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RESEARCH ON OBTAINING AND CHARACTERIZATION OF POLYMERIC MEMBRANES FOR WASTEWATER TREATMENT

Laurenția Geanina TIRON*, Maria VLAD,
Ștefan Cătălin PINTILIE, Ștefan BALTĂ
"Dunarea de Jos" University of Galati, Romania
*e-mail: geanina.tiron@ugal.ro

ABSTRACT

Some of the most common polymeric membranes are used in wastewater treatment. Over the years, these membranes have been studied from different points of view: their aim to improve the retention of impurities, membrane affinity to water and degree of fouling of polymeric membranes. By analysing the surface of the membrane material by chemical characteristics information can be offered regarding the polymer's hydrophilicity or hydrophobicity. Improving membrane properties can be achieved during the stage of obtaining the polymer solution and during the thin film deposition step. To obtain polymeric membranes, the phase inversion method was used, following the influencing factors on membrane properties during the manufacturing process. The performance of membranes was studied using various parameters which lead to different results in terms of flux, permeability and hydrophilicity. This paper presents the influence of different polymer concentration, the influence of relative air humidity and the membrane thickness gradient on membrane flux and permeability.

KEYWORDS: polymeric membranes, pure water flux, relative air humidity, thickness gradient

1. Introduction

Membrane filtration is an important alternative for wastewater treatment and was developped after the XVIIIth century when Abb'e Nolet discovered water permeation through a diaphragm, a phenomenon called osmosis [1]. Widely recognized as the technology used for superior wastewater treatment, membranes provide a physical barrier that effectively removes solids, viruses, bacteria and other unwanted molecules [2].

Membrane water treatment process was applied first in the US and Middle East, but has expanded so much that in the present, to obtain drinking water, there are membranes used all over the world [3]. Membrane technologies are used on a large scale in industries like chemical industry and water treatment [4]. Membrane filtration has become the leading separation technology for water and wastewater treatment in the last 50 years [5].

Water treatment membranes are thin sheets of material (mainly polymers) that are able to separate contaminants based on properties such as size or charge. Water passes through a membrane but not larger particles, microorganisms and other contaminants, depending on their size, are separated and eliminated [6].

Polymeric membranes used in ultrafiltration processes are obtained by applying phase inversion process. The most used polymers are polysulfone (PSF), polyethersulfone (PES) and polyvinylidene fluoride (PVDF). These polymers show a high degree of utilization because it provides high tolerance to pH, chlorine and high temperatures, and are stable from the mechanical point of view [7].

The membrane properties may vary depending on the fabrication steps [8], for example there are many approaches involving either mixing with the hydrophilic components to improve the hydrophilicity of the membrane, or the modification [9] of the surface to improve antifouling [10]. Many factors which can have an influence on the membrane properties were studied by researchers. The most important factors studied are the polymer concentration, relative air humidity and the use of additives in the polymeric casting solution or in the nonsolvent bath (Han and Bhattacharyya, 1994;

Swinyard and Barnie, 1988) [11, 12], the temperature of the nonsolvent bath [13, 14] etc.

A major problem for membranes is fouling. Membrane fouling can be defined as a pollutant deposition to the membrane surface or the absorption of pollutants in the membrane pores [15]. Generally, fouling occurs either on the surface of a membrane or within its pores, and it causes a decrease in flux. There are four major types of fouling: biofouling, scaling, organic, and colloidal [16]. Biofouling results from microbial contamination of feed water and produces a biofilm on the surface of the membrane, which increases the resistance to water permeation. Scaling arises from the precipitation and deposition of salts on the membrane surface. Organic fouling comes from substances such as hydrocarbons which coat the surface and/or plug pores in the porous support layer. Colloidal fouling mainly stems from particles, such as clay or silica, accumulating on the surface of the membrane. Fouling can be controlled to some extent by adding disinfectants, anti-scaling agents, and other pre-treatment steps. However, these are not remedies to the problem, and fouling remains a key area in definite need of improvement for reverse osmosis (RO) membranes [17].

2. Equipment and process

The separation of impurities from the fluid using water flow filtration is achieved by the filters or filter media (permeable porous media) as illustrated in Figure 1 [16].

Using the pressure difference (Δp), the suspension (fluid subjected to filtration) has a flow rate Q that passes through the filter medium. The difference between the pressure of the fluid subjected to the filtration (p_1) and the permeate pressure (p_2) called the pressure drop may be provided by gravity, fluid pressure, filter vacuum downstream.

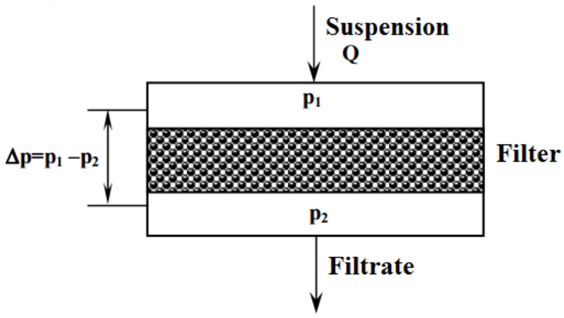
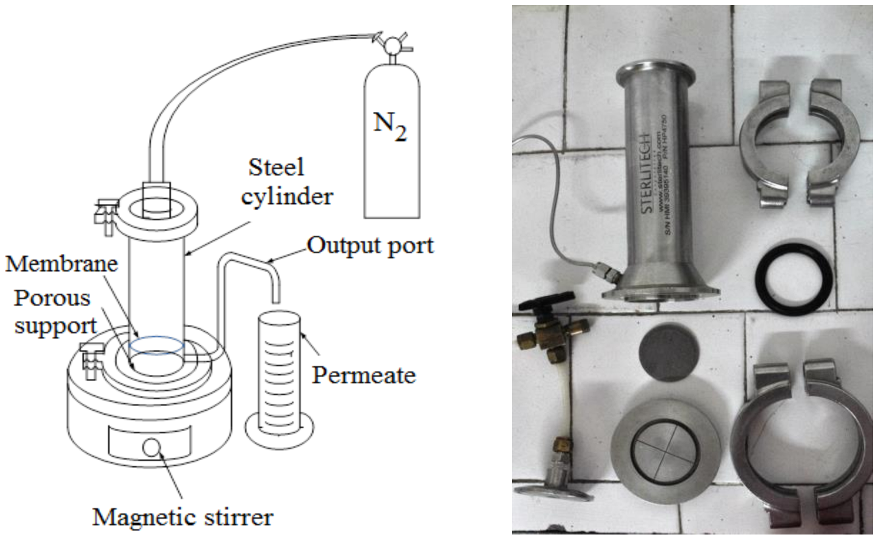


Fig. 1. *The scheme of the filtration principle* [16]

In the dead-end filtration, the influent flow is perpendicular to the membrane (Figure 2). Any solid particles in the influent which is greater than the pore size of the membrane is deposited on the surface, forming a "cake" layer of the solid particles. The fluid passing through the membrane is called filtered [17].



a. b.

Fig. 2. *Dead-End Filtration System: a. filtration plant; b. filtration cell*

The laboratory filtration dead-end system is often conducted in a stirred-cell which is merely a cylindrical vessel, usually made of stainless steel, fitted with a porous support on top of which is placed the membrane [18]. An output port is designed for the filtrate to be collected and weighed on a digital balance. For accurate measurements and efficient data collection, this measurement system can be connected to a personal computer. The flow is calculated by measuring the mass (or the volume if the density is known) of filtrate collected in a known time. The pressure inside the vessel was kept constant by connecting it to a cell with a compressed inert gas (e.g.: nitrogen) [17].

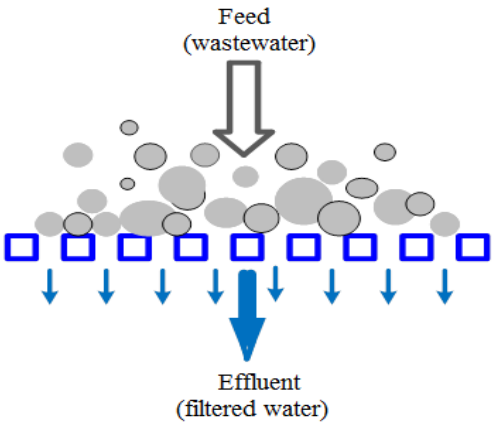


***Fig. 3.** Filtration process in a dead-end stirred-cell* [19]

Pure water permeability is based on the Darcy's Law, which explains that the flow rate of water through a porous medium under the action of a driving pressure ΔP is expressed by the equation [20]

$$dV / (A \times dt) = J = \Delta P / (\eta \times Rm) \quad (1)$$

where:

- J is the linear flux of the fluid (the water volume „V" that passes in the known time „t" through a known area „A") [$L / m^2 \cdot h$];
- ΔP is the pressure gradient [N / m^2] or [bar];
- η is the fluid viscosity [Ns / m^2];
- Rm refers to the permeability of the filter media.

3. Materials used for membrane fabrication

3.1. Types of polymers used to obtain the polymeric membrane

The hydrophilicity of the membrane's surface can be studied using a contact angle analyzer with the sessile drop method by measuring the dynamic contact angle [21].

In the category of hydrophobic materials there are polysulfone (PSF) and polyethersulfone (PES) that are used for ultrafiltration (UF) membranes or for support for the reverse osmosis (RO) membranes. In the category of hydrophilic membranes there are polymers such as polyethylene (PE), polytetrafluoroethylene (PTFE), isotactic polypropylene (PP) or fluoride (PVDF), which are commonly used to obtain the microfiltration membranes [22, 23].

The membrane permeability can be influenced by the type of polymer. Analyzing the results of S.A. Al Malek *et al.*, in their study on the polyethersulfone membranes (15 wt.%), obtained water permeability of 128.2 $L/m^2 \cdot h \cdot bar$, presented in Fig. 1 with PES-1 [24]. The results of the sample PS-1 were obtained by Elizabeth Arkhangelsky *et al.*, using polysulfone with 15 wt.%, resulting pure water permeability of 118.28 $L/m^2 \cdot h \cdot bar$ [25]. In the sample CA, Toraj Mohammadi *et al.* has used cellulose acetate (CA) with 15 wt.% and a value of pure water permeability of about 58 $L/m^2 \cdot h \cdot bar$ [26].

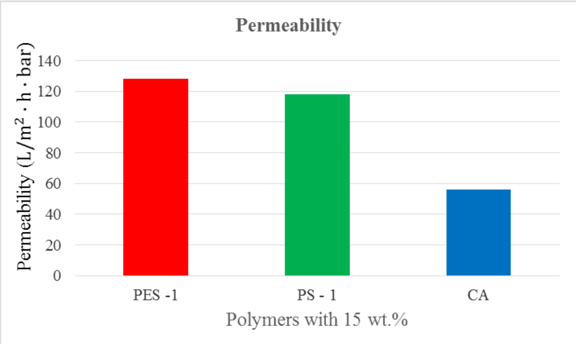


***Fig. 4.** Permeability of polymeric membrane*

If we analyse the three types of membranes obtained from different polymers, with the same concentration, it can be seen that the membrane with polyethersulfone has better permeability than the other membranes, but the polyethersulfone and polysulfone have close values of permeability.

3.2. The influence of polymer concentration used in the membranes manufacture

The concentration is the parameter that has the greatest influence on the properties of the polymer membrane [27] and it may affect the performance of membrane structure and thickness [28].

To observe this phenomenon, three different studies were analyzed for polyethersulfone with different concentrations. The results of sample PES-2 were obtained by S. A. Al Malek *et al.*, with the highest value of permeability [24]. The sample PES-3 was obtained by Jiang-Nan Shen *et al.* In this study, polyethersulfone with 18 wt.% was used and obtained a permeability of 124.6 $L/m^2 \cdot h \cdot bar$ [29]. And Elizabeth Arkhangelsky *et al.* in their study obtained polymeric membranes with 20 wt.% of polyethersulfone and with 50 $L/m^2 \cdot h \cdot bar$ permeability [25].

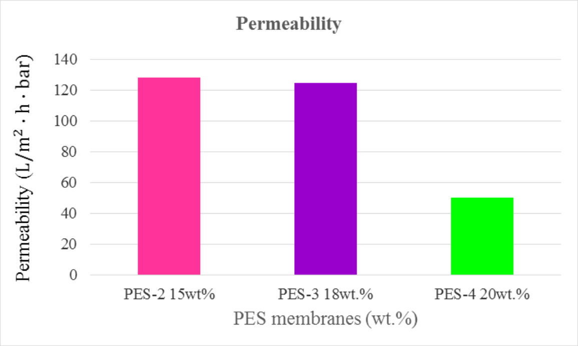


Fig. 5. *The influence of polymer concentration*

3.3. The influence of membrane thickness on the properties of the membrane

A membrane thickness gradient is defined as a flat sheet membrane with a membrane thickness increasing in one direction, which is used to investigate the morphology evolution of the membrane to the membrane thickness.

Experimentally, the gradient of thickness of the membranes is adjusted to the casting with a utility knife, generally being studied the critical structure-transition thickness (Lc) and the thickness of the overall thickness of the structure of a sponge (Lgs). LGS is the thickness of the sponge-like portion below the surface membrane [30].

4. Analysis of the additives used in the preparation of membranes

Polymeric additives (usually a hydrophilic polymer) in a casting solution are also used to increase both porosity and pore size (pore forming agent), and to suppress the formation of macrovoids. However, depending on the polymer used to make the membrane, depending on the solvent and the method of applying the thin film, effects can be observed [31].

Membranes made from hydrophobic materials can be improved by adding copolymer in the membrane matrix solution. The presence of polyethylene glycol (PEG) additive in polymer solution helps form a hydration layer that provides resistance to foulant adsorption [32].

Membranes obtained from polyvinyl chloride (PVC) blended with copolymer (Pluronic F-127) and poly(ethylene oxide) (PEO), used like additive, was studied by Liu *et al.* to increase the antifouling properties [33].

S.A. Al Malek *et al.* studied the pure water flux of membranes obtained from polyethersulfone with 20 wt.% and polyvinylpyrrolidone with 5, 10, 15 and 20 wt.% [24]. Comparing with the membranes with polyethylene glycol having 5, 10, 15 and 20 wt.% in polyethersulfone of 20 wt.% obtained by Ani Idris *et al.* [34], the water flux is higher in the case of polyethylene glycol additive.

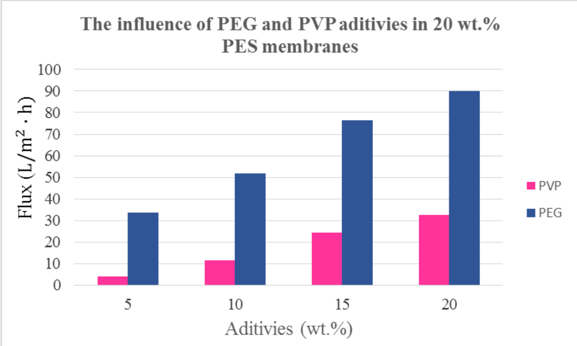


Fig. 6. *The influence of additives on membrane performance*

5. Improving the humidity gradient variation property in the membrane production

Relative air humidity affects membrane performance because during application of polymer solution on a thin film, the cast of this film composition varies by absorbing water vapour. Absorption occurs when the solvent evaporates in the presence of water vapour, dimethylformamide (DMF) and N-Methyl-2-pyrrolidone (NMP) are solvents and absorb a large amount of moisture.

Due to this absorption of water vapour, separation phase occurs in some places of the membrane's surface, preceding the separation phase that occurs when the cast film is placed in a bath of non-solvent with distilled water. Relative air humidity can thus influence the top layer of the surface of the membrane, because the base layer of the membrane is formed only at the time of immersion in the bath of non-solvent.

6. Conclusions

In conclusion, the membranes obtained from polyethersulfone (PES) is one of the most hydrophilic polymer in terms of pure water filtration. Also, the concentration of the polymer has an important influence on the membrane performance. In this situation, the membrane permeability decreases with the increasing polymer concentration. Another important factor influencing the process of obtaining membranes is the addition of additives. The amount of additive and the type of additive in the support layer is an important parameter for membrane permeation.

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