Characterization and application of ceramic membranes prepared from Algerian kaolin

(Caracterização e aplicação de membranas cerâmicas preparadas a partir de caulim argelino)

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Abstract

In this study, a new ceramic membrane type was used for the filtration of colored water. The membrane was prepared from local Algerian kaolin KT2 of Milia-type. The choice of this raw material was dictated by its natural abundance, to form the macroporous support prepared by the slip casting technique. A functional thin film layer (with a pore size of about 0.2 μm) produced by the sol-gel method was deposited on the support to reduce the porosity. A detailed study was conducted because of the importance of this layer and the improvement which brought to the filtration process. Ceramic membranes were tested for the removal of bromophenol red (BR) under a filtration pressure of 3 bar and a duration of 2 h of treatment. The results revealed a rejection rate of 100% for BR, especially after the addition of the inorganic layer. The material was characterized by DTA, TGA, XRD and SEM. The retention and the permeability of BR were also studied.

Keywords: ceramic membrane, bromophenol red, filtration, sol-gel, kaolin, KT2.

Resumo

Neste estudo, um novo tipo de membrana cerâmica foi usado para a filtração de água com cor. A membrana foi preparada a partir de caulim argelino KT2 do tipo Milia. A escolha desta matéria-prima foi ditada pela sua abundância natural, para formar o suporte macroporoso preparado pela técnica de colagem. Uma camada de película fina funcional (com tamanho de poro de cerca de 0,2 μm) produzida pelo método sol-gel foi depositada no suporte para reduzir a porosidade. Um estudo detalhado foi conduzido por causa da importância desta camada e da melhoria que trouxe para o processo de filtração. As membranas cerâmicas foram testadas para a remoção do vermelho de bromofenol (BR) sob pressão de filtração de 3 bar e duração de 2 h de tratamento. Os resultados revelaram uma taxa de rejeição de 100% para o BR, especialmente após a adição da camada inorgânica. O material foi caracterizado por ATD, ATG, DRX e MEV. A retenção e a permeabilidade do BR também foram estudadas.

***Palavras-chave**: membrana cerâmica, vermelho de bromofenol, filtração, sol-gel, caulim, KT2.*

INTRODUCTION

Membrane filtration is increasingly used as a method of separation in many areas. It is based on the application of a pressure difference allowing the transfer of the solvent through a membrane whose pore size ensures the retention of solutes. Recently, ceramic membranes have been used intensively because of their interesting advantages [1]. In general, these membranes are made from expensive metal oxides such as alumina, silica, zircon and titanium [2-6]. The cost of all these materials is high resulting in an increase in the final cost of the prepared membrane. Therefore, the use of less expensive and naturally available materials such as dolomite, kaolin and natural clay [7-9] would be of great interest. Membranes synthesized using the above-mentioned materials sometimes require the addition of certain substances to the raw mixture, such as feldspar, quartz, calcium carbonate, etc., to improve the properties of the inorganic membrane which also increases the cost of the membrane [10]. Nowadays, and under the combined effect of industrial competition and new constraints related to the protection of the environment, the research is based on the development of new low-cost membrane supports, composed mainly of mineral-based raw materials [11-14]. These inorganic membranes are distinguished by their excellent thermal, chemical and mechanical resistance [15-22], long service life and ease of cleaning [23, 24].

In this study, the raw materials usually used were replaced by a natural raw material locally produced, Milia kaolin KT2, a pure product, without any additive added to the raw mixture, in order to reduce the manufacturing costs

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of membrane supports. An inorganic layer was deposited on the membrane supports in order to decrease the pore size. Sol-gel technology is now widely used for shaping ceramics. A metal alkoxide is hydrolyzed and polymerized (polycondensation). The general formula of a metal alkoxide is M(OR)z where M is a metal of valence z. These reactions depend on many parameters such as the temperature and the concentration of the different constituents separately. The gel used was synthesized by the sol-gel technique inspired by the Pechini method. The materials used in this method differ from the commonly used materials (alkoxides) which are too expensive products. The products used were aluminum chlorides and magnesium salts. This can also be contributed to the reduction of the cost. The embedding method for the deposition of the thin layer was used. The main objective of our work was to manufacture macroporous ceramics with high permeability. The membrane supports thus obtained are intended to be used in microfiltration (MF) or ultrafiltration (UF). They allow providing a mechanical strength high enough to withstand the pressure applied to the membrane which varies between 1 to 5 bar. The membrane supports were sintered following a thermal program ranging from 200 to 1200 °C. The parameters porosity, retention rate and flow variation were studied. The average pore size obtained on the tubular membrane supports was about 2 μm, while the pore volume was 38.2%.

MATERIALS AND METHODS

Analysis of raw material: Table I shows the chemical composition of clay using X-ray fluorescence (XRF) analysis. In this study the clay used (kaolin KT2) is intended for the manufacture of ceramics; its composition showed that it consisted essentially of silica (67.9%) and alumina (18.6%). This clay contained significant levels of Fe_2O_3 and K_2O. In addition, other constituents were present in trace amounts.

Elaboration of membrane supports: the membrane supports were prepared from a natural product kaolin KT2 of Milia. The raw product was put in a sprayer type centrifugal mill Pulverisette 14 Classic Line to reduce granulometry. At the end of the operation, the resulted product was in the form of fine powder with a size of about 1 μm. The process of developing the supports essentially comprised the following steps: i) preparation of the suspension from well-milled kaolin mixed with a liquid, i.e. distilled water; the optimal viscosity value was 1.66 cP, which corresponded to the proportions of 300 mL of distilled water for 200 g of kaolin; ii) addition of two drops of sodium silicates used as a deflocculant for the homogenization of the suspension, by the formation of a double electric layer around each particle; iii) the mixture was stirred for a few minutes until a homogeneous suspension was obtained; and iv) the suspension obtained was poured in porous plaster molds which absorbed by capillarity most of the liquid causing the solidification of the paste. *Thickness of the elaborate supports*: the supports thus shaped to different thicknesses (t= 1, 1.5, 2 and 3 min) rested for consolidation and hardening. The synthesized supports were placed on thin surfaces to prevent their deformations and 3 days in open air were sufficient for drying. *Drying*: the drying of the membrane supports led to the consolidation of the green part by eliminating the water introduced during mixing. This drying was accompanied by a first shrinkage [25]. Too fast drying dries the outside of the supports while the inside remains wet because the water has not time to move to the surface. The stresses due to drying shrinkage are therefore inhomogeneous and cause cracks in the structure of the material [26]. The drying rate must not exceed the water migration rate in the material. For this reason, it is essential to control the humidity of the atmosphere during drying. It should be noted that the drying stages are important because it is usually during drying that microcracks occur and decrease the strength of ceramic. After drying, the supports were sintered at 1200 °C.

Sol-gel method: the method followed for the synthesis of the gel was inspired by Pechini's method [27]. It was very simple method for preparing metal oxide powders where polymeric precursors were replaced by metal salts, $MgCl_2.6H_2O$ and $Al(Cl_3)_3.9H_2O$, diethylene glycol and nitric acid. Firstly, a solution was prepared with the metal salts; this solution was stirred at 80 °C; after 2 h an amount of 1 M nitric acid was added to the mixture; then, 10 mL of H_2O was added to promote rapid hydrolysis and produced the metal hydroxide solution; the mixture was submitted always at a high agitation at the same temperature until a homogeneous mixture was formed; after 2 h, 20 mL of diethylene glycol was added to the mixture. This mixture was kept for 3 days with stirring at 80 °C to gel formation. In this process, the molar rate was taken equal to two between the acid and the metal ions. This method allows the metal cations to be mixed at a molecular level and the stoichiometric compositions to be achieved by chelating the metal ions in solution by nitric acid [28-30]. Furthermore, this process offers several advantages in fabrication of ceramic thin films, including low-cost, homogeneous compositions, high purity, and low heat-treatment temperatures [31]. The gel was then deposited on the support using the slip casting method and the double-layer membranes were sintered at 1200 °C.

Table I - Chemical composition of the kaolin clay KT2 of Milia expressed as wt% of equivalent oxides.
[Tabela I - Composição química do caulim KT2 de Milia expressa em % em massa de óxidos equivalentes.]

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	Others	LOI
67.9	18.6	0.88	0.31	2.03	0.39	0.07	0.22	3.92	5.68

LOI - loss on ignition.

Characterizations of materials: the analyzes of crystalline phases were carried out using a diffractometer (PANalytical, X'Pert Pro SW) with copper anticathode (λ=1.5418 Å) and a nickel filter, working voltage of 45 kV and working current of 40 mA, between $2\theta=5°$ up to $2\theta=70°$, with a step of 0.02°; the integration time was 1 s for each step. The thermal stability of the samples was determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a Netzsch STA 449 F3 Jupiter under nitrogen atmosphere at a heating rate of 15 °C/min in the range of 25-1000 °C. The microstructure of sample surfaces was observed by a scanning electron microscope (SEM, Tescan, Mira 3) working at 5 kV as accelerating voltage.

Dye filtration tests: the membrane supports were implemented on a filtration pilot (Fig. 1). The treated solution passed through the membrane support at a pressure of 3 bar using a discharge pump. The permeate was collected at intervals of time for a period of 2 h (time of each operation). The recovered samples were subjected to investigation analyzes. The sintered supports were weighed after immersion in boiling water for 2 h. The absorption rate (A) was determined using the following formula:

$$A(\%) = [(P_h - P_s)/P_h].100 \qquad (A)$$

where P_h is the weight of wet support (after boiling) and P_s is the weight of the dry support. The flow through the membrane was measured as a function of time at the transmembrane pressure value of 3 bar. The permeability characterizes the quantity of water per time and a unit area which crosses the membrane at a given pressure and temperature. A volume measurement was taken with corresponding time. The colored feed solution was prepared with bromophenol red (BR) of analytical grade (BR was a colorful indicator with MW of 512.18 g/mol and formula $C_{19}H_{12}Br_2O_5S$). The retention rate, $R=(1-C_p)/C_o$ where C_o is the initial concentration of the solution and C_p the concentration in the filtrate, of the colored solution was measured in a single-beam UV-visible Easyspec spectrophotometer. The measuring wavelength was λ=575 nm [32, 33].

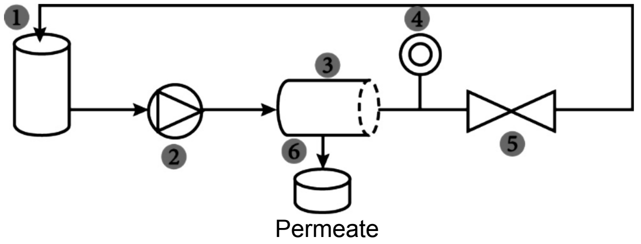

Figure 1: Schematic process used for the filtration system: 1) feed tray; 2) suction and discharge pump; 3) membrane support; 4) manometer; 5) valve to adjust the pressure; and 6) permeate.
[Figura 1: Esquema do sistema de filtragem: 1) bandeja de alimentação; 2) bomba de sucção e descarga; 3) suporte de membrana; 4) manômetro; 5) válvula para ajuste de pressão; e 6) permeado.]

RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction (XRD) pattern of KT2. The analysis of the powder showed the main crystalline phases present in kaolin KT2 and confirmed that its structure was essentially formed by a mixture of two crystalline phases identified as kaolinite and quartz. These crystalline phases were expected in such a type of kaolin [34, 35]. The quantity of other crystalline phases (estimated from the height of the peaks) was in trace amounts, as in the case of free muscovite, which has also been detected [35]. The normative calculation of the mineral compositions of kaolin KT2 gave a percentage of 16% for muscovite, 56% for kaolinite and 23% for quartz. The remaining 5% was attributed to the impurity [36].

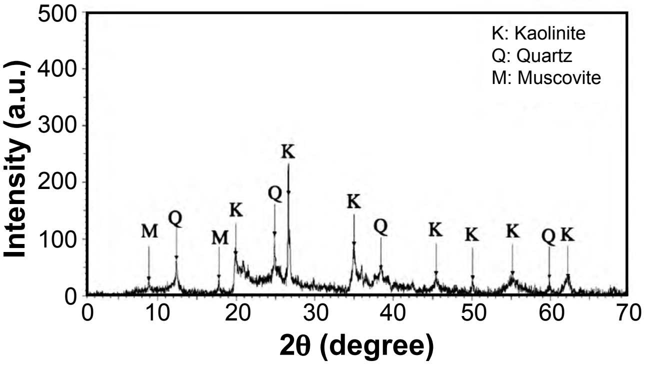

Figure 2: X-ray diffractogram of raw powder kaolin KT2 before sintering.
[Figura 2: Difratograma de raios X da matéria-prima caulim KT2 antes da sinterização.]

The raw material kaolin KT2 undergoes structural evolution and weight loss during its heating; for this reason, the thermogravimetric analysis has been proved useful before any other characterization techniques. The variation of mass informs about possible transformations undergone by the material; for example, a mass loss (decomposition, phase transformation) or a mass gain [37]. The thermogravimetric analysis of KT2 membrane showed that the total weight loss was about 16%. In fact this weight loss consisted of two distinct stages. The first one was attributed to the humidity

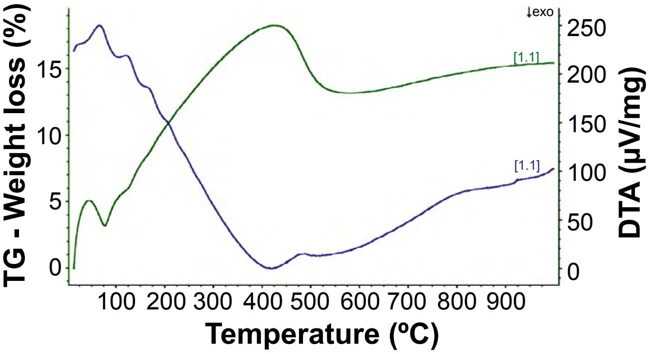

Figure 3: TGA/DTA curves of membrane before sintering.
[Figura 3: Curvas de ATG/ATD da membrana antes da sinterização.]

(water added into the starting mixtures) whereas the second was related to the kaolin chemical composition water loss (by vaporization) itself and from 573 °C there was an increase in the weight of the material due mainly to the formation of mullite and spinel phase and the densification of the material arising from the allotropic transformation of silica quartz from α to β phase. These observations were also confirmed by DTA analysis (Fig. 3). This later exhibits characteristic endothermic peaks, appearing at 85 and 474 °C due to combustion and decomposition of the material [34, 38].

Thermal treatment: the transformations during the sintering treatment have a direct influence on the development of the formed phases [39-42] as well as on the liquid phase [39, 43, 44] likely to form at high temperatures, which is the origin of the recrystallization and secondary mullite formation. The sintering of membrane supports allows the final consolidation of the shaped part after removal by evaporation or carbonization of temporary additions and gives the ceramic supports their definitive dimensions. The results obtained (Fig. 4) showed that there was a good porosity formed at the sintering temperature [45]. The beginning of the densification of the material occurred when the temperature increased [46-49]. The maximum temperature of the heat treatment influences the porosity of the membrane supports. Indeed, from the moment the part of the kaolin begins to melt, the consolidation intervenes and increases with the temperature. A rise of 5 °C/min in temperature up to 200 °C with a 2 h stage caused the complete elimination of the water which was not eliminated during the drying as well as the water possibly absorbed after drying. Between 400-700 °C, the complete elimination of organics occurred. An increase in the temperature until 573 °C corresponded to the transformation of quartz from the α form to the β form. The last increase of the temperature up to 1200 °C, with a holding time of 5 h, the formation of γ-alumina and mullite occurred. Finally, slow cooling of the oven made it possible to avoid any risk of cracking of the elaborated membrane supports [50].

Morphological investigation: to follow the microstructural changes of the ceramic supports obtained after sintering, the micrographs are illustrated in Figs. 4 and 5. It was clearly observed that the morphology of surface and cross-section of sintered samples was similar and both had pores of various shapes. The presence of clear macropores in SEM images of sectional and tubular support profile with similar morphology was already observed in membranes made from kaolin alone [51]. SEM images of the surface and the cross-section showed the absence of macro-defects such as cracks. The material's densification corresponded to an increase in the strength and a decrease of the porosity (2 μm) with respect to the green material. This phenomenon was mainly due to the formation of a vitreous phase formed by the free silica and the melting impurities contained in the clay [52]. During the sintering of the ceramic supports, most of the constituents remained in the solid-state and the densification then resulted from the welding and the change of the shape of the grains. When it happens during solid-phase sintering, densification occurs in three steps: formation of bridges between grains, removal of open porosity and removal of closed porosity until the end of sintering; this last step is the most difficult [53].

Phase identification is of great importance before any membrane manufacturing. Before applying heat treatment,

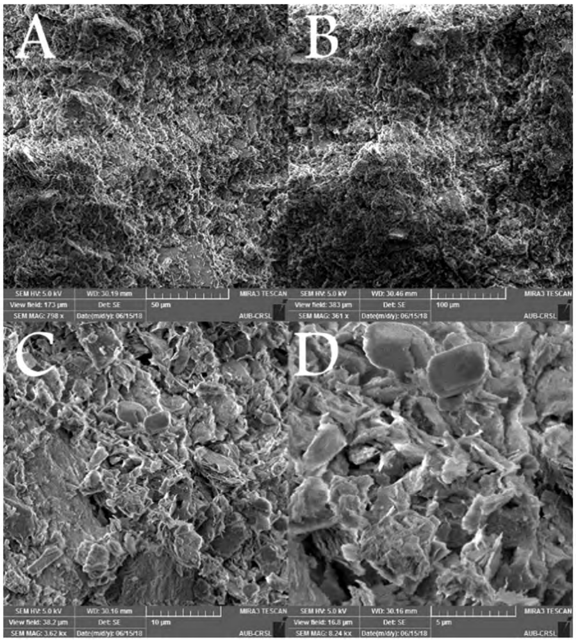

Figure 4: SEM micrographs of the surface (top view) of the sintered membrane.

[Figura 4: Micrografias de MEV da superfície (vista de topo) da membrana sinterizada.]

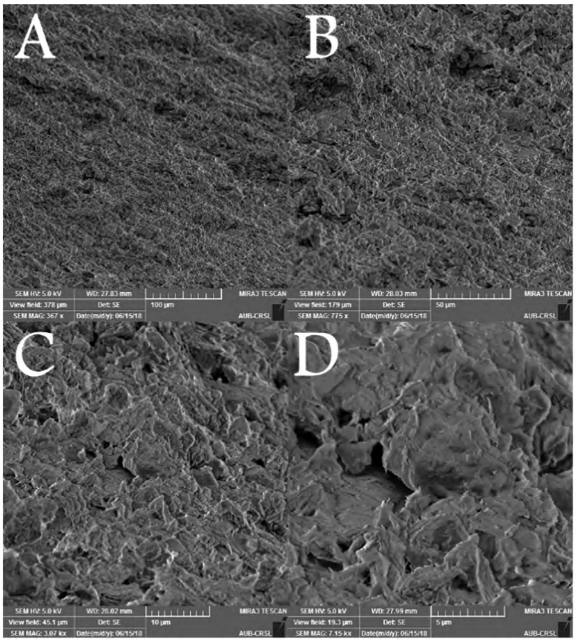

Figure 5: SEM micrographs of the cross-section of the sintered membrane.

[Figura 5: Micrografias de MEV da seção transversal da membrana sinterizada.]

it was seen that kaolinite was the major mineral component. After sintering at 1200 °C, peaks of mullite appeared due to the transformation of metakaolinite. The main phases detected in the membrane support sintered at 1200 °C [54] were mullite and spinel phases as illustrated in Fig. 6.

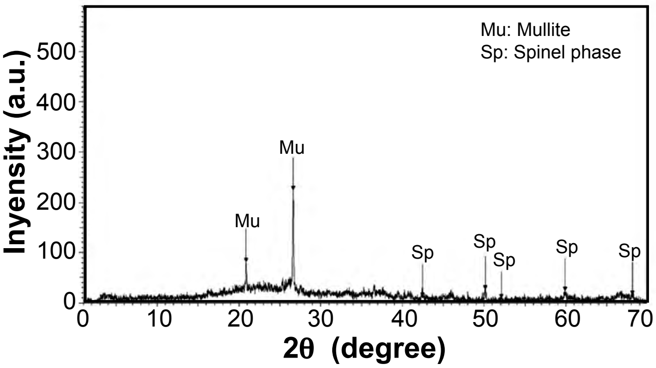

Figure 6: X-ray diffractogram of kaolin KT2 after sintering.
[Figura 6: Difratograma de raios X do caulim KT2 após sinterização.]

Absorption rate of prepared membrane supports: porosity is measured by the ratio of pore volume to total apparent volume. It is the property of a body, of a medium, to have voids interconnected or not, expressed quantitatively by the ratio of the volume of these voids to the total volume of the medium. Porosity is defined both as a characteristic property of a porous medium and as a parameter that expresses it quantitatively (volume ratio, dimensionless). It was deduced from the results that the most important absorption rate was obtained for the membrane support having a thickness of 2.8 mm and corresponding to a slip with a viscosity of 1.66 cP (this value corresponded to 300 mL of distilled water for 200 g of KT2 kaolin) for a casting time of 2 min. The results of absorption rates are shown graphically in Fig. 7.

The SEM images in Figs. 8 and 9 show the surface and the cross-section of the double-layer tubular membrane, respectively. It can be observed the second layer deposited from the sol-gel method. The suspension was deposited on the support using the slip casting method. It was observed a uniform thickness with reduction of porosity which reached 0.2 μm and presented a good adhesion with the ceramic membrane; its surface was homogeneous and without any defects and microcracks and present good consolidation

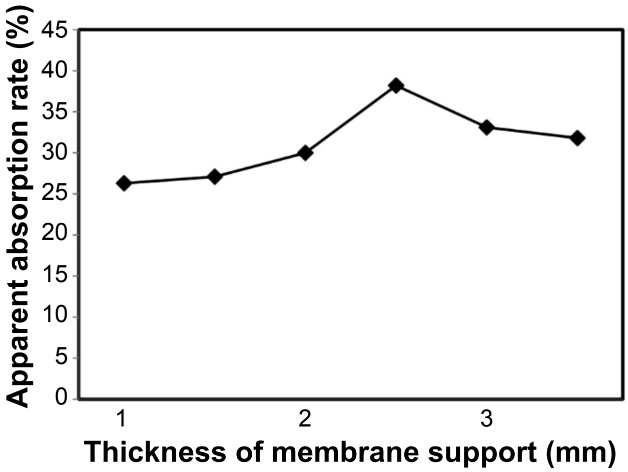

Figure 7: Absorption rate as a function of the thickness of the membrane support.
[Figura 7: Taxa de absorção em função da espessura do suporte da membrana.]

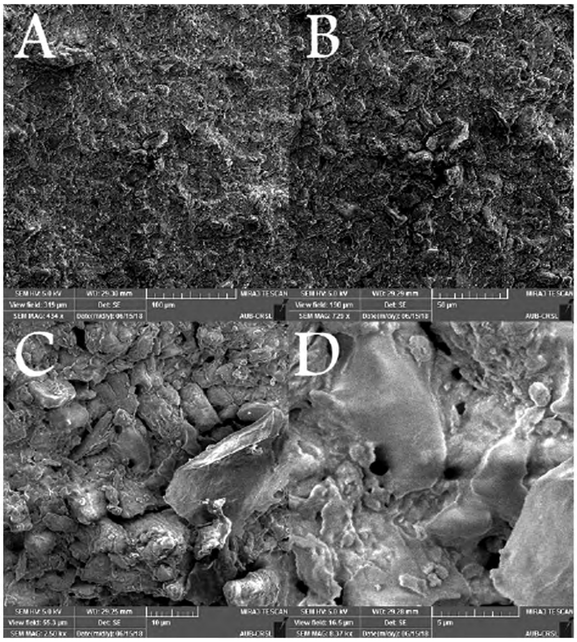

Figure 8: SEM micrographs of the surface of the double-layer sintered membrane.
[Figura 8: Micrografias de MEV da superfície da membrana sinterizada com dupla camada.]

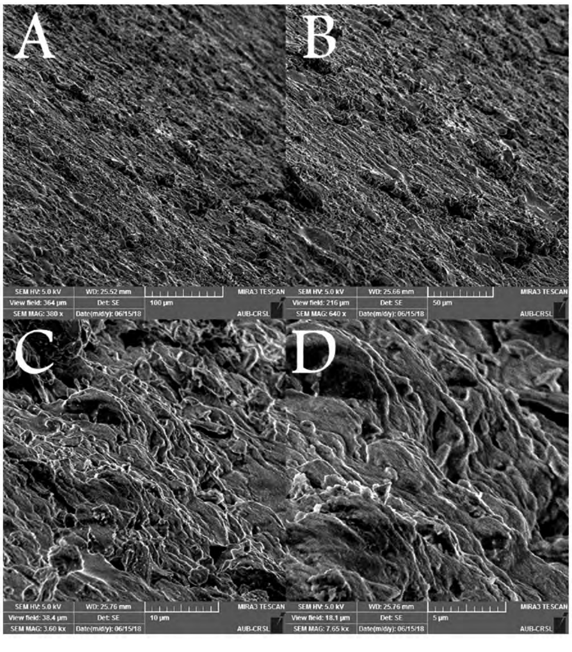

Figure 9: SEM micrographs of the cross-section of the double-layer sintered membrane.
[Figura 9: Micrografias de MEV da seção transversal da membrana sinterizada com dupla camada.]

between particles. Its top surface was characterized by a rough morphological structure. The sintering at 1200 °C generated partial vitrification of the tubular membrane and therefore decreasing the pore volume [55].

Variation of the dye's flow: the result of the flow variation of the dye through the membrane support is shown in Fig. 10a. The decrease in flux observed for BR which reduced the value of 438.9 to 332 L/(h.m^2) confirmed its retention. The permeation flow tended to become weak over time. As the cake layer was formed on the surface of the support, initially it caused low resistance to permeation. At the end of the cycle, the layer of the cake on the surface of the support became thick and resulted in high resistance to permeation. This decrease was associated, in part, with the interactions which can take place between the supports and the solution and in particular with the reduction of the cross-section during the tangential flow.

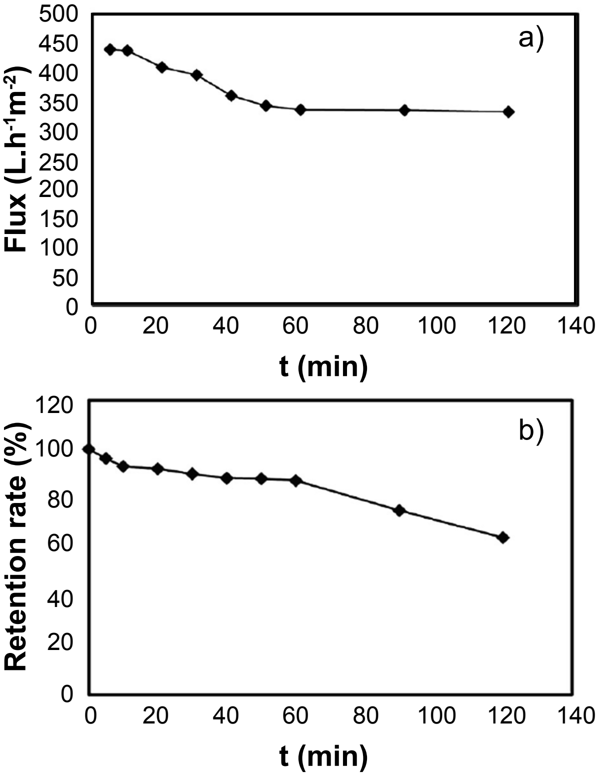

Figure 10: Dye (BR solution) flux through the membrane (a) and retention rate of BR (b) as a function of time.

[Figura 10: Fluxo de corante (solução de BR) através da membrana (a) e taxa de retenção de BR (b) em função do tempo.]

The retention of organic materials on the porous support is conditioned by its own composition, water chemistry and material characteristics. The reaction mechanisms are essentially electrostatic forces. Moreover, the electronic charges carried by the organic materials induce attraction forces with the material if it is charged with the opposite sign, or repulsion forces if the charges are of the same sign. The retention of organic molecules by membranes depends on the molecular size, but also on the charge interactions between membrane and solution. Depending on the nature of the membrane, a higher or lower retention rate can be obtained than expected on the basis of molecular weight or any other size parameter [56]. In our case, the bromophenol red is a neutral dye. A higher retention rate was obtained than expected on the basis of molecular weight and pore size of the surface filtration. The high retention rate during the first minutes was the retention of the membrane support and the molecular weight of the solute. After 1 h the rupture beginning of the membrane support was observed. The results of the change in the retention rate of BR were found to be 92% during the first 20 min. The decrease of this retention rate can also be explained by the fouling of the filtering surface (Fig. 10b). On the other hand, this phenomenon can be attributed to the fact that the dye deposition on membrane surface increased with operating time. The cake formed by the rejected dyes on the membrane surface may operate as additional resistance to the passage of permeate [16, 57].

Variation of dye flow using sintered membrane double-layer support: the results showed that filtration with the modified membrane support had higher retention of BR in comparison with the support alone. This improvement was due mainly to the reduction in the size of the pore diameter and the molecular weight of the solute. 100% removal was observed during the first 40 min of filtration followed by a gradual decrease of up to 98% (Fig. 11b). Another phenomenon can be attributed to the fact that the accumulation of dye on the surface of the membrane

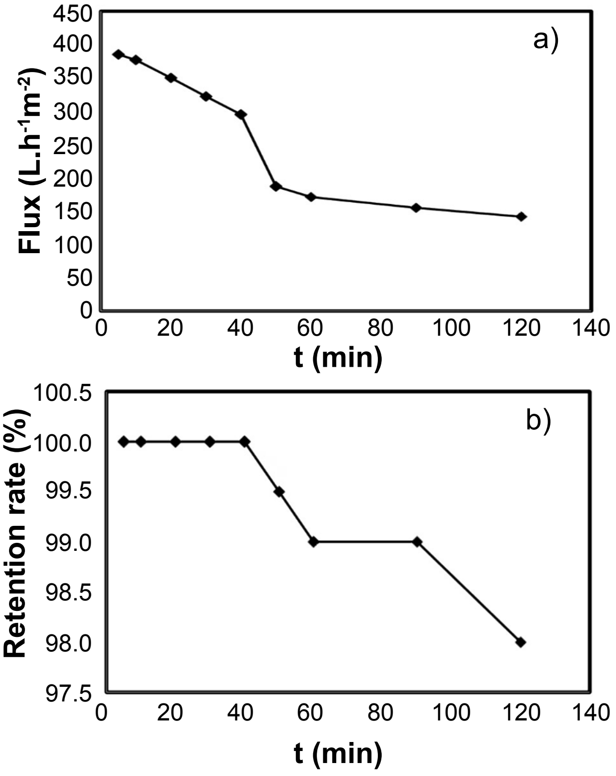

Figure 11: Flux (a) and retention rate (b) of BR as a function of time for the modified support (double-layer).

[Figura 11: Fluxo (b) e taxa de retenção (b) de BR em função do tempo para o suporte modificado (dupla camada).]

increased with the time of operation. This layer formed by the deposition of the dye on the surface of the membrane may constitute an additional resistance to the passage of the dye. We observed a total obstruction of the filtering surface of the double-layer membrane support. A decrease in permeate flux was observed as the filtration time increased (Fig. 11a).

The thin layer prepared by the sol-gel process and added to the filter surface of the support, therefore, reduced the pore size as the deposited film became denser when sintered. There was a decrease in flux as a function of time through the modified medium. This was attributed to the formation of the polarizing layer on the filter surface of the support, contributing to the decrease of the flux and the formation of the cake on the filtering surface of the support (Fig. 12). Conductivity and pH measurements were made on the recovered permeate. The results obtained showed that its characteristics were almost identical to those of distilled water.

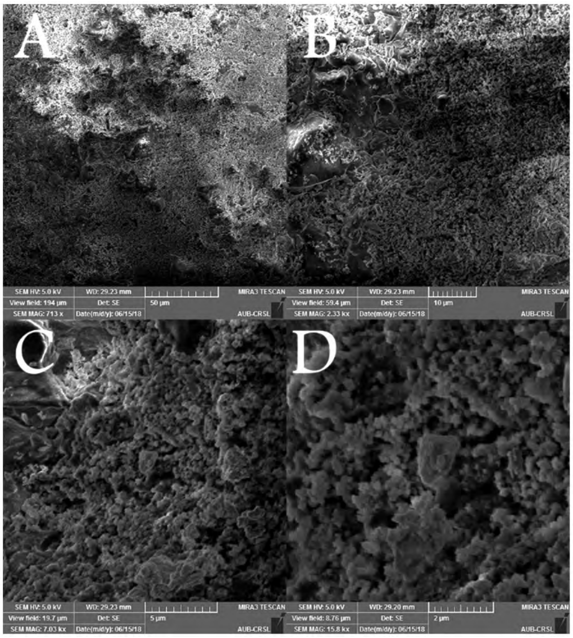

Figure 12: SEM micrographs of the double-layer sintered membrane obstructed with BR.
[Figura 12: Micrografias de MEV da membrana sinterizada com dupla camada obstruída com BR.]

CONCLUSIONS

The purpose of this study was to develop a membrane separation process to treat liquid effluents. Tubular double-layer membranes based on kaolin were prepared. It consisted of alternative support and an intermediate layer. The ceramic supports were prepared by the slip casting method. Prepared substrates sintered at 1200 °C provided good mechanical strength, good porosity (38.2%), average pore size (0.2 µm) after the addition of the double-layer by sol-gel method and good permeability. It was concluded that the prepared membranes were favorable supports for the deposition of a double-layer. The double-layer added to the support significantly improved the retention results. The intermediate layer also had the role of reducing the defects of the support. We were interested in the treatment of bromophenol red (BR) studying its retention. Experimental results showed that the use of ceramic membrane supports, based on KT2 kaolin as membrane for tangential filtration, is encouraging. From the point of view of texture, the results obtained by scanning electron microscopy were promising and suggested the use of this material as a filter element. The new method used for the synthesis of the gel for the preparation of the double-layer improved the use of the membrane support. We observed that the concentration of 10^{-4} M BR reached 100% removal during the first 40 min. This high retention with a high permeability flow which varied between 438.9 and 332 L/(h.m^2) was suitable for the use of these membrane supports for the treatment of dyes and tangential filtration. The water returned by the filtration system was in compliance with the standards governing the discharge of wastewater into the wild. The idea of sol-gel inspired by the Pechini's method used for the first time in gel synthesis is only a beginning in the synthesis of a multitude of gel in this field.

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