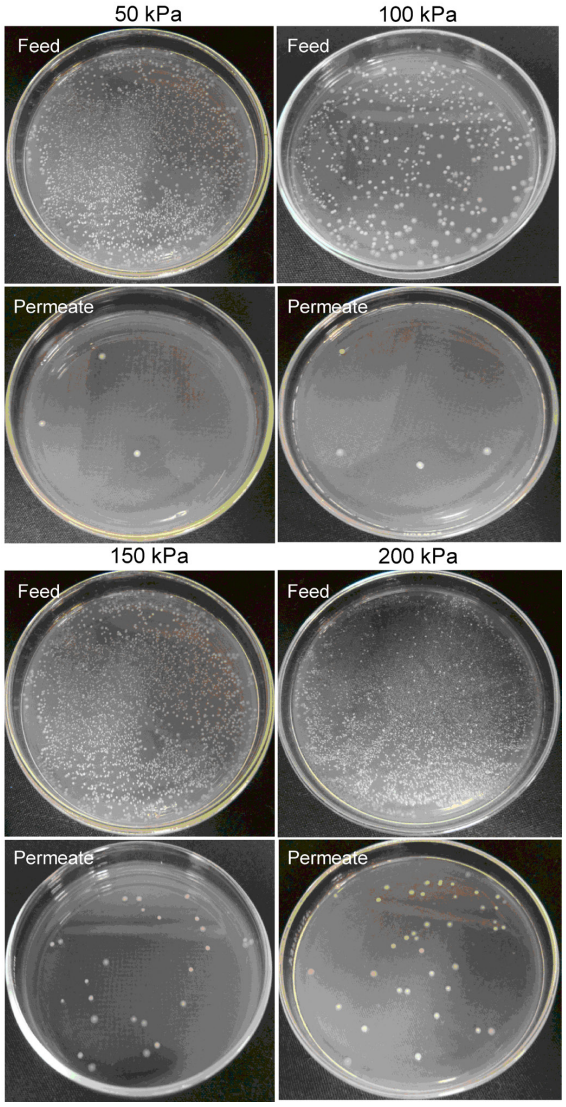

Figure 9. Images of Petri plates inoculated with feeds and permeates from experiments reported in Figure 7 after incubation.

Figure 9 shows the images of *E. coli* colonies incubated in Petri plates that had been inoculated with the permeated and feed streams from filtration experiments reported in Figure 7. The significant retention of bacteria could be seen. However, the results obtained show that the rejection of *E. coli* by membrane is insufficient, since water for human consumption must be free of microorganisms. By obtaining a log reduction of less than 2 the membrane proves to be ineffective for bacteria control. These results were expected by the previous pore size distribution characterization that showed the existence of a large fraction of membrane pores above 0.45 μm.

4. Conclusions

The characterization of ceramic membranes showed a free material cracks, however with pores distributed unevenly. The flux rate with distilled water resulted in an average of $1.9x10^2$ $L{\cdot}m^{-2}{\cdot}h^{-1}$ and retention of the protein was 46, 76 and 89% for trypsin, egg albumin and bovine serum albumin, respectively. The SEM showed an irregular structure and pore malformed. Despite this characteristic, it was demonstrated that the ceramic membrane is highly selective and can be used in microfiltration process using solutes with molecular weight above 69 kDa.

The permeation tests of *E. coli* solution with the ceramic membrane showed fluxes around 400 $L{\cdot}m^{-2}{\cdot}h^{-1}$ at 200 kPa transmembrane pressure (TMP). At this TMP a decrease over time occurred while for lower TMPs (150, 100 and 50 kPa) no or a minor flux decrease was observed. By cleaning the membrane with sodium hypochlorite it was possible to recover 89% of the permeate flux. The retention of *Escherichia coli* ranged from 66% to 99% for different pressures and as the pressure was increased was decreased retaining the microorganism. Therefore, the use of mullite in bacteria-retaining membrane processes evaluated in this study showed an efficiency poor, but transmembrane flux comparable to other materials proposed in the literature.

Acknowledgments

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