Journal of Materials, Processes and Environment
December edition. Vol. x. N° x. (20xx)
ISSN : 2335-1020

Removal of Pharmaceutical Pollutants using a Membrane Hybrid Matrix

ABSTRACT— In this work, hybrid carbon-polymeric membranes were synthesized by an immersion-precipitation method using polysulfone (PSf) as the membrane matrix, methylcellulose (MC) as pore forming agent and commercial powdered activated carbon (PAC) as inorganic adsorbent additive. All the components were dissolved in N-methylpyrrolidone (NMP) to prepare the casting solutions. The surface hydrophilicity of the prepared membranes was determined by measuring water contact angle. The effect of methycellulose and activated carbon on the morphology of the membranes was examined by scanning electron microscopy. Hybrid membranes performances were tested in terms of water permeability and rejection of selected pharmaceuticals at a concentration of 10 ppm. Results showed that the hydrophilicity of the hybrid membranes was improved by methylcellulose and activated carbon component. The asymmetric structure of the prepared membranes was more porous by adding activated carbon. The water permeability of the hybrid membranes was better than non-hybrid ones. A high rejection rate was obtained with hybrid carbon-polymeric membranes compared with membranes without carbon.

Keywords: *Hybrid membrane, Methylcellulose, Powdered activated carbon, Pharmaceuticals removal*

I. INTRODUCTION

The global water challenge will become greater as the population and economies of the countries develop. In the coming years, the world's population is expected to grow and, as a result, domestic, agricultural, industrial and energy demands on water resources will continue to grow. More than ever, existing water resources need protection and new resources must be developed in order to meet the growing demand for water in the world. This will require better water treatment technology.

Treating water using lower cost purification technologies, using less energy and minimizing the impact on the environment makes axis of new research **[1,2]**.

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Membrane technologies, in particular, are favored over other water treatment technologies because of their distinct advantages, such as improved water quality, non-use of chemical additives and compact modular construction with excellent separation efficiency.

Unfortunately, the conventional polymeric membranes can hardly achieve the aforementioned properties due to the inherent limitations in material properties. One of the most promising solutions is the introduction of inorganic component into polymeric matrix and combines their advantages together **[3-5]**.

In this work, flat sheet polymeric membranes with a hybrid matrix were prepared based on polysulfone using organic and inorganic additives *via* phase inversion method. The first one is a cellulosic derivative, methylcellulose, used for the first time as a basic biopolymer additive **[6]**, acting as a pore agent and having the property of

improving surface hydrophilicity. The second one is a commercial powdered activated carbon, used as an additional additive giving rise to a membrane hybrid matrix.

The effect of methylcellulose and activated carbon on the performances of polysulfone membranes was evaluated using scanning electron microscopy, contact angle, water permeability and rejection studies of pharmaceutical molecules.

II. EXPERIMENTAL

II.1. Materials

Polysulfone (PSf, Udel P-3500, M_w: 35000 Da) used as membrane material was supplied by Solvay Advanced Polymer (Belgium). Methylcellulose (MC, M_n~63000 Da, vis.1500 cps) from Aldrich was used as an organic additive. A commercial powdered activated carbon (PAC, purity ≥ 97.0%) from Merck, having a specific surface area of 625.726 m^2g^{-1} and a total pore volume of 0.519 cm^3g^{-1}. The BET surface area and total pore volume were determined using nitrogen gas adsorption analyzer at 77K with an ASAP 2010 instrument (Micromeritics). N-methyl-2-pyrrolidone (NMP, 99%) from Fluka was used as solvent directly without any further purification. Paracetamol from Sigma-Aldrich and Metronidazole from Fluka were used as model molecules of pharmaceuticals pollutants.

II.2. Membrane preparation

Flat sheet polysulfone based membranes were prepared by the phase inversion method using the immersion precipitation method reported in the literature **[7,8]**. This technique is the most widely used in the preparation of porous ultrafiltration and microfiltration membranes. Membranes were formed by respecting the amounts of based polymer and additives shown in table I and following the steps described below:

- The polysulfone is first dissolved with magnetic stirring in NMP at room temperature. Then amount of MC and PAC were added to the polysulfone solution, still under stirring, until a homogenous mixture is obtained (24h)
- The obtained solution is left without stirring until the air bubbles disappear and then spread on a glass plate. The film thus formed is immersed immediately in a coagulation bath of distilled water maintained at 25 °C, it separates from the glass plate after a few seconds.

Table 1. Composition of the casting solutions (wt %)

Membranes	PSf	MC	PAC	NMP
PSf	16.0	0.0	0.0	84.0
PSf-1	16.0	1.0	0.0	83.0
PSf-1/2.5	16.0	1.0	2.5	80.5

II.3. Membrane characterization

II.3.1. Contact angle

This method is often used to evaluate the hydrophilic/hydrophobic nature of membrane surface. The principle of this technique is based on the deposition of a drop of water (3 µl) using a precise syringe on the surface of a membrane simple in contact with air. The membrane simples were previously washed with distilled water and dried in air before the measurement. The contact angle was measured using a GBX DIGIDROP goniometer "Digitizer of droplets" at three different locations for each sample and the average was reported.

II.3.2. Scanning electron microscopy

The cross section morphologies of the membranes were observed by an electron microscope (SEM) (Philips ESEMXL 30). Before SEM analysis, the membrane samples were cut into appropriate size, frozen in liquid nitrogen and fractured.

II.3.3. Hydrodynamic characterization

Filtration experiments were performed using a dead end filtration stirred cell (Model 8050, 50ml, Amicon) connected to a nitrogen pressure. Each fresh membrane was compacted before use. The compaction was carried out with deionized water for 30 minutes at 1 bar. The pure water flux was measured in a range of pressure of 0.6

to 4 bars. For each membrane, several discs were tested and the average pure water flux was reported.

II.3.3.1. Pure water flux (PWF)

The pure water flux was calculated using Eq. (1)

$$J = V/ (A \times \Delta t) \qquad (1)$$

Where J ($L.m^{-2}.h^{-1}$) is the pure water flux, V (L) is the volume of filtrate, A (m^2) is the membrane area and Δt (h) is the filtration time.

Hydraulic permeability (Ph) was obtained from the slope of the plot of J and ΔP and was calculated using Eq.2 **[9].**

$$P_h = J/\Delta P \qquad (2)$$

II.4. Removal of pharmaceuticals

The filtration tests were carried out with flat sheet membranes placed in a filtration cell. All the experiments were carried out at a constant pressure of 1 bar and at room temperature.

Solutions of Paracetamol and Metronidazole were prepared in distilled water at a concentration of 10 ppm. The drug concentration in feed and permeate solutions was measured by UV spectrophotometer "LAMBDA 20, Perkin Elmer".

III. Results and Discussion

III.1. Hydrophilic /Hydrophobic character

The measurement of the contact angle gives an indication of the surface hydrophilicity. It is one of the most important parameter that can affect the water flow of membranes. As presented in Fig.1, the contact angle of the membranes modified with MC and PAC is lower than that of the membrane prepared with pure PSf. It decreased by 4° by adding the MC to the PSf membrane matrix, and by 9° when adding PAC to the membrane containing MC.

During the immersion/ precipitation process, the MC can diffuse on the membrane surface due to its good solubility in water, leading to the improvement of wettability on the membrane surface due to its hydrophilic groups (OH) **[9]**. The variation in the contact angle of the membrane hybrid matrix containing PAC can be explained by the fact that during phase inversion process, the PAC particles having hydrophilic groups (OH) migrate spontaneously towards the membrane/water interface, which reduces the surface tension of the surface **[10,11]**.

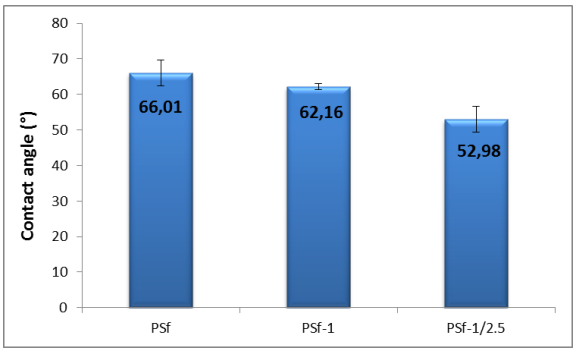


Fig.1. Contact angle of the membranes

III.2. Morphology of the membranes

The structure of the membrane is affected by the composition of the casting solution, where the nature and concentration of additives play important roles in the modification of the membrane properties. To evaluate the morphology of the membranes, the cross-sections of different membranes were characterized by SEM images and presented in Fig.2. It can be seen that the membranes exhibit an asymmetric structure with a dense skin in the top layer and open pores (macrovoids and finger like pores) at the sublayer.

The cross-sectional morphology of the PSf membrane display both finger like pores and macrovoids near the bottom. This structure is formed by an instantaneous demixing produced between the surface of the polymer casting solution and water coagulation bath which results a formation of polymer reach phase and poor phase **[12,13].**

Compared with PSf membrane, the structure of the membrane containing MC become more porous with more regular finger like pores. Generally, water soluble polymers have been considered as pore-formers during membrane formation **[14].** It is assumed that most of water soluble polymers can be leached out of the casting film and the site where the polymer exists becomes micropores in the prepared membrane.

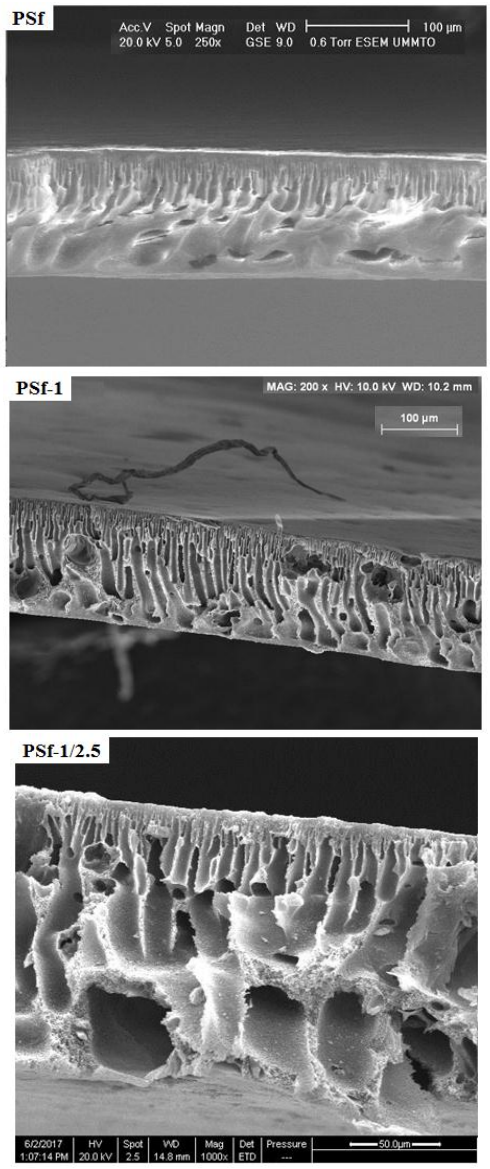


Fig.2. Cross-section SEM images of the prepared membranes

The structure of the membrane mixed matrix containing PAC was completely changed from finger like structure to macrovoids structure. This macrovoids are obtained in the vicinity of transition from delayed demixing to instantaneous demixion and their number increases when the concentration of non -solvent (water) in substructure is higher **[15].**

III.3. Pure water flux

The effect of MC and PAC on PWF is shown in Fig.3. It can be seen that PWF increases with increasing in transmembrane pressure linearly.

This result means that the transport through a membrane is described by Darcy's law and the flow regime of the fluid is laminar, which is generally the case in porous media. The variation of the water flux could be explained by the porosity and the hydrophilicity of the membranes.

The permeabilities of the membranes are 4.71, 28.19 and 132.24 $L.m^{-2}.h^{-1}.bar^{-1}$ respectively for PSf, PSf-1 and PSf-1/2.5 membranes. It is clear that the permeability has been improved by adding the MC and the PAC to the casting solutions.

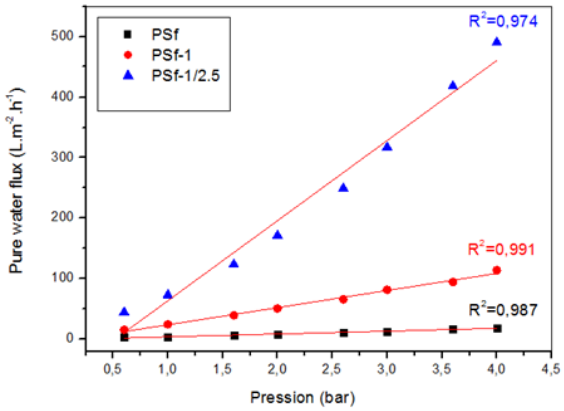


Fig.3. Effect of MC and PAC on pure water flux at different transmembrane pressure (ΔP 0.6-4 bar)

III.4. Removal of pharmaceuticals

The results of the experiments of the removal of pharmaceuticals conducted using MC modified membranes and mixed matrix membranes are summarized in Fig.4. It can be

seen that the retention of Paracetamol and Metronidazole was improved with the membrane containing PAC. The rejection increased from 16.44 to 31.91% for Paracetamol, and from 3.39 to 24.8% for Metronidazole. However, the low rejection rate can be due to the difference in molecular weight of pharmaceuticals compared to the membrane pore size.

In addition to pore size, adsorption at the membrane surface is one of the main mechanisms of ultrafiltration to remove micro-pollutants. therefore, the increase in removal rate using carbon-polymeric membranes means that the introduction of PAC particles into the membranes matrix has improved their retention capacity.

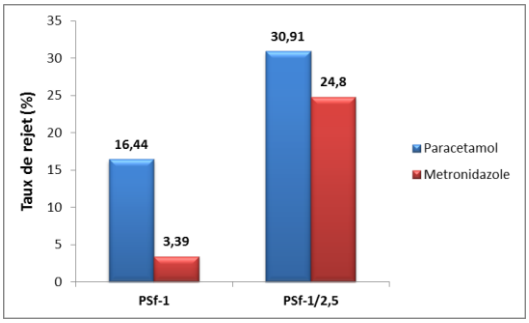


Fig.4. Removal of pharmaceuticals using mixed and non-mixed matrix membranes

IV. Conclusions

In order to study the effect of activated carbon as an additive on membrane structure and performances, polysulfone based membranes were prepared via phase inversion method. The morphology of the modified membranes shows an asymmetric structure with a dense skin at the surface and both finger like pores and macrovoids penetrating the membrane cross section when methylcellulose and activated carbon were added to polysulfone solutions respectively. The measurement of contact angle shows an improvement in the surface hydrophilicity. The hydrodynamic characterization reveals that the membranes had the behavior of porous media and that their permeability to water could be described by Darcy's law.

Filtration tests of aqueous solutions containing pharmaceutical molecules carried out on membranes prepared with and without activated carbon showed a clear improvement of the elimination of theses micropollutants by the hybrid membranes in comparison with the non-hybrid ones.

The results obtained in this work suggest that incorporation of powdered activated carbon into the membrane matrix may be a promising additive in the formation of membranes used for the treatment of industrial effluents.

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