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Production and application of porous membrane for removal of contaminants in treated water

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ABSTRACT. Due to several factors caused by urban and industrial growth worldwide, water supply problems have become increasingly complex, with difficult and costly solutions. The use of membrane filters is one of the newest unit operation options being incorporated into the water and sewage treatment process. This work involves the study of the production of a polymeric asymmetric porous membrane to be used in the removal of possible abiotic or biological contaminants remaining after the post-treatment of drinking water, as well as the assessment of the membrane life span. The phase inversion process was used to produce the membrane, using a polymer solution consisting of polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA), and NN-Dimethylformamide as a solvent. KCl salts were incorporated as additive, and a polyester polypropylene sheet was used as support. The membrane was tested in a transverse flow module. The tests demonstrated that the membrane presented an effective barrier to abiotic contaminants, with an average flux of 342 kg h^{-1} m^{-2} and life span of 48h, as well as to biologic contaminants such as *Escherichia coli*.

Keywords: membrane production, water, contaminants.

Produção e aplicação de membrana porosa para a remoção de contaminantes presentes em água tratada

RESUMO. Em função de vários fatores ocasionados pelo crescimento urbano e industrial mundial, problemas cada vez mais complexos e de solução difícil e onerosa, tem se originado em águas de abastecimento. O uso de membranas filtrantes é uma das opções mais recentes de operação unitária que está sendo incorporado no processo de tratamento de água e esgoto. O presente trabalho envolve o estudo da produção de membrana polimérica porosa assimétrica para ser utilizada com o intuito de se remover prováveis contaminantes abióticos e/ou biológicos remanescentes do pós-tratamento da água potável, bem como, avaliar o tempo de vida útil da membrana. O processo usado para a produção de membrana foi o de Inversão de Fase, utilizando a solução polimérica constituída de Fluoreto de Polivinilideno (PVDF), de Polimetacrilato de Metila (PMMA) e como solvente, N-N-Dimetilformamida. Como aditivo os sais de KCl foram incorporados na solução, e como suporte, a folha de poliéster polipropileno foi empregada. A membrana produzida foi testada em um módulo de fluxo perpendicular. Os ensaios demonstraram que a membrana produzida apresentou uma eficiente barreira aos contaminantes abióticos com fluxo médio de 342 kg h^{-1} m^{-2} e tempo de vida útil de 48h, bem como, aos biológicos como a bactéria entérica *Escherichia coli*.

Palavras-chave: produção de membrana, água, contaminantes.

Introduction

The increasing demands of drinking water standards lead to a necessity to increase the efficiency of the treatment processes that are currently employed. In this sense, the use of membrane technology for micro, ultra, and nanofiltration and reverse osmosis has become an attractive option. Thus, the membrane filtration process has been widely used in industries and basic sanitation companies for the production of drinking water, brackish water desalination, water hardness and color removal, and wastewater treatment and reuse (HABERT et al., 2006).

In the study by Ribeiro et al. (2004), polymeric membranes of PVDF (polyvinylidene fluoride) and PSF (polysulfone) were prepared in order to make water potable by removing *Escherichia coli*. These membranes retained, in general, 95% of the enteric bacteria, with permeate fluxes around 300 kg h^{-1} m^{-2}, although the most efficient membrane, produced with 17% PVDF, achieved total removal of *E. coli* at a flux of 284 kg h^{-1} m^{-2}.

According to Schneider and Tsutiya (2001), the possibility of scaling up and the continuous improvement of membrane systems are important factors that enabled the construction of larger scale systems – today, in developed countries, membrane systems are being designed to replace conventional water treatment systems in large scale (7.0 m^3 s^{-1}). However, as also occurs in conventional filters, the permeate flux obtained by membrane filtration decays with time. According to Petersen (1993), the decline in flux or permeation rate is the greatest problem in the wide deployment of the membrane process for water and wastewater treatment. This decline is attributed to the formation of a secondary type of membrane under the primary membrane, due to the presence of solids in the feed (MUHAMMAD; ANDERSON, 1997).

The disadvantage of composite membranes, according to Petersen (1993), is that their synthesis is more expensive than that of homogeneous asymmetric membranes. In this case, the cellulose acetate membrane still maintains a low demand for applicability in water treatment, based on its high cost. For most applications of reverse osmosis, however, the high cost of manufacturing composite membranes is more significant than the resulting characteristics of these membranes. Many studies have been done on microporous polysulfone membranes for application in water treatment, which indicate good performance as ultrafiltration membranes.

Considering the membrane technology for water treatment, this study aimed to produce a membrane to be employed in removing abiotic (suspended or dissolved solids, responsible for producing color and turbidity) and biological (*Escherichia coli*) contaminants remaining in the water, in the post-treatment for the final consumer. In addition, the time, in hours, in which the filtration through the membrane remained stable without the need for cleaning was also evaluated.

Material and methods

Membrane preparation

The blend membrane was synthesized using polymeric materials in the proportion of 8% polyvinylidene fluoride (PVDF) and 1% polymethyl methacrylate (PMMA). Reagents (Aldrich) were used as received and their high purity (reagent grade) was relevant to make as accurate as possible the studied concentrations.

PVDF and PMMA, together with KCl, were dissolved in NN-Dimethylformamide in a thermostatic stirrer at a controlled temperature of 45ºC. After complete dissolution, the polymer solution was aged for 48h and then spread on a polyester-polypropylene sheet, with the aid of a glass rod and plate. Thereafter, the assembly was immersed in distilled water at room temperature (25°C) and dried at the same temperature, according to Ribeiro et al. (2007). However, additional immersion in distilled water in order to remove the remaining solvent from the membrane, as performed by the author, was not done in this study, in order to evaluate its influence on the characterization of the membrane.

Determination of permeate flux

Figure 1 shows the gravitational system, in which the membrane produced was tested with a driving force around 0.3 atm. The water used for the tests was from the Sanepar (Paraná Sanitation Company) treatment plant in Maringá, Paraná State, Brazil, which had dissolved and suspended solids when drawn from a distribution reservoir. This water was stored in the main tank (1), which supplied the lung tank (2), which was placed at 3.5 m above the floor. The water level in the tank was kept constant by the bypass (3). The membrane produced was adapted to the filtration module (4), allowing perpendicular filtration and obtaining the permeate (5).

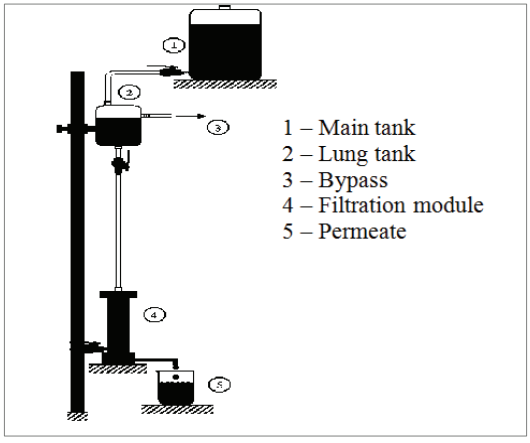

Figure 1. Gravitational system.

For the experimental evaluation of the membrane life span, using the same gravitational system, several discontinuous tests were carried out (the module was fed with water at different time intervals). Thus, the assessment was conducted until the flux reached 5% of its initial value. Each test lasted approximately 120 min. While the module was not in operation, it was kept completely filled with distilled water to maintain the hydration of the membrane.

This way, the permeate flux (J) was determined by Equation 1 for all flux analyses, according to Mello et al. (2010).

$$J = \frac{V_p}{t.A_m} \quad (1)$$

where:

Vp = permeate volume;

t = time;

A_m = membrane area.

The reproducibility of the polymeric membrane synthesis was evaluated through tests to analyze the permeate flow using different membranes synthesized under the same physical and chemical conditions, using distilled water.

Degree of retention of compounds by the membrane

The degree of retention indicates the membrane capacity to retain molecules. Through the determination of the concentration of compounds in the feed water and in the permeate, which were obtained by physicochemical analysis, the degree of retention of the compounds was calculated using Equation 2, according to Schneider and Tsutiya (2001).

$$R\% = 100 - (C_p/Cc) \times 100 \quad (2)$$

where:

R% - percent retention;

C_p - compound concentration in the permeate;

Cc - compound concentration in the feed.

Analyses of the samples

In order to assess the degree of retention of abiotic contaminants (dissolved or suspended solids), responsible for producing color and turbidity in water, physicochemical analyses were performed according to Eaton et al. (2005), to determine undesirable compounds in the feed (water that had previously undergone potabilization treatment). These analyses were also performed after each 2 L of permeate had been collected in the gravitational system shown in Figure 1. Table 1 lists the equipment used to assess the physicochemical parameters of the feed water.

Table 1. Parameters and methods.

Physicochemical parameter	Equipment
Color (Units PtCo APHA)	HACH DR/2010
Turbidity (NTU)	Turbidimeter HACH 2100 P
TDS* (mg L^{-1})	Oven

*Total dissolved solids.

To evaluate the microbiological retention, the method of Eaton et al. (2005) was used to analyse sterile water obtained by reverse osmosis that had been contaminated with faecal bacteria *E. coli* at 1.1 x 10^2 cfu 100 mL^{-1} (colony forming units 100 mL^{-1}) and then filtered through the produced membrane.

Determination of the apparent mean pore radius of the membrane

According to Ribeiro et al. (2007), the apparent mean pore radius of the membrane was determined using Equation 3. However, to calculate the percent retention of BSA (bovine serum albumin - with a molecular mass of 67,000 Daltons and an average radius of 40 Å) Equation 1 was applied, using the protein concentrations determined by the method of Lowry.

The concentrate and permeate concentrations were determined based on a calibration curve (absorbance x protein concentration), from the absorbance readings on a Shimadzu UV - 1203 spectrophotometer, for a single molecular mass of BSA.

$$r = 100.\left(\frac{a}{R(\%)}\right) \quad (3)$$

where:

r: mean pore radius of the membrane;

a: mean radius of the solute (BSA) of known molecular mass and diameter;

R(%): BSA percent retention.

Results and discussion

Table 2 presents the mean values of the physicochemical characteristics of the water samples, as well as the Maximum Allowed Values (MAV) according to ordinance 518/04, from the Brazilian Ministry of Health (BRASIL, 2004). Figure 2 shows the degree of retention of color, turbidity, and TDS as a function of permeate volume.

Table 2. Maximum Allowed Values (MAV) and mean measured values of the physicochemical parameters.

Parameter	Feed water (average)	MAV Ordinance 518
Color (Units PtCo APHA)	13	15
Turbidity (NTU)	1.02	1.00 – 5.00
pH	7.53	5.40 – 9.50
TDS* (mg L^{-1})	119	1000

*Total dissolved solids.

It can be observed in Figure 2 that the degree of color and turbidity retention was around 85 and 70%, respectively, during the period of permeate

collection. However, the degree of TDS retention showed an increase during the tests. This was probably due to the formation of deposits of some compounds on the membrane surface, acting as a second membrane, which allowed greater retention of these compounds over time.

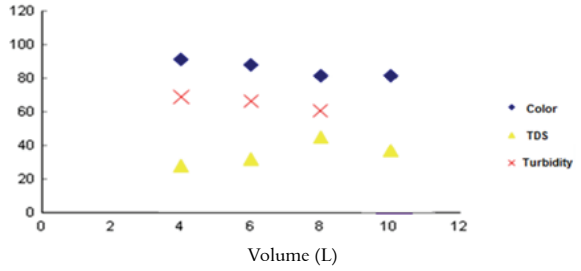

Figure 2. Degree of retention of color, turbidity, and TDS, as a function of permeate volume.

Figure 3 shows the final aspect of the membrane after its use as filtering medium in the filtration module, without being washed. The formation of a deposit on the membrane surface is clear.

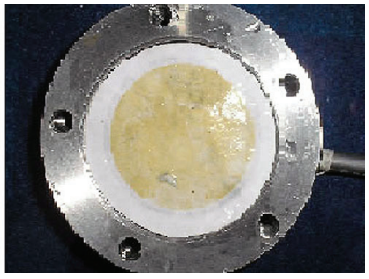

Figure 3. Membrane supported on the base of the filtration module.

In the microbiological evaluation of the permeate, no colony-forming units of *E. coli* were detected, that is, total retention of the bacterial mass of 1.1 x 10^2 cfu 100 mL^{-1} of *E. coli* was obtained with the membrane produced with a PVDF concentration near 8.5%. Ribeiro et al. (2007) prepared PVDF membranes with higher polymer concentrations (12 to 17% PVDF), which removed virtually all the bacterial mass of the same species. Therefore, it is possible to synthesize a PVDF membrane with lower apparent mean pore radius and capable of retaining the enteric bacteria, using lower polymer concentration.

Thus, the membrane synthesized in the present study was found to be able to retain 32.6% of BSA, showing apparent mean radius of 122.7 Å.

Permeate flux data collected using membranes M1 and M2, synthesized in the same chemical and physical conditions to evaluate the accuracy of the polymeric synthesis, is presented in Figure 4. Both membranes were evaluated for 2h using distilled water under the same conditions. The initial flux (1852 kg h^{-1} m^{-2} for M1 and 1816 kg h^{-1} m^{-2} for M2) dropped to 495 and 493 kg h^{-1} m^{-2}, respectively.

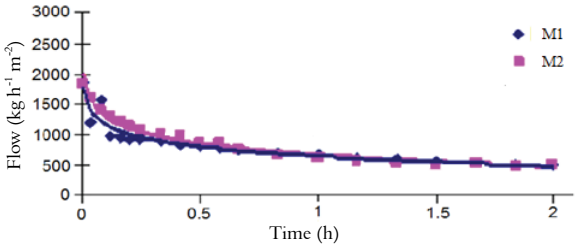

Figure 4. Permeate flux profile using distilled water.

Based on the results obtained using distilled water, the technique used to produce the membrane was found to be accurate, that is, it was possible to reproduce a membrane that promoted a permeate flux profile that was similar to that of the original membrane.

Figure 5 shows the data collected during the first 2h test with membrane M1 using water from the Sanepar distribution reservoir. It was observed that the permeate flux, which initially was 1,077 kg h^{-1} m^{-2}, decreased with time, stabilizing at approximately 434 kg h^{-1} m^{-2}.

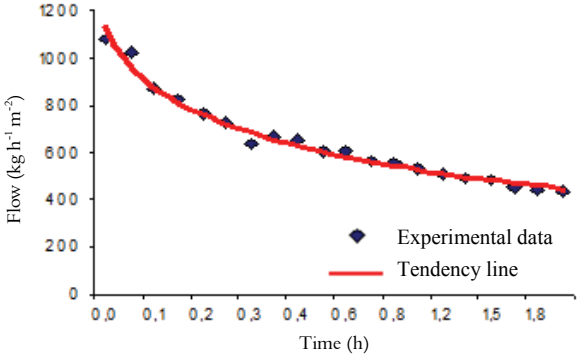

Figure 5. Permeate flux profile obtained in the first test.

The stabilized permeate flux obtained by Ribeiro et al. (2004), with a similarly produced membrane, was 321 kg h^{-1} m^{-2} at a pressure of 3 atm. Therefore, the stabilized flux obtained with the membrane prepared in the present research, with a gravitational pressure of 0.3 atm, was significantly higher. Thus, one can verify that the physicochemical properties of the membranes can be changed, probably by modifying the synthesis process.

Figure 6 shows the permeate flux behavior during all tests. It can be seen that after 48h the permeate flux decreased to 5% of its initial value, but a recovery was observed at the beginning of each partial test during the evaluation of the membrane life span.

This recovery was achieved during the resting periods of the membrane module, when it was completely filled with distilled water. Most likely, the compounds deposited on the membrane surface were suspended or solubilized in water. Thus, the formation of deposits, which leads to membrane fouling, was mitigated, promoting a slight increase in permeate flux at the beginning of each test.

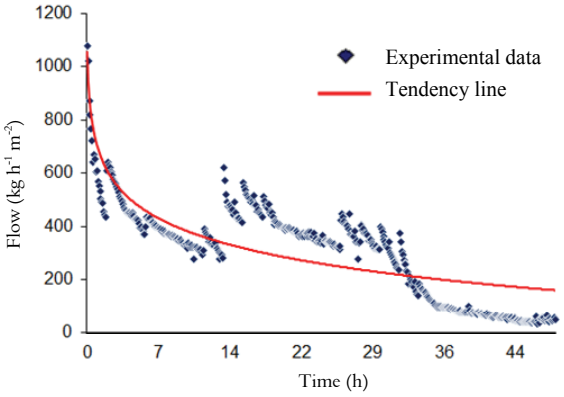

Figure 6. Permeate flux tests in a 48h time span.

It is also observed in Figure 6 that the permeate flux presented an average value of 342 kg h^{-1} m^{-2} between 4 and 32h. After this period the membrane began to lose its efficiency significantly, until the flux decreased to 5% of its initial value, 43 kg h^{-1} m^{-2}. However, as the membrane was not washed during the experiment, it is not clear wether the flux decay was caused by the reversible formation of deposits, or also, according to Mohammadi et al. (2002), by fouling (irreversible formation of deposits).

Conclusion

It was concluded that changes in the physicochemical conditions of membrane synthesis affect the performance of the filtration process. Thus, the membrane produced in this work was efficient for the retention of abiotic contaminants (dissolved or suspended solids), as well as biological contaminants (enteric bacteria *Escherichia coli*) of water. The retention efficiency was 85% for color, 70% for turbidity, and 30% for TDS. The microbiological retention (*E. coli*) of the membrane was complete, as the enteric bacteria was not found in the permeate. The studied membrane was found to be reproducible and to have a life span of 48h, with a final permeate flux of 5% of the initial value, without washing. The permeate flux remained almost constant at 342 kg h^{-1} m^{-2} for 28h.

In conclusion, the filtration process with polymeric membranes presents itself as a promising unit operation for the retention of contaminants that remain after drinking water treatment.

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