„Dunărea de Jos” University of Galaţi
Doctoral School of Fundamental and Engineering Sciences

DOCTOR OF PHILOSOPHY DEGREE
PhD THESIS

-Summary-

Contributions regarding fabrication and characterization of organic membranes used in wastewater treatment

Ph.D. Student,
eng. Laurenția Geanina TIRON (PINTILIE)

Ph.D. Supervisor,
Prof. univ. dr. eng. Maria VLAD

Series I5: Material Engineering No. 12
GALAŢI
2018

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Series I5: Materials Engineering No. 12

GALAȚI

2018

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INTRODUCTION

Water consumption in industrial and agricultural environments (about 90% of total global consumption) represents the largest quantity of potable water used.

The amount of water consumed at industrial and agricultural levels may decrease, but it is not a long-term method to overcome this crisis. Another option, more reliable at this time, is waste water treatment and reuse within the industry. An important drawback to the implementation of this method is the cost and space required for a conventional water treatment plant used in industries.

In the past years, it is desirable to implement membrane wastewater treatment technologies. This field is a developing branch due to the variety of raw materials used in the production processes, but also to the parameters that influence the properties of the membranes, implicitly the quantity and quality of the treated waters.

Improving the membrane performance is in continuous development, so in the doctoral thesis entitled "Contributions for the obtaining and characterization of organic membranes for waste water treatment", manufacturing membranes with different parameters was followed and their properties depending on the concentration of polymer, the thickness the applied solution layer and the additive addition have been determined.

The research in the doctoral thesis aimed to obtain the polymeric membranes used in the treatment processes through the phase inversion method. These membranes were analyzed for permeation properties (water flow, compaction resistance, permeability, flow of retaining solutions) according to the membrane fabrication parameters. The most important property of the membranes is the capacity to treat wastewater and was determined by the study of dye retention performance (Methylene Blue and Congo Red).

The results on membrane permeation properties were correlated and explained by characterization studies of morphology, surface topography, hydrophilicity, porosity, and chemical composition analysis.

The experimental researches were carried out locally in the laboratories of "Dunărea de Jos" University of Galati, the Faculty of Engineering and through external collaboration with Technical University "Gh. Asachi ", Faculty of Materials Science and Engineering, Department of Materials Science for Surface Topography Survey by Atomic Force Microscopy (AFM).

This work is developed in six chapters, which include, in order, the following:

In Chapter 1 entitled "Overview of current research on the obtaining and characterizing of organic membranes for wastewater treatment", a study that included a brief introduction to membrane technology and bibliographic information on research in the field has been conducted, more precisely on the parameters of manufacture of membranes which influences the permeation properties. Also, the results obtained by other authors in this field research are mentioned, which represented the basis for establishing the new research directions approached in the doctoral thesis. Thus, it has been observed that polysulfone is a polymer that offers a number of advantages to membrane properties but instead has a segment still in development to obtain the maximum membrane performance. So far, polysulfone membranes have been obtained with concentrations up to 20 wt%. Instead, higher polymer concentrations were avoided since this type of membrane has a lower permeability. The membrane properties can also be influenced by the thickness of the applied solution layer in the membrane production process. The influence of this parameter on the membrane performance has not been studied, especially for the type of membranes researched within this thesis, but in the literature there are studies on the influence of the thickness of the solution layer on the membrane morphology.

Recently, various methods have been discovered to increase the flux of solution through the membrane. In this paper the improvement of the membrane properties by adding additive to the polymer solution were studied. The influence of the polyvinylpyrrolidone additive has been investigated, as is clear from the literature but it appears that has not yet been determined an optimal concentration of the additive to improve the properties. Moreover, most of the researches focused on high concentrations of additive added to the polymer solution without determining the evolution of the properties depending on the addition of polyvinylpyrrolidone.

Chapter 2 entitled " Materials, methods and experimental procedures" presents the materials used in the research activity, the methods, the experimental procedures and the means of investigation, in order to obtain and characterize the organic membranes for wastewater treatment. Detailed work on permeation properties testing and membrane characterization techniques from structural, physical and chemical point of view is detailed.

In Chapter 3 entitled "Experimental research on the role of obtaining membranes for wastewater nanofiltration" the experimental plan on how to obtain the polymer solution and manufacture the membranes with the variation of the production parameters are presented, namely with different concentrations of polysulfone in the polymer solution, with different thicknesses of the applied polymer solution layer and with the addition of different concentrations of polyvinylpyrrolidone. In the polymer membrane production stage the phase inversion method was applied by immersion into the coagulation bath of the thin film polymer solution.

Chapter 4 entitled "Experimental results on the role of main factors affecting membrane properties" presents the experimental results on the evolution of membrane properties according to the main factors specific to membrane technologies, and the obtained results are correlated with the fabrication parameters. The experimental study on the permeation properties analysis was performed in a "Dead-End" filtration cell by perpendicular flux to the membrane surface. Thus, the evolution of the distilled water flux, the permeability variation, the flux of the solution with Methylene blue and Congo Red solution, the relative flux and membrane retention capacity related to the polysulfone concentration difference, the difference in the thickness of the solution layer and the addition of the polyvinylpyrrolidone additive were conducted.

Chapter 5, entitled "Characterization of organic membranes resulting from experimental research", presents the experimental research on the influence of the production parameters on the contact angle, the porosity and the structure of the membranes obtained, researches based on SEM analysis (both surface and cross-section view) and AFM analysis. Correlation of permeation properties with physical, chemical and structural properties was achieved by determining the hydrophilicity, roughness and morphology of the manufactured membranes.

Chapter 6 presents the general conclusions, original contributions and future research directions.

The results obtained from the experimental researches were presented in scientific papers that were discussed in workshops, national and international conferences in the specialty field or published in indexed international databases (BDI), ISI Proceedings Volumes and ISI journals.

CHAPTER 1

OVERVIEW OF CURRENT RESEARCH ON THE OBTAINING AND CHARACTERIZATION OF ORGANIC MEMBRANES FOR TREATMENT OF WASTEWATER

1.1. General notions

A membrane can be characterized as a thin film or thin layer, that has the property of selectivity between two phases that can be in liquid, gaseous or vapor phase. More specifically, a membrane is a separation structure between two different phases and acts as a selective barrier in a system with certain physico-chemical properties [1].

Membrane separation technology enjoys a broad application segment that is classified as a clean industry, both in terms of manufacturing industry, energy consumption and in terms of environmental protection. It provides the possibility of substitution of consecrated processes [7], for example chemical treatment, ion exchange and distillation [6].

1.2. Membrane processes for water treatment

Membrane separation technologies are only achieved through applying a driving force to the solution of interest. The driving forces used are: pressure difference (ΔP), difference in concentration (ΔC), temperature difference (ΔT) or electric potential difference (ΔE) [17].

The pressure difference is the driving force used in wastewater treatment processes. After applying pressure on the feed solution, water passes through the membrane and leaves the pollutant particles or molecules in concentrated form on the membrane surface. Currently, filtration processes based on the use of membranes in water treatment applications in the industrial and municipal show a significant increase in market value and implementation [2].

Removing pollutants by applying membrane filtration processes is an innovative method with very good results, but the decrease in flow due to membrane fouling is still a point of interest for researchers [18]. Fouling is the deposition of pollutants on the membrane surface and structure [19].

1.2.1. Membrane classification

The membranes exhibit a very wide range depending on the material (natural or synthetic), of membrane dimensions (primarily thickness), differing according to their structure (homogeneous or heterogeneous) and the type of membrane transport (active or passive). In terms of passive transport, it is driven by pressure, solution concentration and applied electrical difference. Thus, membranes can be classified by various criteria [21].

1.2.2. Methods of membrane filtration

The process of separating impurities from liquids using membrane technology is achieved by the flow of fluids (eg. polluted water) through the filters or filter media (permeable porous media).

Using the pressure difference Δp as the driving force, the feed solution (the fluid subjected to the filtration) has a flow Q which produces the flow through the filter medium. The difference between the pressure of the fluid subjected to filtration (p_1) and the pressure of the filtered fluid (p_2) called pressure drop can be ensured by: gravitational force, fluid pressure, applied pressure on the feed solution [25].

1.3. Membrane processes using the pressure gradient

Separations through this membrane type can be divided into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Each of these processes is based on pressure action and pore size [37].

As can be seen in Table 1.2, the four processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) have as their driving force different pressures, being called barometric processes.

Tabel 1.2. Baromembrane processes and their characteristics. Adapted after [37]

Membrane process	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (OI)
Driving force [bar]	0.1 – 3	2 – 10	10 – 30	20 – 100
Particle size retained [µm]	0.1 - 10	0.02 – 0.1	0.0001-0.001	≤0.0001

1.4. Membrane fabrication

The most important fabrication processes underlying membranes are sintering, lamination, track-etch, phase inversion, and coating of ultra-thin layers.

1.4.1. Processes for technical membranes obtained by phase inversion

The phase inversion process is among the most used and underlies the method used to obtain asymmetric membranes [96]. The homogeneous polymer solution passes from the viscous liquid state into a two-phase system, namely a polymer-rich phase (solid state) and a liquid phase forming the membrane pores. The solid phase represented by the polymer is the one that forms the structure of the membrane [97].

1.5. Factors that influence the membrane fabrication process

1.5.2. Influence of the polymer concentration used in the manufacture of membranes

The parameter with the greatest influence on the membrane properties is the concentration of the polymer [204]. Polymer concentration affect membrane performance, structure and thickness [205].

The main aspect that is influenced by increasing the polymer concentration is the viscosity of the solution used to obtain the membrane

1.5.3. Influence of membrane thickness on membrane properties

Experimentally, the gradient of membrane thickness is controled in the casting process with a special knife. In general, the total thickness (Lc) and thickness of the sponge structure (Lgs) are studied. Lgs is the thickness of the sponge-like portion beneath the active layer at the surface of the membrane [221].

Over the last two decades, researchers have studied the effect of the homogeneous membrane thickness on separation performance for different binary mixtures; the flux turned out to be inversely proportional to the thickness of the membrane and the selectivity remains almost unaffected.

1.5.4. Analysis of additive types used for the preparation of membranes

The method of addition is done during preparation by simple addition of the polymer solution under continuous stirring to aditivulu [227,228,229]. The addition method is carried out during the preparation of the polymer solution by the simple addition with continuous stirring of the additive [149,155].

1.6. Partial conclusions

Studies on the preparation and characterization of organic membranes have shown that the polymer nature used to obtain asymmetric membranes used in wastewater treatment processes is a defining feature of the permeation properties.

An important aspect in the membrane production process is the control of the polymer concentration in the casting solution. Research in the field of membrane processes has focused particularly on the study of membranes with small polymer concentrations, thus very few research over the influence of high polymer concentrations.

Another important parameter in the process of obtaining organic membranes is the thickness of the applied polymer solution layer. The thickness of the polymer solution layer has not been studied sufficiently in terms of influence on membrane properties.

It has been shown that the membrane properties can also be influenced by the addition of additives in the composition of the polymer solution. A very important aspect is the membrane retention capacity that has not been sufficiently studied for certain conditions for obtaining and using them.

CHAPTER 2

MATERIALS, METHODS AND EXPERIMENTAL PROCEDURES

2.1. Materials used

Any change that may occur in one or more stages of the membrane manufacturing flow may result in a final product with different properties. Therefore, it is very important to clearly identify the solutions to be used and to precisely control all the parameters of membrane fabrication.

2.2. Polymeric membrane production stages

The membranes were obtained by applying the immersion precipitation method, which is based on the phase inversion technique. The polymer solution was obtained by adding the polymer with a well known concentration to a certain amount of NMP solvent.

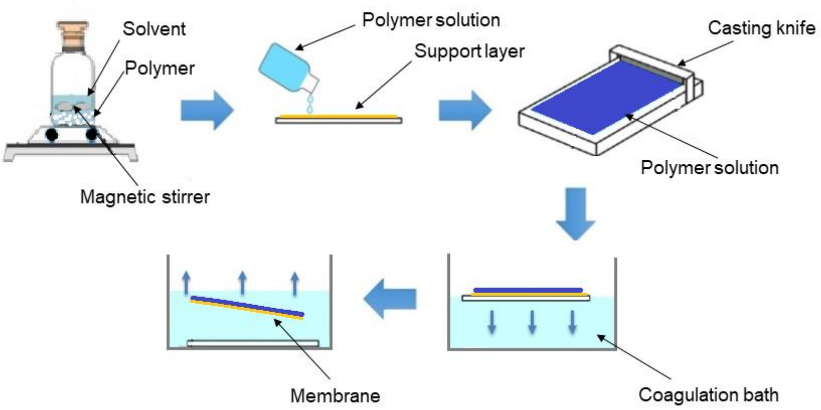


Figure 2.4. The steps for preparing polymeric membranes

The polymer solutions were obtained by dissolving different concentrations of polysulfone polymer (PSf) in the N-methylpyrrolidone (NMP) solvent. The casting solution is set to continuous stirring for 24 hours at 1200 rpm, as shown in Figure 2.4. In the case of modified polymer solutions with additives, firstly the PVP polymer and NMP solvent are allowed to stirring for one hour. The additive amounts have been previously established and, after complete dissolution of the PVP in solvent, the PSf polymer was added to the solution under continuous stir for 24 hours. After this period of continuous stirring, the solution is casted into thin films followed by immersion in a coagulation bath with distilled water for 15 minutes.

2.3. Devices used to obtain and test the membranes

2.3.3. Dead-End Filtation Cell

The Dead-End filtration is the model where the water flow direction is perpendicular to the surface of the membrane. The water is driven through the membrane by an applied pressure.

The total volume of water that is filtered by the membrane from the Dead-End cell is known as permeate.

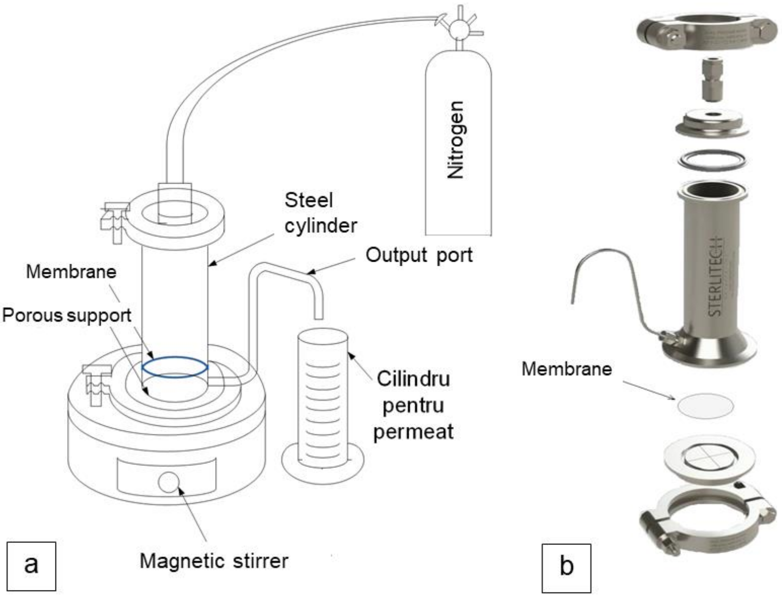


Figure 2.7. Dead-End filter cell: a. Filtering installation scheme; b.composition of the cell [279]

2.4. Methods of membrane properties investigation

2.4.1. Flux and permeability tests

The distilled water flux is the amount of water passing through the membrane dependent of membrane surface area and filtration time. Thus, following the measurements, the water flux (J_W) passing through the membrane can be calculated by the formula [201]:

$$J_W = \frac{V}{A \times \Delta t} \tag{2.1}$$

Where: J_w – flux of distilled water (L/m^{2}h), V – permeate volume (mL), A – membrane active area (m^2), Δt – filtration time of the permeate volume (s).

The pure water permeability was calculated with the equation (2.2) [287]:

$$PWP = \frac{V}{\Delta t \cdot A \cdot \Delta P} \tag{2.2}$$

Where ΔP is the working pressure.

After extracting the distilled water flux values, the dye solution flux was calculated, also, with respect to equation (2.1). Subsequently, relative flux was calculated with the ratio between dye solution flux and distilled water flux, in order to understand the fouling occurence during the filtration of dye solutions.

The relative flux was calculated by applying the equation (2.3) [288]:

$$J_R = \frac{J_C}{J_W} \tag{2.3}$$

Where: J_R – relative flux, J_C – dye solution flux, J_W – flux of distilled water.

2.4.2. Study on retention capacity

Retention is the property of the membrane to separate the solids from a solution. In this study, this property was analyzed by filtering a solution of a methylene blue dye with a molecular weight of 319.8 g·mol^{-1} and a Congo Red dye solution with a molecular weight of 696.6 g·mol^{-1}, both having a concentration of 10 ppm (parts per million). The retention ratio (R) was calculated using the following equation:

$$\mathrm{R}\,\% = \left(1 - \frac{\mathrm{C_f}}{\mathrm{C_0}}\right) \times 100 \tag{2.5}$$

Where C_0 represents the dye concentration in the feed solution (10 ppm) and C_f is the permeate concentration.

2.5. Techniques for membrane characterization

2.5.1. Scanning Electron Microscopy (SEM)

In SEM analysis, two-dimensional (2D) images of the surface of the membrane or its section is obtained by irradiating the membrane sample with an electron beam. To characterize the surface and section-view of the membranes, all the samples were coated with gold. For sectional analysis, the samples were prepared by breaking the membranes after immersion in liquid nitrogen. The images were obtained with the Philips FEI, QUANTA 200 SEM microscope.

2.5.2. Atomic Force Microscopy (AFM)

Surface roughness analysis of the manufactured membranes was performed with the Nanosurf easyScan 2 non-contact atomic force microscope. By studying the images made by the atomic force microscope, the morphology of the membrane surfaces can be observed and the roughness can be determined.

2.5.3. Contact angle measurements

The goniometer is used to measure the static contact angle, advancing and removing the contact angle and surface tension [316]. The analysis consists in observing the contact angle of a drop of liquid placed on a solid surface whilst measuring the contact line of the droplet formed [317]. To study the hydrophilicity of the membranes obtained, the OCA 15EC, DataPhysics goniometer device was used.

2.5.4. Raman spectroscopy

The Raman spectrum is given by the frequency light-scattered intensity by a photoelectric system. The resulting signal of the detector is amplified and transformed into a suitable shape for frequency plotting.

For the analysis of obtained samples in this thesis, a 785 nm Raman spectrometry system of StellarNet Inc was used [334].

2.6. Partial conclusions

In the study of polymer membranes applied in water treatment, polysulfone polymer and the solvent N-methylpyrrolidone were used to obtain the reference membranes. For membrane preparation, the phase inversion method was used by immersing the polymer solution film in a coagulation bath.

Thus, the obtained membranes show the point of interest for studying the distilled water flux, membrane permeability, and retention capacity. Membrane performance is closely related to structural features.

CHAPTER 3

EXPERIMENTAL RESEARCH ON THE ROLE OF OBTAINING MEMBRANES FOR NANOFILTRATION OF WASTEWATER

3.1. Motivation and experimental plan

Membrane processes are among the newest and most advantageous methods of wastewater treatment due to the reliability and high degree of adaptation of the membranes, depending on the industry in which they are applied or the degree of contaminants separation. Due to the wide diversity of membrane types and application areas, research on the improvement of membrane processes is an important point of interest [335].

In particular, the influence of three parameters of membrane production was studied: polysulfone concentration in the polymer solution (23, 25, 27 and 30 wt.(%)); the thickness of the applied polymer solution (100, 150, 200 and 250 μm) and addition of polyvinylpyrrolidone (0.5, 1, 1.5 and 2 wt.(%)).

3.2. Fabrication and properties of membranes depending on polymer concentration

3.2.1. Preparation of solutions with different polymer concentrations

Regarding the manufacture of the polymeric membranes, a polymer solution composed of polysulfone and N-methylpyrrolidone was obtained.

The concentration of polysulfone and N-methylpyrrolidone, respectively, was calculated according to the density of each material so as to obtain the four concentrations of the polymer in solution, which are presented in Table 3.1.

Tabel 3.1. The composition of the polymer solution

Polysulfone [wt.(%)]	**N-methylpyrrolidone [wt.(%)]**
23	77
25	75
27	73
30	70

Each solution was obtained at room temperature (23 ° C) using the same type of electro-magnetic stirrer set at 1200 rpm.

3.2.2. Obtaining of membranes with different polymer concentrations

The manufacturing process of thin films complied with the following steps:
- the glass plate with a support layer was positioned on the applicator (Figure 3.4 - a.);
- the support layer was wetted with N-methylpyrrolidone solvent;
- the excess of sovent was removed (Figure 3.4 - b);

- the thickness was fixed and the casting knife was positioned at the end of the applicator (Figure 3.4-c);
- pouring of the polymer solution onto the support layer (Figure 3.4 - d);
- casting of the thin film polymer film onto the support layer using the applicator and the casting knife (Figure 3.4 - e);
- the glass support with the applied film was immersed in the coagulation bath (distilled water) for 15 minutes (Figure 3.4 - f);
- the obtained membrane was washed with distilled water to remove the solvent residues.

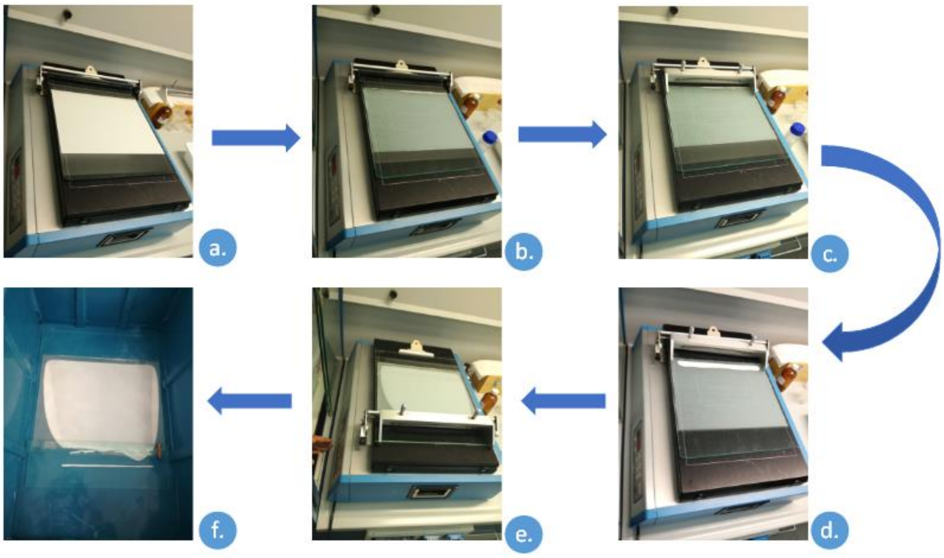


Figure 3.4. Technological procedure for the casting of thin films

After the phase inversion is complete, the membranes were stored in distilled water for 24 hours followed by the measurement of the final thickness. The measurements were made on 6 different samples at five points (Table 3.2).

Table 3.2. The thickness of the membranes according to the PSf concentration

PSf concentration [wt.(%)]	**The thickness of the membranes (with the support layer) [µm]**	**Standard deviation**	**Degree of thickness reduction [%]**
23	260.8	5.77	34.07
25	271.4	4.41	31.29
27	282.6	6.83	28.50
30	303.4	2.71	23.18

* The support layer thickness is 145 µm and the wet film thickness of casted solution was 250 µm

By increasing the polymer / solvent ratio, the amount of solvent is lower and the reduction in thickness of the membrane is lower. This is shown in Table 3.2 and Figure 3.5, so that by increasing the concentration of the polymer, the membranes are thicker. Figure 3.5 shows sectional images of the membranes, performed with the Olympus CX31 optical microscope with a magnification of 4X. To observe the sections of the samples, a surgical scalpel was used for cutting.

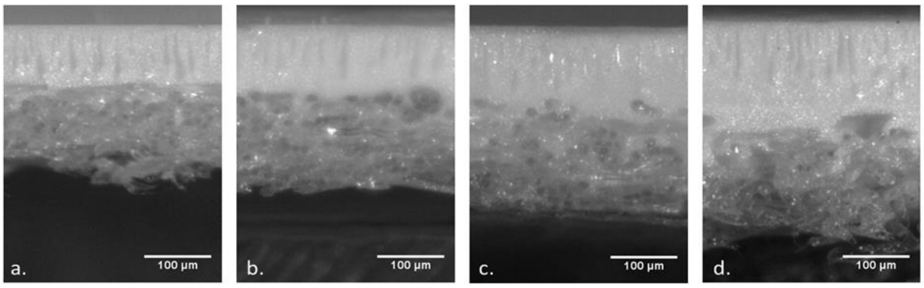


Figure 3.5. Variation of membrane thickness: a. 23 wt.% PSf; b. 25 wt.% PSf; c.27 wt.% PSf; d. 30 wt.% PSf

After the membranes were obtained, they were analyzed in Chapters 4 and 5 in terms of permeation performance and were characterized in terms of morphological structure, surface roughness, hydrophilicity and membrane porosity.

3.3. The study of the influence of membrane thickness

3.3.1. Obtaining the solutions for membranes with different thicknesses

The polymer solutions used for the production of membranes with different thicknesses are composed of polysulfone (PSF) with 27 wt.(%) and 73 wt.(%) N-methyl pyrrolidone. In order to obtain the solutions, the operating mode set out was observed in subsection 3.2.1.

3.3.2. Manufacture of membranes with different thicknesses of applied polymer solution film

To analyze the effect of the applied polymer solution thickness, membranes with four different thicknesses were manufactured, as can be seen in Table 3.3.

Table 3.3. Film thickness of applied polymer solution

Polysulfone [wt.(%)]	N-methylpyrrolidone [wt.(%)]	Polymer solution film thickness [μm]]
27	73	100 150 200 250

Following the phase inversion, the polymer layer is compacted and a reduction in membrane thickness is obtained, as shown in Table 3.4 and can be observed in Figure 3.9. The phase inversion time from the start of this process to the full demixing of the solvent is directly proportional to the thickness of the membrane [206].

Table 3.4. Thickness reduction after phase inversion method for the membranes with 27 wt.(%) PSf

Casted wet film thickness [μm]	Membrane thickness (with support layer) [μm]	Standard deviation	Reduction of thickness [%]
100	236.6	3.41	3.42
150	265.2	4.26	9.96
200	277.8	3.66	19.53
250	282.4	2.92	28.50

* The thickness of the support layer is 145 μm. The reported casted wet film thickness was not with the support layer.

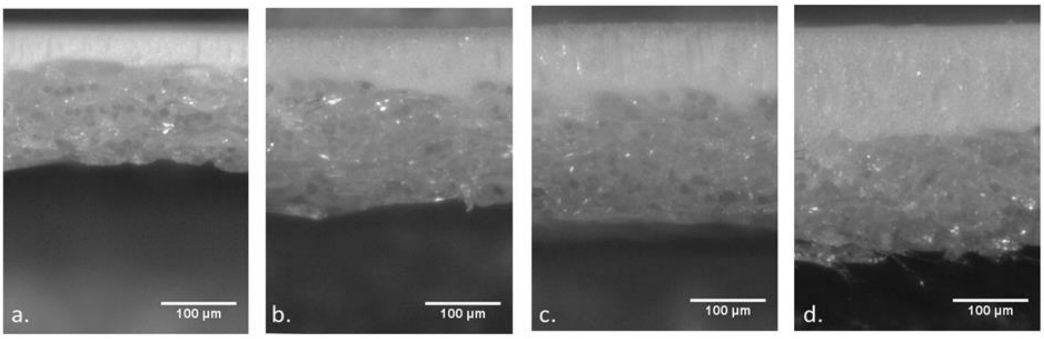


Figure 3.9. Optical microscope observations of thickness variation of membrane polymer solution layer with 27 wt.% PSf: a. 100 μm; b. 150 μm; c. 200 μm; d. 250 μm

The increase in membrane thickness corresponds to the increase in applied film mass, which means a time when the water penetration velocity was higher than that of the solvent extraction. On the other hand, the reduction in the thickness of the membrane may correspond to the dissolution of the solvent in the polymer solution caused by the phase inversion rate hence the diffusion of the solvent in water. The different thicknesses influences the properties and characteristics of the membranes, these aspects being of interest in the following chapters.

3.4. Preparation of membranes with additive blended in the polymer solution

3.4.1. Solution preparation with additive addition

The influence of PVP additive was analyzed by using the polysulfone solution with 27 wt.% and N-methylpyrrolidone solvent with 73 wt.%. By adding the four concentrations of PVP (Table 3.5), the weight of polysulfone and N-methylpyrrolidone was equally reduced as the total solution was 100%.

Table 3.5. Added polyvinylpyrrolidone concentrations in the polymer solution

Additive	**wt.%**
PVP (polyvinylpyrrolidone)	0.5
	1
	1.5
	2

3.4.2. Manufacture of membranes with polyvinylpyrrolidone addition

The polyvinylpyrrolidone blended membranes were obtained by applying a thin film of 150 μm polymer solution to a polyester support layer and immersed in distilled water. The support layer was previously wetted with NMP solvent.

During the phase inversion step, the solvent is replaced by the distilled water from the coagulation bath resulting in different thickness of the obtained membranes compared with the initial casted wet thickness. The support layer has a thickness of 145 μm and after application of the polymer solution film, the membrane would have 295 μm but the final thickness is less than the theoretical thickness.

Table 3.6. The thickness of the membranes with addition of PVP additive

PVP concentration [wt.(%)]	**The thickness of the membranes (with the support layer) [µm]**	**Standard deviation**	**Degree of thickness reduction [%]**
0.5	222.6	6.58	24.54
1	234.8	6.87	20.40
1.5	244.8	5.54	17.01
2	256.8	2.83	12.94

*The thickness of the support layer is 145 µm and the film thickness of the casted solution is 150 µm.

By increasing the concentration of PVP in the polymer solution, the higher concentration of the additive membrane has a greater thickness than the membrane with 0.5 wt.% PVP. The variation of membrane thickness according to the addition of PVP additive is shown in Table 3.6 and Figure 3.11.

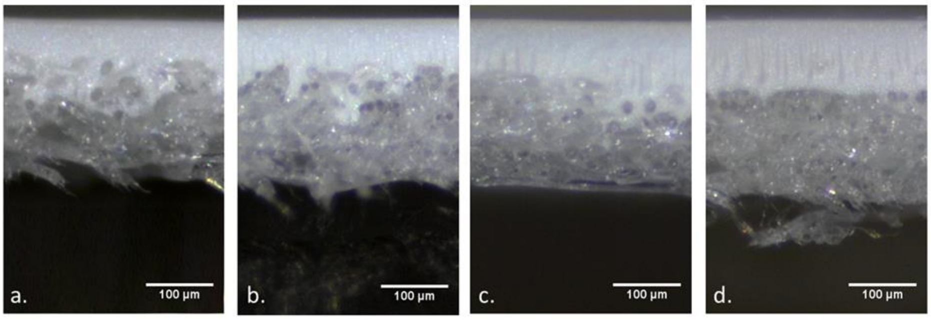


Figure 3.11. The variation of the membranes thickness with PVP addition: a. 0.5 wt.(%); b. 1 wt.%; c. 1.5 wt.%; d. 2 wt.%

3.5. Partial conclusions

The membranes were obtained by the phase inversion method by immersing the polymer solution film in a coagulation bath composed of distilled water.

The variable parameters in the process for preparing the membranes were: concentration of PSF in the polymer solution from 23 to 30 wt.%, the applied thickness of the polymer solution (from 100 to 250 µm) and the addition of various concentrations of PVP (from 0.5 to 2 wt.%).

After the membranes were obtained, their thickness was measured in a solid state. Thus, it has been observed that the final thickness of the membranes is less than the theoretical thickness by casting the film on the support layer.

CHAPTER 4

EXPERIMENTAL RESULTS ON THE ROLE OF MAIN FACTORS INFLUENCING THE MEMBRANE PROPERTIES

4.1. Experimental plan

In this chapter, experimental researches regarding the determination of membrane properties with different parameters are included such as polymer concentration, thickness of the polymer solution layer, addition of additive and its concentration. The following analysis was carried out to achieve the objectives: Membrane Distilled Water Flux; Membrane permeability; Dye retention flux; Relative flux; Dye retention capacity.

4.2. Distilled water flux determination for the studied membranes

4.2.1. Determining the flux of distilled water depending on the concentration of the polymer

In Figure 4.1 it is observed that at higher polymer concentrations the flux of distilled water is lower. The stable values of the distilled water flux, the membrane with 30 wt.(%) shows the smallest water flux, about 43 (L/m^2·h). According to literature, the reduction of polysulfone concentration produces an increase in water flux [341]. A decrease of 10%, 16.66% and 23.33% of polymer concentration (27, 25 and 23 wt.(%) PSf) produces a flux increase of approximately 118%, 272% and 539%.

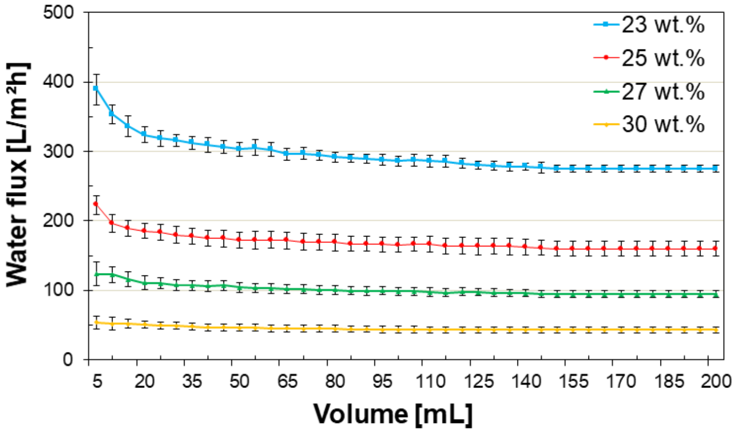


Figure 4.1. Influence of polysulfone concentration on the distilled water flux of the studied membranes

4.2.2. Influence of polymer layer thickness on the flux of distilled water

The four different types of membrane thicknesses of the polymer layer (100, 150, 200 and 250 μm) were tested in the perpendicular filtration cell and it was observed that the distilled water flux is inversely proportional to the thickness of the membrane, as can be seen in Figure 4.3.

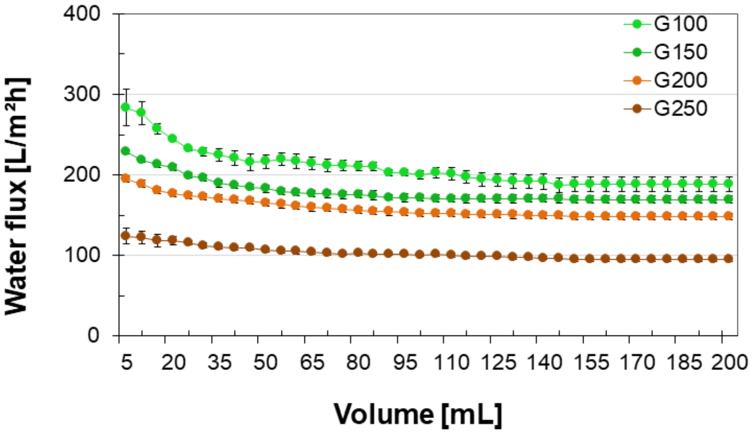


Figure 4.3. The influence of the thickness (G) of the applied solution films on the distilled water flux for membranes with 27 wt.(%) PSf

By increasing the thickness of the polymer solution layer, the membrane opposes more resistance due to the higher thickness, and the passage of the distilled water becomes more difficult, so the flux of distilled water decreases.

4.2.3. The variation of the membrane distilled water flux depending on the polyvinylpyrrolidone additive

The membranes modified with additive were analyzed from the distilled water flux point of view. The four membrane types based on the polysulfone solution of 27 wt.(%) to which 0.5; 1; 1.5 and 2 wt.(%) polyvinylpyrrolidone was added as an additive, were studied.

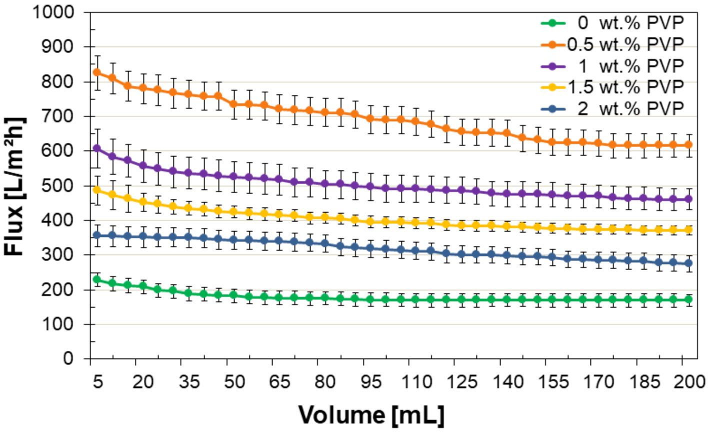


Figure 4.5. Flux of distilled water through membranes with addition of PVP additive

The distilled water flux of the membranes presents an inverse-proportional relationship with the increase in concentration of PVP in the polymer solution. In Figure 4.5 it is observed that the permeate flux is increased approximately three times for the membrane with addition of 0.5 wt.(%) PVP compared to the membrane with 27 wt.(%) PSf whitout additive. When the amount of additive increases above the 0.5 wt.(%) (1, 1.5 and 2 wt.(%) PVP), the distilled water flux decreases, whereas 2 wt.(%) PVP exhibits a flux of approximatly 2 times higher than the water flux of membrane without additive.

4.3. Experimental research on permeability of the studied membranes

4.3.1. Variation of membrane permeability depending on polymer concentration

The high concentration of polysulfone in the application solution results in a higher viscosity, and dispersion time of the solvent in the coagulation bath is slower. Demixing delay produces more and more pores in the membrane structure [346]. The membranes obtained from solutions with lower concentration of polymer show larger pores, which offers higher permeability, also [347].

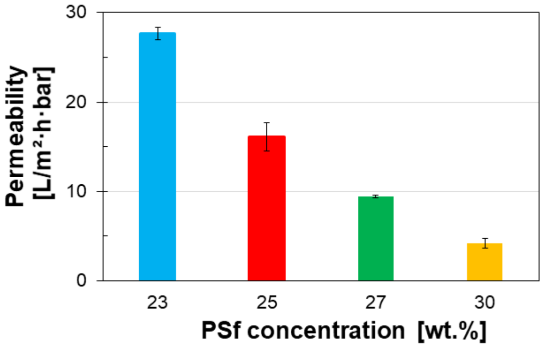


Figure 4.8. Permeability of membranes with different polysulfone concentration

4.3.2. Influence of polymer layer thickness on membrane permeability

Membrane performance on permeability is influenced by the thickness of the casted polymer solution film, which produces differences in membrane structures, namely in their morphology.

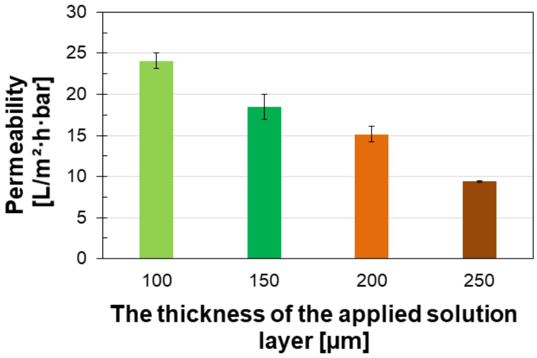


Figure 4.9. Permeability evolution of membranes with different thicknesses of polymer solution film

The additional increase in membrane thickness produces a higher top layer, which provides greater compaction resistance, but a lower permeability. The permeability of the membranes with different thicknesses of the polymer solution layer is shown in Figure 4.9.

4.3.3. Study on the nature of the additive in the polymer solution over membrane permeability

The results of the permeability study on membranes with addition of additive retained the inversely proportional trend, since at high concentrations of PVP a decrease in permeability was observed. However, the permeability of the membrane with the additive is much higher than the permeability of the membrane without additive (Figure 4.10) [349].

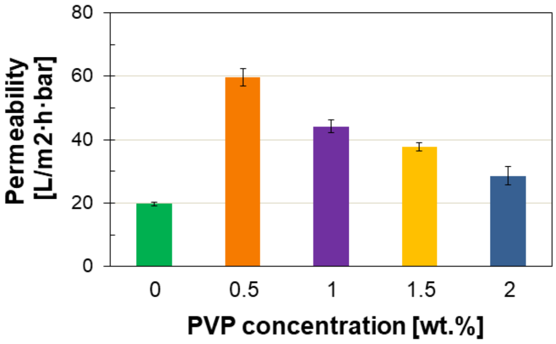


Figure 4.10. Influence of PVP concentration on membrane permeability

Increasing the concentration of PVP in the polymer solution beyond the maximum performance creates a denser structure of the membrane, which leads to a decrease in permeate flux and permeability.

4.5. Variation of relative flux

4.5.1. Influence of the polymer concentration over the evolution of the relative flux

Membranes with a concentration of 23 and 25 wt.(%) PSf have a relative flux lower compared to the other two types of membranes (Figure 4.14).

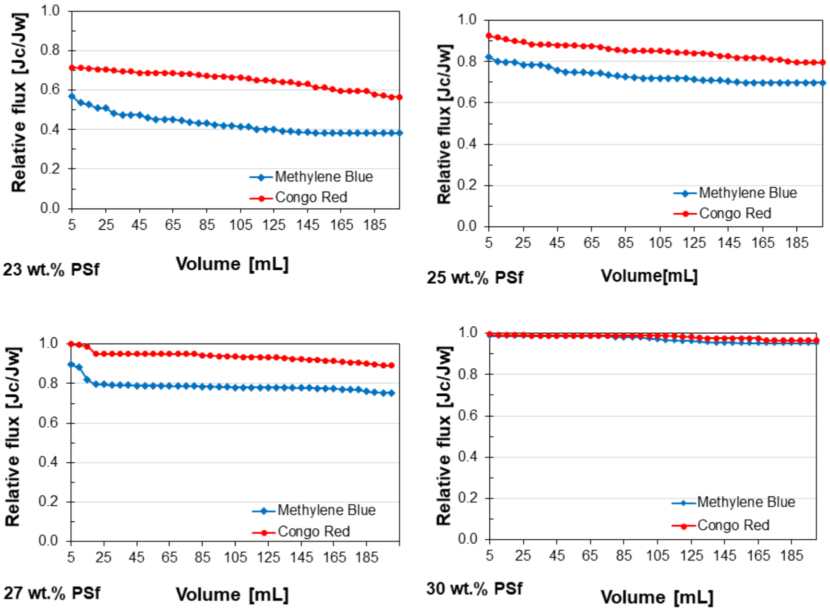


Figure 4.14. Evolution of relative flux of membranes with different concentration of PSf

The membrane with 30 wt.(%) PSf has the highest and most stable relative flux, with the lowest fouling. For the membrane with 27 wt.(%) PSf, the retention of 200 mL of dye also has a low fouling phenomenon.

It is noted that all four types of membranes show a better relative flux for the retention of Congo Red dye.

4.5.2. Variation of relative flux depending on the thickness of applied polymer layer

As depicted in Figure 4.15, the relative flux of the membranes with different thicknesses of applied polymer layer show almost the same trend and values, the lowest fouling being for the highest thickness membrane, the fouling resistance being about 0.03% higher than the other membranes.

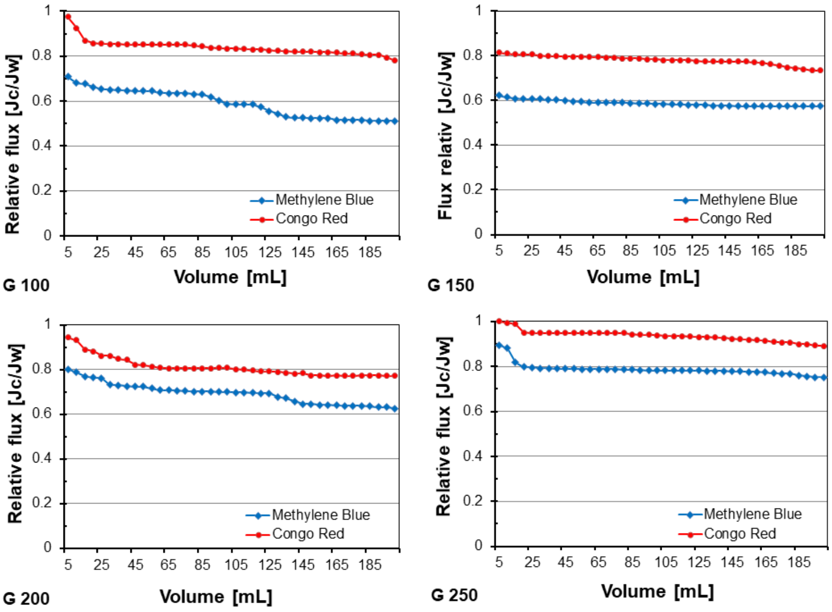


Figure 4.15. The influence of the polymer layer thickness (G) on the relative flux recorded through the membranes by 27 wt.(%) PSf

Following the ratio between distilled water flux and retention flux of dye solutions of the membrane with 27 wt.(%) PSf and with different thicknesses of polymer layer (100, 150, 200 and 250 µm), it was observed that, in all four cases, the relative flux is close to the ideal value of low fouling.

4.5.3. Determination of relative flux depending on polyvinylpyrrolidone additive concentration

When analyzing Figure 4.16, it is noted that the membrane with 2 wt.(%) PVP addition exhibits a relative flux close to value 1, meaning that this membrane has the lowest fouling in the case of 10 ppm methylene blue solution filtration.

Due to the presence of polyvinylpyrrolidone on the surface but also in the membrane matrix, its hydrophilic property causes a lower fouling tendency than the pure membrane. The higher concentration of PVP in the membrane composition, the fouling is reduced, as evidenced by the relative flux tests.

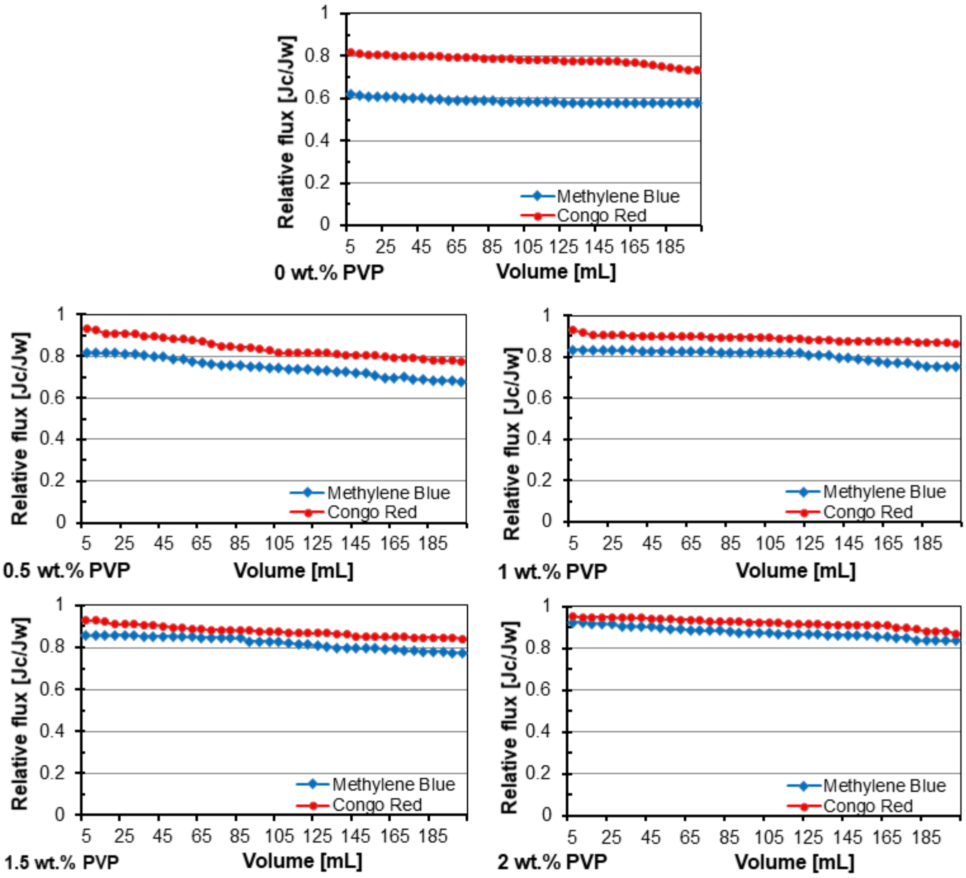


Figure 4.16. Relative flux for membranes with different concentrations of PVP

4.6. Retention capacity of studied membranes

4.6.1. Retention capacity evaluation depending on polymer concentration

The retention degree of the membranes with different polymer concentrations was studied. Figure 4.17 shows that membranes with higher polysulfone concentrations have a higher retention for both types of dye solutions [351].

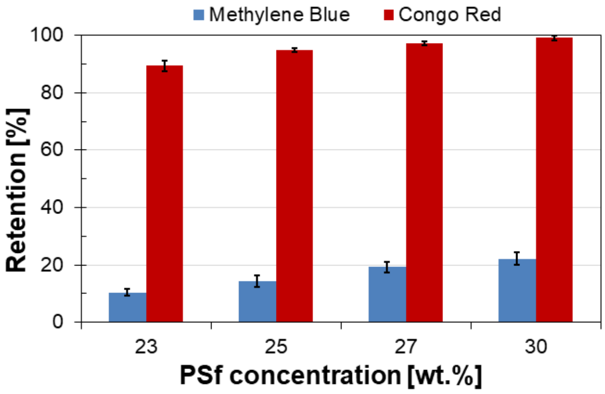


Figure 4.17. Retention of polymeric membranes based on polysulfone concentration

The variation of the polymer concentration in the membrane composition leads to differences in pore size and porosity, so increasing the polymer concentration produces a decrease in distilled water flux and improves the retention capacity [355].

4.6.2. Determination of the retention capacity of membranes with different thicknesses

By analyzing the membrane retention capacity of 27 wt.(%) PSf in Figure 4.18, it is noted that the retention increases with membrane thickness while permeability decreases.

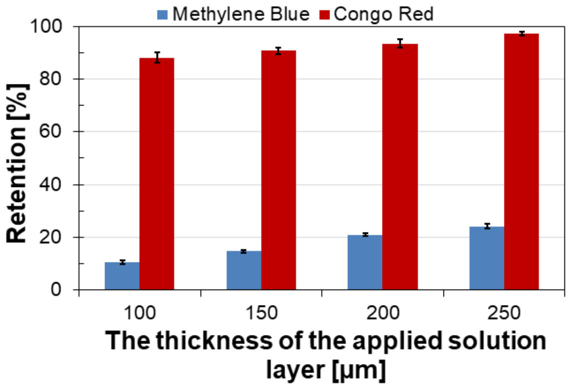


Figure 4.18. The influence of thickness (G) of polymer layer on dye retention capacity for membranes with 27 wt.(%) PSf

In the case of the Methylene Blue solution, the retention decreases by approximately 50% with the reduction in thickness. For membranes with a thickness of 100 µm, the retention is 10.51%, while the 250 µm thick membrane has a retention value of 24.02%. Conversely, the capacity of retaining the Congo Red dye with the studied membranes does not differ greatly depending on the thickness of the polymer solution layer.

4.6.3. Study on the ability to retain dyes for membranes with polyvinylpyrrolidone additive

In Figure 4.19 it is observed that by the addition of polyvinylpyrrolidone an improvement in the membrane retention capacity has been achieved since the retention is influenced by the size of the membrane pores.

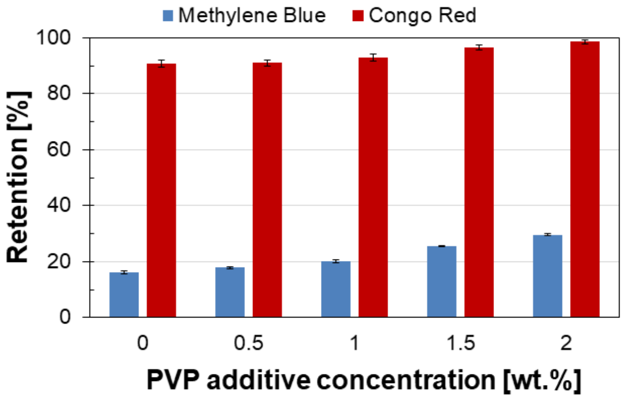


Figure 4.19. Capacity of retaining dyes for membranes with different concentrations of PVP, in wt.(%)

Due to the increase in PVP concentration, the phase inversion process in the coagulation bath between the solvent and distilled water slows down. First, dissolution of the additive in the distilled water takes place, suppressing the formation of pores on the surface of the membranes, forming a denser active layer. A structure with an increased porosity was formed under the upper membrane layer. At higher additive concentrations, the membranes exhibit smaller and lesser pores at the surface, resulting in an increase in retention capacity.

4.7. Partial conclusions

The results obtained from the research revealed that the flux of distilled water decreased when the polysulfone concentration increased from 23 to 30 wt% (%) by about 85%. Regarding the membrane retaining capacity of 23, 25, 27 and 30 wt.(%) PSf, an improvement in dye retention was observed by increasing the concentration of polymer in the membrane composition.

The analysis of membranes obtained with variations in thickness of polymer solution layer in terms of the distilled water flux shows that by increasing the thickness, water flux decreases. By determining the retention capacity of membranes with different thicknesses of the polymer layer it has been observed that it increases by only 10% with the increase in thickness.

The addition of PVP improves the membrane permeability, as well as the retention of dye solutions. This is very important because, for membranes without the addition of PVP additive, the two properties (permeability and retention) were inversely proportional.

CHAPTER 5

CHARACTERIZATION OF ORGANIC MEMBRANES OBTAINED IN THIS STUDY

5.1. Membrane hydrophilicity

5.1.1. Influence of polymer concentration on hydrophilicity of membranes

Although membranes are obtained from the same type of polymer, it has been observed that the membranes with higher concentrations of PSF tend to a more hydrophobic nature, this being influenced by the surface roughness of the membranes. Thus, membranes with higher concentrations of polymer has a lower roughness and a higher contact angle. According to the results of Zhang et al. [353], the hydrophilicity of the membranes is closely related to the surface roughness of the membranes. The hydrophilic membranes have a high roughness, and the hydrophobic membranes have a lower surface roughness.

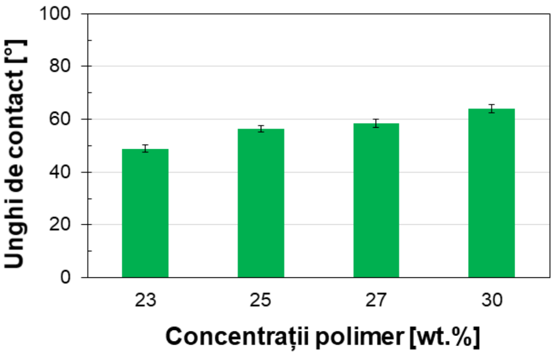


Figure 5.1. Hydrophilicity analysis of membranes with different concentrations of PSF by the contact angle method

A more hydrophobic surface means that the membrane exhibits a low affinity to water (mainly to hydrophilic compounds) and creates a poor interface in polar solutions.

5.1.2. Variation of the contact angle depending on the thickness of applied polymer layer

As can be seen in Figure 5.2, the contact angle between the water drop and the membrane surface shows an insignificant difference with increasing thickness, which means that the hydrophilic property is not considerably influenced by the thickness of the solution layer applied.

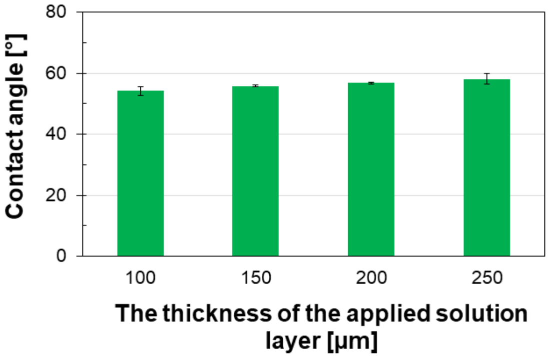


Figure 5.2. Evolution of hydrophilicity according to the thickness of polymer solution layer

5.1.3. Study on the influence of additive over membrane hydrophilicity

In Figure 5.3. it is noted that the membranes with additive possess lower contact angle because the polyvinylpyrrolidone creates higher pores by volume, which makes the water to easily penetrate the pores of the membrane. This shows that PVP-modified membranes have higher hydrophilic nature than the membrane with no additive, due to the fact that polyvinylpyrrolidone is a hydrophilic polymer. This evolution of hydrophilicity was also observed by Saljoughi E. et al. (2009) in its research, by the addition of PVP additive with 3 and 6 wt.(%) in the cellulose acetate solution, which increasses the hydrophilic nature of the membranes [240].

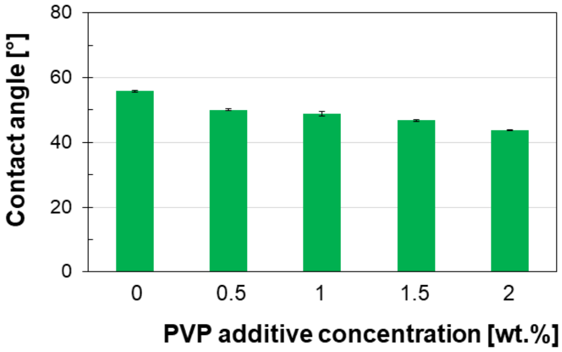


Figure 5.3. Influence of PVP addition on membrane hydrophilicity

The high performance of the membranes that can be verified by the coexistence of high permeability and selectivity, where these two properties are ensured by a remarkable balance of hydrophilicity and porosity [26]. Increasing hydrophilicity is an advantage as it improves the properties of permeability and fouling resistance of membranes [358].

5.2. Porosity of studied membranes

5.2.1. Influence of polymer concentration on membrane porosity

If the polymer solution has a lower percentage of solvent, at the moment of phase inversion between NMP (solvent) and water (non-solvent) fewer pores are produced, which means that the membrane has a lower porosity structure. Thus, for the formation of the porous structure, the solvent in the polymer solution plays a very important role because it facilitates pore formation.

By increasing the concentration of PSf with 2 wt.(%), the porosity decreases approximately 25%. By comparing the membranes with 23 and 30 wt.(%) PSf, a 49% decrease in porosity was observed.

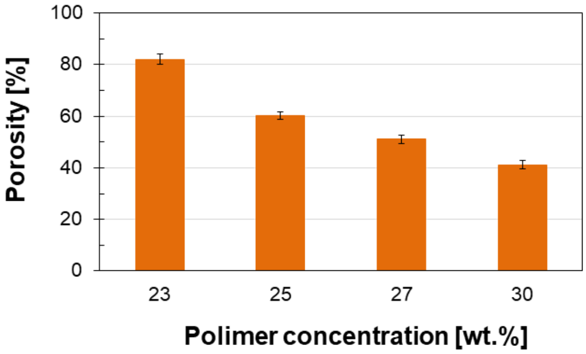


Figure 5.4. Porosity variation depending on the concentration of PSF in the membranes

5.2.2. Evolution of porosity depending on the thickness of applied polymer layer

As the membrane porosity is greater, the membrane exhibits less mechanical strength due to the pore fractions, these areas reduce the mechanical properties of the membrane. In the case of PSF membranes with 27 wt.(%) of different thickness, it has been observed that the variation in porosity is insignificant.

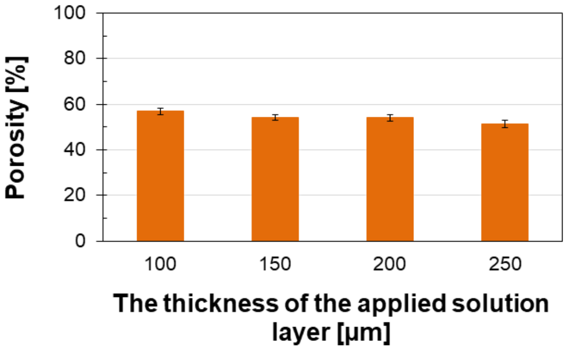


Figure 5.5. Porosity of membranes with different thicknesses of the solution layer

5.2.3. Variation of membrane porosity by additive addition

In the case of studied membranes, the evolution of porosity based on the concentration of PVP is influenced by the soluble character of the additive in the coagulation bath (distilled water), a phenomenon that slows down the transition from the liquid state to solid state of the thin film. The concentration of the additive increases, the porosity is higher, which means that the PVP assits the progress of pore formation which determine higher porosity. Increased porosity leads to increased flux and permeability.

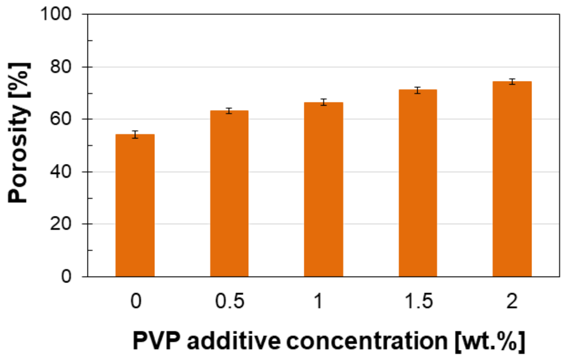
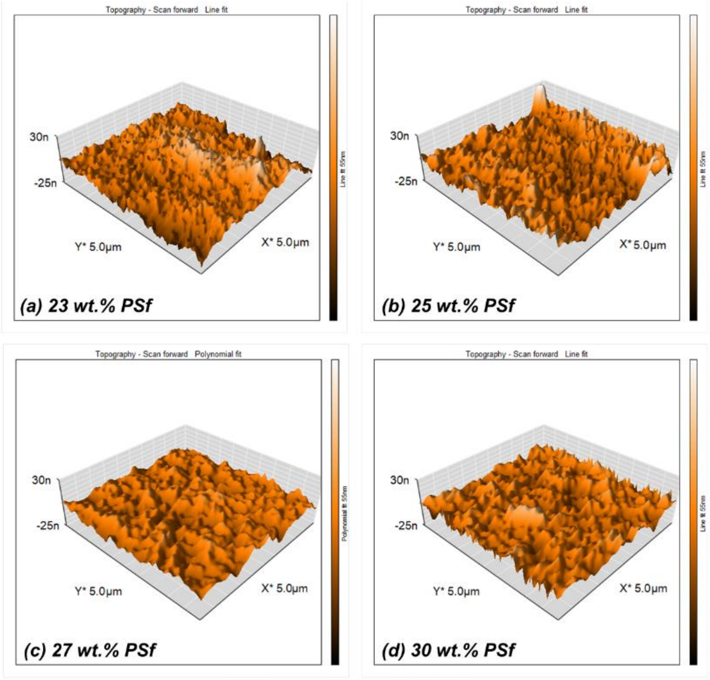


Figure 5.6. Influence of PVP addition in membranes on the evolution of porosity

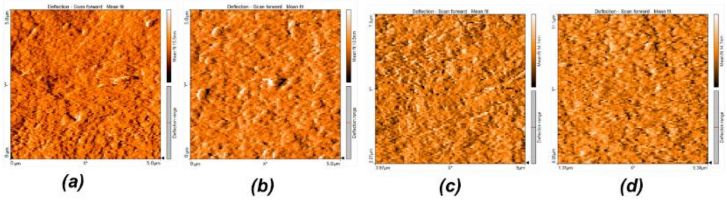
5.3. Membrane surface analysis by atomic force microscopy (AFM)

5.3.1. Analysis of atomic force microscopy (AFM) of membranes of different polymer concentrations

In membrane 3D surface AFM images, the brightest area illustrates the highest point on the surface of the membrane, and the dark regions represent the valleys or membrane pores [367]. The surface roughness variation of the 3D and 2D membranes is shown in Figure 5.7.



I. Topographic analysis 3D



II. Topographic analysis 2D

Figure 5.7. AFM images for membranes obtained with four different concentrations of PSf: I. Topographic 3D Analysis; II. Topographic 2D analysis

In Table 5.1. it can be noticed that the difference between the roughness values is lower at higher concentrations of PSf, thus increasing the polymer concentration from 23 to 25 wt.(%) PSf the roughness declines from 5,543 nm to 4,193 nm and for membranes with 27 and 30 wt.(%) PSf the difference is lower as it decreases from 3,306 to 3,096 nm.

Table 5.1. Surface roughness of membranes with different PSf concentrations

PSf concentration [wt.(%)]	**Surface Roughness [nm]**	**Standard deviation**	**Linear roughness [nm]**	**Standard deviation**
23	5.54	±0.56	6.38	±0.77
25	4.19	±0.24	4.58	±0.09
27	3.30	±0.48	3.66	±0.15
30	3.09	±0.31	2.26	±0.61

Yi-Fan Zhao et al. (2013) observed that the surface roughness influences the hydrophilicity of the membrane, since if the membrane has a higher roughness, the contact angle will be lower [370].

5.3.2. Atomic force microscopy analysis on membranes with different thicknesses of the applied polymer layer

The ratio of polymer and solvent used in the thin film application solution influences the roughness, because the phase inversion by diffusion of the solvent into the coagulation bath produces the porosity and the roughness of the membrane.

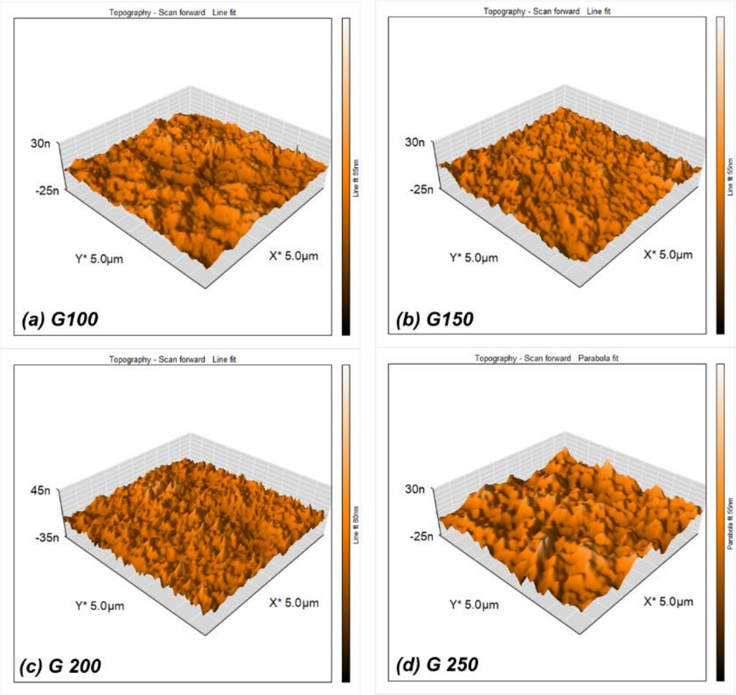
Table 5.2 shows that the roughness of the membranes obtained at different thicknesses of the solution layer decreases slightly by increasing the thickness from 100 to 250 µm.

This decline of the roughness can be correlated with the increase of the contact angle, these two parameters being inversely proportional [370].

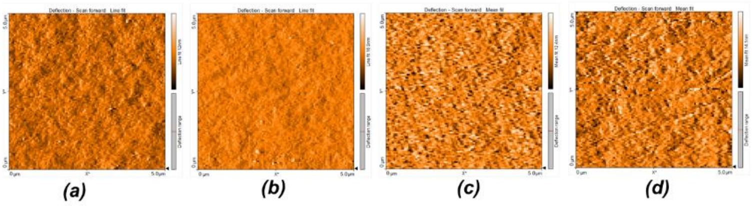
The differences in surface roughness are obtained due to different speed of dissolution of the solvent, this is due to different thickness. Having a lower thickness of the polymer solution layer, the solvent dissolves more readily as water from the coagulation bath penetrate immediately into the applied film.

Table 5.2. The surface roughness of the membranes with variations thickness of the solution layer of 27 wt.(%) PSf

Polymer solution layer thickness [µm]	**Surface Roughness [nm]**	**Standard deviation**	**Linear roughness [nm]**	**Standard deviation**
100	3.96	0.50	3.96	0.09
150	3.85	0.51	3.87	0.21
200	3.41	0.08	3.78	0.15
250	3.30	0.48	3.64	0.15



I. Topographic analysis 3D



II. Topographic analysis 2D

Figure 5.8. AFM images of 27 wt.(%) PSf membranes with different coating thicknesses: I. Topographic 3D analysis; II. Topographic 2D analysis

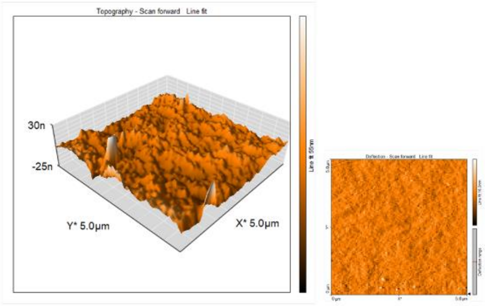
5.3.3. Topographic analysis of membranes with different concentrations of polyvinylpyrrolidone additive

In the study of additive-modified membrane properties, it was observed that the addition of 0.5 wt.(%) PVP in the solution of 27 wt.(%) PSf improved these properties, but by increasing the additive concentration, the permeability and water flux showed lower values. This is due to the change in morphology, porosity and roughness. While maintaining the same trend, membrane roughness decreases by increasing from 0.5 to 2 wt.(%) PVP.

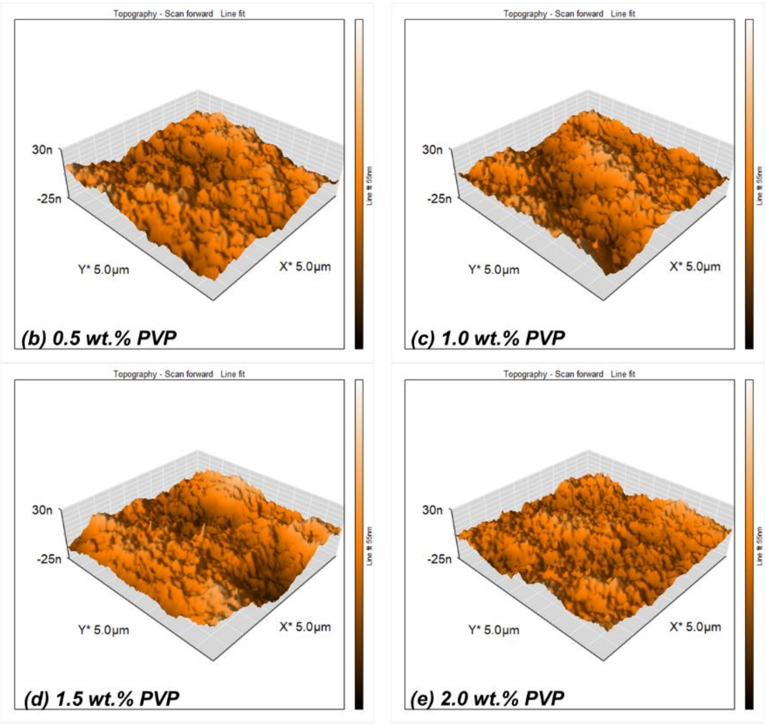
The recorded values for the surface roughness of non-additive and additive membranes are shown in Table 5.3.

Table 5.3. The influence of PVP additive in PSf solution with 27 wt.(%) on membrane roughness

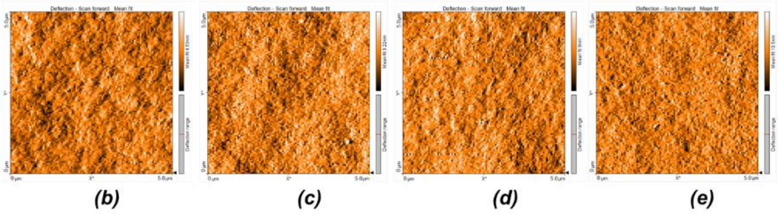
PVP additive concentration [wt.(%)]	**Surface Roughness [nm]**	**Standard deviation**	**Linear roughness [nm]**	**Standard deviation**
0	3.85	0.51	3.87	0.21
0.5	6.53	0.48	7.39	0.27
1	5.69	0.70	6.03	0.61
1.5	4.55	0.36	5.40	0.85
2	4.11	0.30	4.46	0.46



(a) 0 wt.% PVP



I. Topographic analysis 3D



II. Topographic analysis 2D

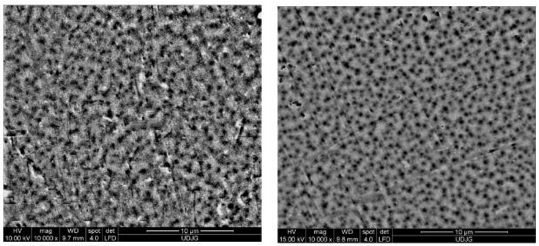
Figure 5.9. Roughness analysis by AFM microscopy of PVP-added in the solution of 27 wt.(%) PSf membranes: I. Topographic 3D analysis; II. Topographic 2D analysis

Analyzing AFM 2D images, the darker areas represents the membrane pores. By increasing the PVP concentration from 0.5 to 2 wt.(%), pore presence is lower on the surface of the membrane, which correlates with SEM surface images. Instead, it has been observed that the porosity of the membranes increases by increasing the PVP concentration, but the porosity is higher in the lower layer of the membrane, due to the formation of the very dense layer on the surface of the membranes.

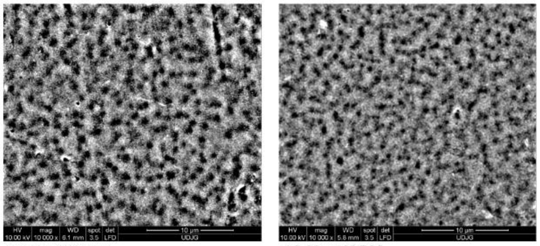
5.4. Determination of membrane morphology by electronic microscopy

5.4.1. Study on morphology evolution of the polymer concentration on the membranes

As regards the surface morphology of the polysulfone membranes with different concentrations, Figure 5.10 reveals that the membranes with low concentrations of polymer showed higher porosity. The 23 and 25 wt.(%) PSf membranes have a structure with larger pores, confirming that their water flux and permeability is higher.



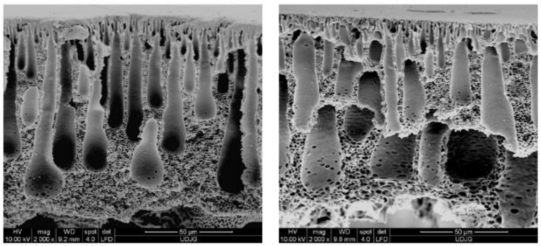
(a) 23 wt.% PSf *(b) 25 wt.% PSf*



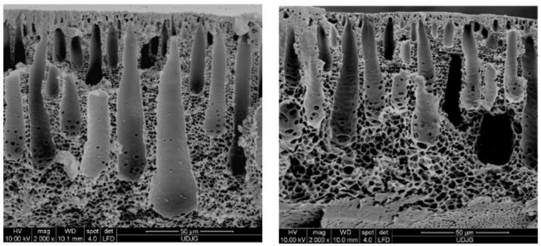
(c) 27 wt.% PSf *(d) 30 wt.% PSf*

Figure 5.10. Surface SEM images: a. PSf 23 wt.(%), b. PSf 25 wt.(%), PSf 27 wt.(%) și PSf 30 wt.(%)

Analyzing the membrane cross-section it was observed an asymmetric structure consisting on a dense top layer and a porous substrate. The substrate appears to have elongated cavities as well as macrovoid structure (sponge-like).



(a) 23 wt.% PSf *(b) 25 wt.% PSf*



(c) 27 wt.% PSf *(d) 30 wt.% PSf*

Figure 5.11. Cross-section SEM images of membranes with different polysulfone concentrations

Membranes manufactured with the phase inversion method generally have asymmetric structures and their formation is closely related to the affinity between NMP and water, leading to instantaneous demixing. Such morphological structures were also obtained by Holda et al. (2013) in the study of PSf membranes dissolved in N-methylpyrrolidone (NMP) and tetrahydrofuran (THF) solvents. They observed that the thickness of the surface layer increases and the number of macrovoids decreases to higher concentrations of polymer [373].

5.4.2. Influence of the polymer layer thickness on the morphological structure

The porous asymmetric structure of the membranes can be obtained mainly by the phase inversion method by the transfer of the solvent from the casting solution to the non-solvent in the coagulation bath, in our case NMP and water, also called demixing (phase separation).

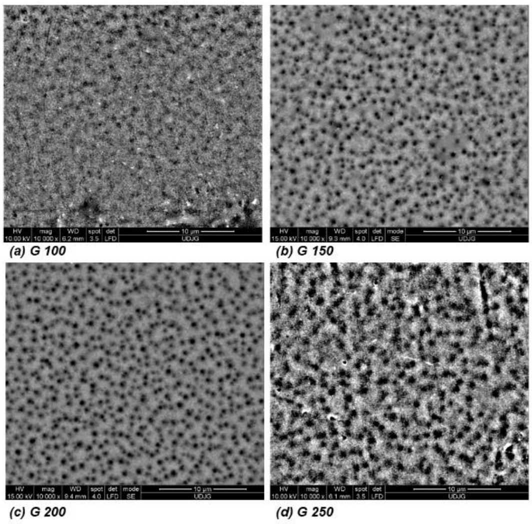

(a) G 100 *(b) G 150*
(c) G 200 *(d) G 250*

Figure 5.12. SEM observation over the influence of the polymer layer thickness (G) on the surface morphology of the membranes

The thickness of the applied polymer solution layer is directly proportional to the thickness of the top layer of the membrane and inversely proportional to the formation of elongated pores [375,218].

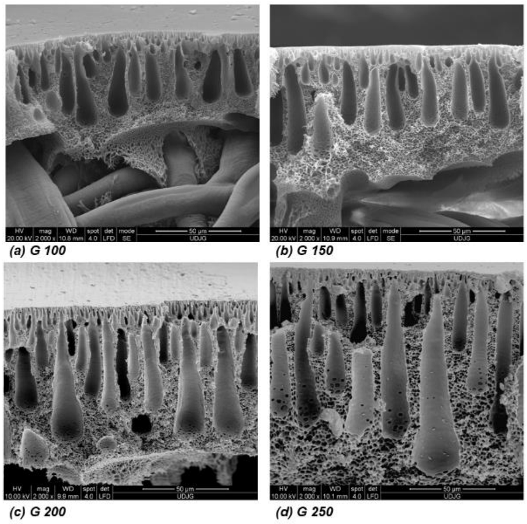

(a) G 100 *(b) G 150*
(c) G 200 *(d) G 250*

Figure 5.13. Section view SEM images for studying the influence of thickness (G) of the polymer layer on membrane morphology

The membranes formed, as seen in Figure 5.13, have an asymmetric structure consisting of a dense top layer and a porous substrate. The substrate has elongated cavities (finger-like).

It can be seen that the thinner membranes exhibit a macroporous formation which tends to form several elongated tear-like pores (the base has a larger diameter and are shorter) and the thick membranes have a finger-like structure. According to Holda et al. (2013), macrovoid structures in the form of tears are formed at higher polymer concentrations [373].

5.4.3. Determination of the morphology of the membranes modified with additive

Figure 5.14 shows the surface SEM images of the membranes with the four concentrations of polyvinylpyrrolidone (0.5, 1, 1.5 and 2 wt.(%) PVP) and the unmodified membrane, so it can observed the influence of the additive on the surface morphology of the obtained membranes.

In the case of 0.5 wt.(%) PVP membrane, a much dense surface porosity was obtained compared to the simple PSf membrane, since the additive has a positive role in pore formation. This phenomenon has also been studied by Jung et al. (2004) for polyacrylonitrile (PAN) / dimethylsulfoxide (DMSO) membranes with PVP addition [376].

Additionally, by further increasing the additive concentration, it has been observed that the surface of the membranes exhibits less easily visible pores with a much denser layer, which explains the decrease in the flux of distilled water and the higher retention capacity.

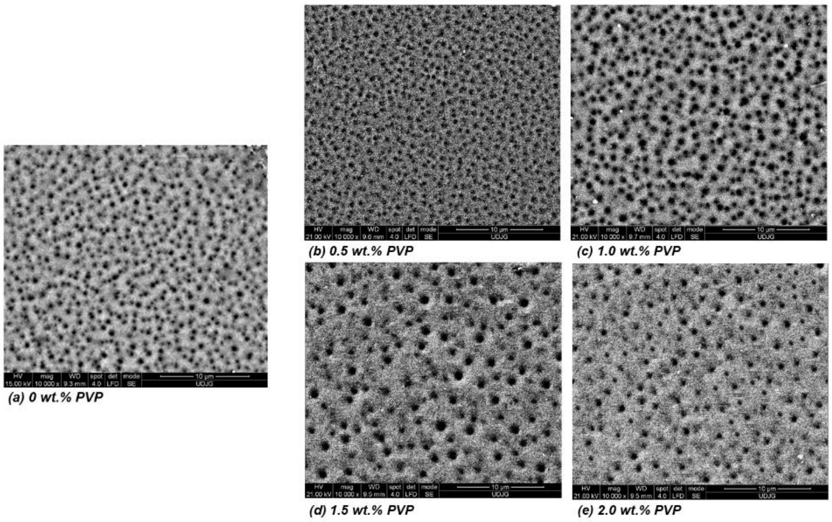
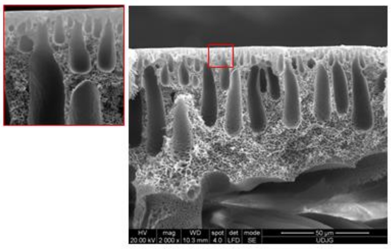

(a) 0 wt.% PVP
(b) 0.5 wt.% PVP
(c) 1.0 wt.% PVP
(d) 1.5 wt.% PVP
(e) 2.0 wt.% PVP

Figure 5.14. SEM images of membrane surfaces with addition of PVP additive

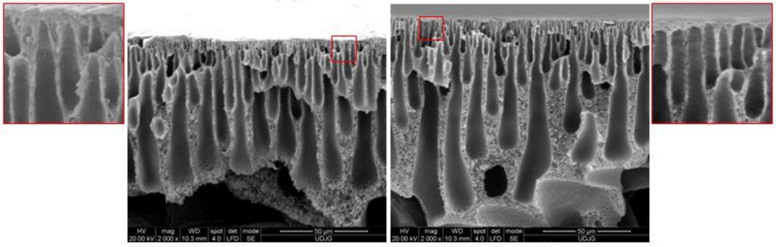
By analyzing the cross-section morphology, it can be seen how the pores in the lower layer are more elongated and intermediate pores were formed in the case of PVP-added membranes compared to those without additive.

The morphology of the cross-sectional structure of the membrane PSf concentration of 27 wt.(%) and the addition of PVP with concentrations between 0 and 2 wt.(%) is shown in Figure 5.15.

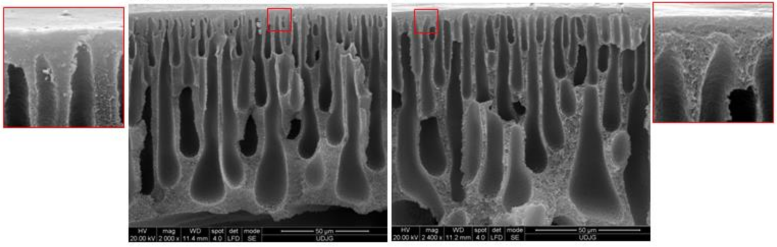
The influence of PVP additive on the membrane structure was also analyzed by Saljoughi et al. (2009) obtaining structures with more elongated and porous macrovoids [239].



(a) 0 wt.% PVP



(b) 0.5 wt.% PVP *(c) 1.0 wt.% PVP*



(d) 1.5 wt.% PVP *(e) 2.0 wt.% PVP*

Figure 5.15. Cross-section SEM images of the membranes with the addition of additive PVP

The increase in porosity in the membrane structure can be explained by increasing the water affinity [380], as a result of the addition of PVP additive.

5.5. Compositional analysis by energy dispersion X-ray spectroscopy on membranes blended with PVP additive

From the SEM-EDX analysis of PVP additive membranes, the following main elements were identified: carbon, oxygen, sulfur and nitrogen. Sulfur is a specific element of the polysulfone polymer matrix, and the presence of nitrogen demonstrates the addition of PVP in the polymer solution.

Table 5.4 shows the mass percentage of the elements. An important aspect is the increase in the concentration of nitrogen in the membrane composition with the increase in the addition of PVP from the polymer solution.

Table 5.4. EDX analysis of membrane with PVP, [wt.(%)]

PVP additive concentration [wt.(%)]	**Elements [wt.(%)]**			
	Carbon (C)	Oxygen (O)	Sulfur (S)	**Nitrogen (N)**
0	76.56	14.21	9.23	**0**
0.5	73.49	12.00	8.85	**5.66**
1	71.66	13.34	8.31	**6.69**
1.5	70.42	13.63	8.16	**7.79**
2	68.44	14.68	7.91	**8.97**

5.6. Raman spectroscopy on membranes with 27 wt.(%) PSf concentration and addition of PVP

According to the literature, Raman band with the maximum amplitude of the vibrations with the wavelength of 798 cm^{-1} is attributed to C-H stretching vibration [383,385] characteristic for polysulfone.

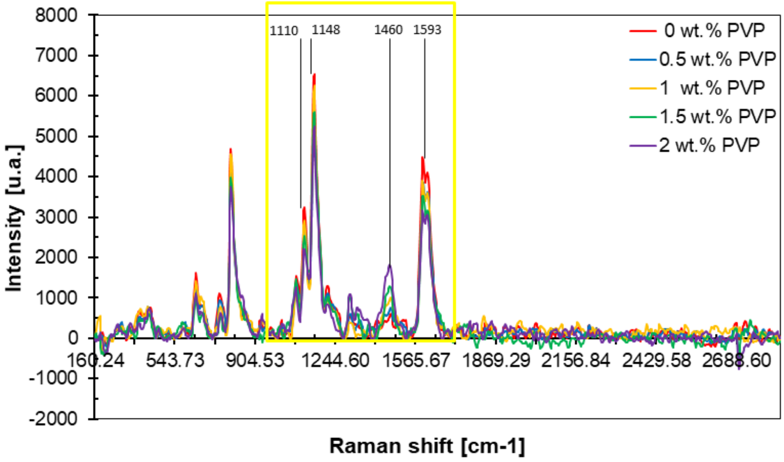


Figure 5.18. Raman spectrum for membranes with different PVP concentrations

The Raman spectrum of the N = N aromatic vibration frequencies is prominent in the spectrum in the vibration band with the wave numbers ranging from 1380-1463 cm^{-1} [387]. This bond is present in the Raman band with a vibration peak having the wavelength of 1460 cm^{-1} for all modified membranes.

5.7. Partial conclusions

The hydrophilicity of the studied membranes was determined by the contact angle method. Thus, it has been observed that by increasing the concentration from 23 to 30 wt.(%) PSf, the membranes are more hydrophobic due to the surface pores, more precisely the membrane roughness.

Comparing the AFM analysis surfaces on membranes with a concentration of 23, 25, 27 and 30 wt.(%) PSf shows that the membranes with the highest concentration of polymer have less roughness.

By electronic microscopy it has been observed that the solvent has an important role in the formation of the membrane structure. Since the higher concentration of N-methylpyrrolidone (23 wt.(%) PSf membrane) has led to the formation of a porous structure and to the formation of larger pores compared to lower solvent membranes.

SEM images of surface membranes and in cross-section allowed the study of the influence of thickness gradient on membrane properties. Surface images of membranes obtained by scanning electron microscopy show that at larger thicknesses the pores are rarer and at smaller thicknesses the membrane exhibits higher pore-density.

Addition of the PVP additive to the solution with 27 wt.(%) PSF improves the permeation properties. A comparison of non-additive and PVP-modified membranes shows that the presence of the additive forms a more hydrophilic surface with a lower contact angle.

The surface roughness of the modified membrane increases by the addition of 0.5 wt.(%) PVP than the roughness of the additive-free membrane. Further, the roughness decreases by increasing the concentration of PVP.

PVP membranes show more elongated pore formations and a top layer of high-density sponge structure.

CHAPTER 6

GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND NEW RESEARCH DIRECTIONS

6.1. General conclusions

In this paper we aimed to obtain the organic membranes used in waste water treatment, the determination of the permeation properties and the characterization from their structure point of view. The purpose of this research was to evaluate the influence of the production parameters on permeation performance, structure, morphology, topography, hydrophilicity and chemical composition.

Different solutions obtained by dissolving polysulfone (PSf) in a solvent (N-methylpyrrolidone) and were used to obtain membranes by phase inversion method through immersing the polymer solution films into the coagulation bath. Different parameters in the membrane production process have been varied to improve their properties. The parameters of interest in this study were the variation of polysulfone concentration from 23 to 30 wt.(%), the thickness of the 27 wt.(%) PSf solution from 100 to 250 µm and the addition of PVP at concentrations of 0.5 to 2 wt.(%) in the solution of 27 wt.(%) PSf casted with a thickness of 150 µm.

After obtaining the membranes, these were studied as follows:

1. By analyzing the flux of distilled water and the permeability of the obtained membranes, it was observed that membranes with different concentrations of PSf, the highest values of water flow and permeability were obtained with the 23 wt.(%) PSf membrane.

2. From membrane thickness results, when the 27 wt.(%) PSf solution layer thickness varies, these properties are improved for membranes with the lower layer thickness.

3. By adding the PVP additive it was observed that the permeation properties are improved, the highest permeability was obtained by the membrane with 27 wt.(%) PSf and 0.5 wt.(%) PVP. Increasing the PVP concentration over the 0.5 wt.(%) PVP in the polymer solution, a decrease of the permeability and of the distilled water flux was observed, but their performance is not lower than the membranes without additive.

4. Due to the different molar masses of the two dye solutions, it was observed that the flux of the Congo Red solution is higher than the flux of methylene blue dye solution for all studied membranes.

5. The membrane retention capacity of Methylene Blue and Congo Red solutions tests has shown that the studied membranes reach the molecular weight reduction threshold (MWCO) for Congo solution Red filtration because of the higher molecular weight.

6. Dye retention is enhanced by increasing the polymer concentration, by increasing the thickness of the solution layer and by adding the polyvinylpyrrolidone additive. In contrast, for membranes with PVP additive, both permeability and dye retention are improved.

7. It has been observed that at low PSf concentrations the membranes are more hydrophilic, but by varying the thickness of the polymer solution layer this property has not been influenced.

8. A significant impact on membrane hydrophilicity was the addition of PVP additive, a hydrophilic, water-soluble polymer. By increasing the concentration of PVP in the solution of 27 wt.(%) PSf, it has been observed that the contact angle is lower, so the membrane is more hydrophilic.

9. The obtained membranes recorded higher roughness at low concentrations of PSf, but also in the case of membranes with PVP added.

10. Analyzing membranes with different concentrations of PSf, their roughness is higher at low concentrations because the active layer is not very well dissolved and the surface of the membranes exhibits greater porosity.

11. The morphological structure of the membranes was analyzed by SEM images, and asymmetric structure formation was observed for all types of membranes obtained.

12. By increasing the concentration of PSf, the active layer exhibits smaller pores and the same dimension without interconnected pores. In the case of thickness variation membranes, it is observed that the active layer is also formed to the thickness of 100 μm of the applied solution.

13. The chemical composition of additive-modified membranes was studied by EDX and Raman analysis. Thus, the presence of nitrogen in the obtained membranes and uniform distribution in the membrane structure was observed. By determining the Raman spectrum, the N = N group was observed after the addition of PVP in the polymer solution.

6.2. Original contributions

The research topic approached by the author of the PhD thesis is part of a new research direction in Romania, namely, the obtaining and characterization of organic membranes aiming at the development of membrane technologies applied in wastewater treatment processes.

The contributions of the author can be quantified in:

1. To carry out a bibliographic study focused especially on the literature on the production and characterization of polymeric membranes with high concentrations of polysulfone (PSf) polymer, N-methylpyrrolidone (NMP) solvent and polyvinylpyrrolidone (PVP) additive.

2. Obtaining polymeric membranes used in waste water treatment processes by the phases inversion method by immersion in the coagulation bath, which is a new process in Romania. This technology is more developed in the southern region of the world, relying mainly on reverse osmosis processes. Instead, technologies based on nanofiltration processes are used very little, being continually progressing.

3. In the present study, polymer membrane with higher polymer concentrations were obtained than those achieved so far in the other experiments and was shown that membranes with a higher concentration of 25 wt.(%) exhibit good permeation PSf (water flux, permeability, retention capacity). In the framework of the researches, analyzes regarding the properties of permeability and retention correlated with the hydrophilicity, topography and structure referring to membrane morphology were carried.

4. In order to reduce production costs of the resulting membranes, four different thicknesses of the polymer solution layer were studied. This aspect, in the literature, has not been studied and correlated in terms of the effect of the thickness of the solution layer on the permeation properties and the physical characteristics of the membranes. This study demonstrated that membranes with 27 wt.(%) PSF exhibited similar morphological aspects for layer thicknesses ranging from 100 to 250 μm. According to some literature data, a higher thickness of the applied polymer film is needed to develop the active layer of the membrane structure. From the research carried out in the thesis it was found that polysulfone membranes show an asymmetric (morphologically) structure from the thickness of 100 μm of the applied layer of polymer solution.

5. Improvement of permeation performance was achieved by adding the polyvinylpyrrolidone additive. The novelty of this study is due to the use of low concentrations of polyvinylpyrrolidone PVP additive (between 0.5 and 2 wt.(%)), which obtained improved properties (permeability, water flow, water retention capacity, hydrophilicity, surface

roughness) as compared with literature. Thus, experimental research has highlighted that there is no need for a large amount of PVP additive in the PSf / NMP solution to obtain membranes with superior properties to those without the additive.

6. Membrane retention capacity was determined using two different dye solutions (Methylene Blue and Congo Red) at a concentration of 10 ppm. In the present study, it has been shown that by the addition of the polyvinylpyrrolidone PVP additive, both the permeability and the membrane retention capacity are improved. Instead, the study of membrane properties without additive showed an inversely proportional trend between permeability and retention.

7. The correlation results on hydrophilicity, surface roughness and morphology of the membranes with the addition of polyvinylpyrrolidone reveals that the membrane surface is smoother, justifying the water flux decrease by concentration increase of PVP, although the membrane is hydrophilic. These properties are influenced by the obtaining of less roughness and dense porous structure on the membrane surface.

8. The research on the preparation and characterization of polymeric membranes with high concentrations of polysulfone polymer PSf, N-methylpyrrolidone (NMP) solvent and addition of polyvinylpyrrolidone (PVP) additive focused on the determination of the permeation properties and correlation with the physical, chemical, structural properties of the polymeric membranes for wastewater treatment using modern investigation methods based on analyzes: SEM, AFM, UV-VIS, EDAX, RAMAN.

6.3. New research directions

The study presented in this thesis will be further developed through the following studies:

- Application of the membranes obtained in this study for the treatment of industrial wastewaters;
- Expanding research by using higher concentrations of PVP to determine the maximum concentration to have a positive impact on the membrane properties;
- Improving the membrane properties by blending nanoparticles into the polymer solution;
- Determination of the impact produced by the addition of the PVP additive to another type of polymer solution on membrane properties;
- Evaluation of the impact of other types of additives in the PSf / NMP polymer solution on the permeation properties and on the physico-chemical characteristics of the membranes.

SCIENTIFIC ACHIEVEMENTS

Scientific publications on the research topic

Publications in WOS Journals

1. *Laurenţia Geanina TIRON*, Ştefan Cătălin PINTILIE, Andreea Liliana LAZĂR, Maria VLAD, Ştefan BALTĂ, Marius BODOR, **INFLUENCE OF POLYMER CONCENTRATION ON MEMBRANE PERFORMANCE IN WASTEWATER TREATMENT**, Materiale Plastice 55 Issue: 1 (2018) 95-98, ISSN: 0025-5289, Factor de impact - 1,248

2. Ştefan Cătălin PINTILIE, *Laurenţia Geanina TIRON*, Andreea Liliana LAZĂR, Maria VLAD, Iulian Gabriel BÎRSAN, Ştefan BALTĂ, **THE INFLUENCE OF ZnO/TiO2 NANOHYBRID BLENDING ON THE ULTRAFILTRATION POLYSULFONE MEMBRANES**, Materiale Plastice 55 Issue: 1 (2018) 54-62, ISSN: 0025-5289, Factor de impact - 1,248

ISI Proceedings Volume Publications

1. *Laurenţia Geanina TIRON*, Marius BODOR, Maria VLAD, Ştefan Cătălin PINTILIE, Ştefan BALTĂ, **THE INFLUENCE OF MANUFACTURING FACTORS ON THE POLYSULFONE MEMBRANE PROPERTIES**, Energy And Clean Technologies Conference Proceedings, SGEM 2016, International Multidisciplinary Scientific GeoConference-SGEM, VOL II (2016) 157-164, doi: 10.5593/sgem2016B42, ISSN:1314-2704, ISBN 978-619-7105-64-3

2. *Laurenţia Geanina TIRON*, Ştefan Cătălin PINTILIE, Maria VLAD, Iulian - Gabriel BÎRSAN, Ştefan BALTĂ**, CHARACTERIZATION OF POLYSULFONE MEMBRANES PREPARED WITH THERMALLY INDUCED PHASE SEPARATION TECHNIQUE,** IOP Conf. Series: Materials Science and Engineering, 209 (2017) Art. No.012013, doi:10.1088/1757-899X/209/1/012013

3. *Laurenţia Geanina TIRON*, Ştefan Cătălin PINTILIE, Maria VLAD, Ştefan BALTĂ, Andreea Liliana LAZĂR, **THE INFLUENCE OF THE POLYSULFONE CONCENTRATION ON MEMBRANE RETENTION PROPERTIES**, Nano, Bio, Green and Space - Technologies for a Sustainable Future, SGEM 2017, International Multidisciplinary Scientific GeoConference-SGEM, Vol. 17 Issue 61 (2017) 391-398, DOI:10.5593/sgem2017/61, ISSN 1314-2704, ISBN 978-619-7408-12-6

4. *Laurenţia Geanina TIRON*, Maria VLAD, Ştefan BALTĂ, **RESEARCH ON HYDROPHILIC NATURE OF POLYVINYLPYRROLIDONE ON POLYSULFONE MEMBRANE FILTRATION,** IOP Conf. Series: Materials Science and Engineering, 374 (2018) 012059 doi:10.1088/1757-899X/374/1/012059

5. *Laurenţia Geanina TIRON*, Eliza DANĂILĂ, Gina Genoveva ISTRATE, Ştefan BALTĂ, Maria VLAD, **RETENTION CAPACITY OF POLYSULFONE MEMBRANE IN**

WASTEWATER TREATMENT, Nano, Bio, Green and Space - Technologies for a Sustainable Future, SGEM 2018, International Multidisciplinary Scientific GeoConference-SGEM, Vol. 18 Issue 6.1 (2018) 433-440, doi.org/10.5593/sgem2018/6.1, ISSN 1314-2704, ISBN 978-619-7408-50-8

Publications in Indexed International Databases (BDIs)

1. Laurenția Geanina TIRON, Maria VLAD, Ștefan Cătălin PINTILIE, Ștefan BALTĂ, **RESEARCH ON OBTAINING AND CHARACTERIZATION OF POLYMERIC MEMBRANES FOR WASTEWATER TREATMENT**, The Annals Of "Dunarea De Jos" University Of Galati Fascicle Ix. Metallurgy And Materials Science, 2 (2016) 9-13, ISSN 1453 – 083X;

Conferences and Workshops

Workshop participations:

1. Laurenția Geanina TIRON, Ștefan Cătălin PINTILIE, Maria VLAD, Ștefan BALTĂ, **THE INFLUENCE OF POLYVINILPYRROLIDONE ON THE PERMEATION PROPERTIES OF POLYSULFONE MEMBRANES** *"Ecotehnologii în ingineria materialelor /Tehnologii fără reziduuri"* (prezentare orală), Mai 2017

2. Laurenția Geanina TIRON, Ștefan Cătălin PINTILIE, Maria VLAD, Ștefan BALTĂ, **INFLUENCE OF POLYMER CASTING THICKNESS ON THE MEMBRANE PROPERTIES,** *"Best Available Technologies for Environmental Protection and Safety at Work in Materials Engineering"* (poster), Noiembrie 2017

Participations at National Conferences:

1. Laurenția Geanina Tiron, Maria VLAD, Ștefan Cătălin PINTILIE, Ștefan BALTĂ, **RESEARCH ON OBTAINING AND CHARACTERIZATION OF POLYMERIC MEMBRANES FOR WASTEWATER TREATMENT,** *Scientific Conference of the Doctoral Schools SCDS – UDJG 2016, Universitatea „Dunărea de Jos", Galați* (prezentare orală), Iunie 2016

2. *Laurenția Geanina TIRON*, Ștefan Cătălin PINTILIE, Ștefan BALTĂ, Maria VLAD, **INFLUENCE OF POLYMER CASTING THICKNESS ON THE MEMBRANE PROPERTIES,** *Scientific Conference of the Doctoral Schools CDS – UDJG 2017, Universitatea „Dunărea de Jos", Galați* (prezentare orală), Iunie 2017

3. *Laurenția Geanina TIRON*, Ștefan BALTĂ, Maria VLAD**, THE INFLUENCE OF POLYVINYLPYRROLIDONE ADDITIVE ON PSF MEMBRANES PROPERTIES**, *Scientific Conference of Doctoral Schools CDS – UDJG 2018, Universitatea „Dunărea de Jos", Galați* (prezentare orală), Iunie 2018

Participation in International Conferences:

1. *Laurenția Geanina TIRON*, Maria VLAD, Ștefan Cătălin PINTILIE, Ștefan BALTĂ, **INFLUNCE OF FACTORS FROM THE MANUFACTURING PROCESS ON THE PROPERTIES OF POLYMERIC MEMBRANES USED IN WASTEWATER TREATMENT,** *3rd*

International Conference New Trends In Environmental And Materials Engineering TEME 2057, Galați (prezentare orală), 21 -23 Octombrie 2015

2. *Laurenția Geanina TIRON*, Marius BODOR, Maria VLAD, Ștefan Cătălin PINTILIE, Ștefan BALTĂ, **THE INFLUENCE OF MANUFACTURING FACTORS ON THE POLYSULFONE MEMBRANE PROPERTIES,** *16th International Multidisciplinary Scientific GeoConference SGEM 2016, Bulgaria* (poster), Iulie 2016

3. Ștefan Cătălin PINTILIE, *Laurenția Geanina TIRON*, Andreea Liliana LAZĂR, Maria VLAD, Iulian - Gabriel BÎRSAN, Ștefan BALTĂ, **THE INFLUENCE OF NANOPARTICLE TYPE ON THE ORGANIC-INORGANIC MEMBRANES USED FOR WASTEWATER TREATMENT,** *3rd International Conference on Desalination using Membrane Technology, Spania* (poster), Aprilie 2017

4. *Laurenția Geanina TIRON*, Ștefan Cătălin PINTILIE, Andreea Liliana LAZĂR, Maria VLAD, Ștefan BALTĂ, Marius BODOR, **INFLUENCE OF POLYMER CONCENTRATION ON MEMBRANE PERFORMANCE IN WASTEWATER TREATMENT,** *29th European Symposium on Applied Thermodynamics – ESAT 2017, București* (poster), Mai 2017

5. Laurenția Geanina TIRON, Ștefan Cătălin PINTILIE, Maria VLAD, Iulian - Gabriel BÎRSAN, Ștefan BALTĂ, **CHARACTERIZATION OF POLYSULFONE MEMBRANES PREPARED WITH THERMALLY INDUCED PHASE SEPARATION TECHNIQUE**, *International Conference on Innovative Research, Iași* (prezentare orală), Mai 2017

6. *Laurenția Geanina TIRON,* Ștefan Cătălin PINTILIE, Maria VLAD, Ștefan BALTĂ, Andreea Liliana LAZĂR, **THE INFLUENCE OF THE POLYSULFONE CONCENTRATION ON MEMBRANE RETENTION PROPERTIES,** *17th International Multidisciplinary Scientific GeoConference SGEM 2017, Bulgaria* (poster), Iunie 2017.

7. *Laurenția Geanina TIRON*, Ștefan Cătălin PINTILIE, Ștefan BALTĂ, Maria VLAD, **RESEARCH ON MEMBRANES WITH DIFFERENT THICKNESSES AND CONCENTRATIONS OF POLYSULFONE WITH APPLICATION ON WASTEWATER TREATMENT,** *4rd International Conference New Trends In Environmental And Materials Engineering - TEME 2017, Galați* (prezentare orală), Octombrie 2017

8. *Laurenția Geanina TIRON*, Maria VLAD, Ștefan BALTĂ*,* **RESEARCH ON HYDROPHILIC NATURE OF POLYVINYLPYRROLIDONE ON POLYSULFONE MEMBRANE FILTRATION**, *International Conference on Innovative Research – Euroinvent ICIR 2018 Iasi* (prezentare orală), Mai 2018

9. *Laurenția Geanina TIRON*, Eliza DANAILA, Gina Genoveva ISTRATE, Ștefan BALTĂ, Maria VLAD, **RETENTION CAPACITY OF POLYSULFONE MEMBRANE IN WASTEWATER TREATMENT,** *18th International Multidisciplinary Scientific GeoConference-SGEM 2018, Bulgaria* (prezentare orală), Iulie 2018

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