

**„Dunărea de Jos” University of Galați**  
**Doctoral School of Mechanical and Industrial Engineering**



# **PhD THESIS**

**-Summary-**

## **The influence of nanoparticle type and size on the composite polymeric membranes used in wastewater treatment**

**PhD candidate,**  
**eng. Ștefan Cătălin PINTILIE**

**PhD Supervisor,**  
**Prof. univ. dr. eng. Iulian Gabriel BÎRSAN**

**Series I6: Mechanical Engineering No. 48**

**GALAȚI**

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## Table of contents

Table of contents.....	v
Introduction.....	viii
<b>CHAPTER I. MEMBRANES USED IN WASTEWATER TREATMENT.....</b>	<b>1</b>
1.1. Membrane technologies. General notions .....	1
1.2. Mass transfer models through membranes.....	1
1.3. Membranes classifications according to the driving force used.....	1
1.3.4. Membrane processes based on pressure gradient .....	2
1.4. Membrane Operating Modes .....	2
1.4.1. Direct flux .....	2
1.4.2. Tangential flux .....	3
1.5. Membrane classification according to the used materials .....	3
1.5.1. Organic membranes .....	3
1.5.2. Inorganic membranes .....	3
1.5.3. Organic-inorganic composite membranes.....	3
1.6. Types of membrane morphologies .....	3
1.7. Methods for obtaining polymeric membranes .....	4
1.7.3. Phase inversion method .....	4
1.8. Partial conclusions.....	4
<b>CHAPTER II. NANOCOMPOSITE MEMBRANES. STATE OF THE ART.....</b>	<b>5</b>
2.1. Nanomaterials and nanocomposites. General notions.....	5
2.2. Nanocomposite membranes.....	5
2.3. Influence of nanoparticle type and concentration on membrane properties .....	6
2.3.1. Titanium dioxide nanoparticles .....	6
2.3.2. Zinc oxide nanoparticles .....	6
2.4. Influence of nanoparticle size on membrane properties.....	6
2.5. Influence of nanoparticle shape on membrane properties.....	6
2.6. Review on mechanical properties of membranes used in water treatment .....	6
2.7. Partial conclusions.....	7
<b>CHAPTER III. MATERIALS, METHODS AND EXPERIMENTAL PROCEDURES.....</b>	<b>8</b>
3.2. Membrane fabrication process.....	8
3.2.1. Polymer solution preparation .....	8
3.2.2. Membrane formation by phase inversion method .....	9
3.3. Membrane characterization .....	10
3.3.1. Scanning Electron Microscopy (SEM) and Elemental Analysis with X-ray Dispersive Spectrometry (EDX) .....	10
3.3.2. UV-VIS spectrophotometry analysis .....	10
3.3.4. Atomic force microscopy (AFM) analysis .....	10

3.4.1. Contact angle analysis.....	10
3.5. Permeation tests .....	10
3.6. Retention tests .....	11
3.7. Degree of fouling analysis .....	11
3.8.1. Elongation-at-break .....	11
3.8.2. Tensile strength.....	11
3.7. Partial conclusions.....	12
<b>CHAPTER IV. MORPHOLOGICAL, TOPOGRAPHIC AND STRUCTURAL CHARACTERIZATIONS OF THE STUDIED NANOCOMPOSITE MEMBRANES.....</b>	<b>13</b>
4.1. Influence of the crystalline structure of titanium dioxide nanoparticles on membrane properties .....	13
4.1.1. SEM and EDX analysis of the studied membranes.....	13
4.1.3. Analysis of hydrophilic character by contact angle method.....	16
4.1.5. Atomic force microscopy (AFM) results .....	17
4.2. Influence of zinc oxide nanomaterial shape on membrane properties.....	17
4.2.1. SEM and EDX analysis of the studied membranes.....	17
4.2.3. Analysis of hydrophilic character by contact angle method .....	19
4.2.5. Topographic characterization of membranes by atomic force microscopy (AFM).....	19
4.3. Influence of zinc oxide nanoparticle size on membrane properties .....	19
4.3.1. Electronic scanning microscopy (SEM) and EDX analysis on studied membranes.....	20
4.3.3. Analysis of hydrophilic character by contact angle method .....	23
4.3.5. Atomic force microscopy (AFM) results .....	24
4.4. Partial conclusions.....	24
<b>CHAPTER V. EXPERIMENTAL RESULTS ON THE INFLUENCE OF NANOPARTICLES ON MEMBRANE PERFORMANCE.....</b>	<b>26</b>
5.1. Study of membrane properties on the influence of the crystalline structure of titanium dioxide nanoparticles.....	26
5.1.1. Determination of permeation properties.....	26
5.1.2. The retention capacity of the studied membranes.....	26
5.1.3. Fouling studies of the resulted membranes .....	27
5.1.4. Mechanical properties of the studied membranes.....	28
5.1.5. Determination of total membrane performance .....	30
5.2. Determination of membrane properties resulting from blending of zinc oxide nanomaterials of different forms .....	31
5.2.1. Permeation tests.....	31
5.2.2. The retention capacity of the studied membranes.....	31
5.2.3. Fouling studies of the resulted membranes .....	32
5.2.4. Mechanical properties of the studied membranes.....	33
5.2.5. Determination of total membrane performance.....	34
5.3. Analysis of the influence of zinc oxide nanoparticle size on membrane properties .....	35
5.3.1. Permeation tests of the studied membranes.....	35

5.3.2. Congo Red dye degree of retention .....	35
5.3.3. Study on the degree of membrane fouling .....	36
5.3.4. Mechanical properties of the studied membranes .....	37
5.3.5. Determination of total membrane performance .....	39
5.4. Partial conclusions .....	39
<b>CHAPTER VI. FINAL CONCLUSIONS, PERSONAL CONTRIBUTIONS AND NEW RESEARCH DIRECTION .....</b>	<b>40</b>
6.1. Final conclusions .....	40
6.2. Personal contributions .....	41
6.3. New research directions .....	42
<b>Bibliography .....</b>	<b>43</b>
<b>ANNEX 1 .....</b>	<b>48</b>
<b>ANNEX 2 .....</b>	<b>49</b>
<b>Scientific achievements .....</b>	<b>50</b>

## Introduction

Even since the first appearance of unicellular organisms, water has played a crucial role in the evolution of life on Earth and hence the humanity. A clear evidence of the importance of water in the development of civilizations is the position of settlements next to natural waters. Human society has always relied on access to water resources, which is essential to ensure favorable conditions for a sustainable development.

One of the main issues that dominates the 21<sup>st</sup> century is the pollution of natural waters, which pose a risk to the environment and to the population health.

Various water treatment technologies have emerged over the decades promising to solve this increasing water crisis. Also, most industries have implemented wastewater reuse systems to prevent their spillage into natural waters.

Among the most promising technologies for wastewater treatment and drinking water production is membrane technology. Membrane processes offer more advantages compared to conventional water treatment processes, such as: ensuring the permeate quality for a wide range of uses, not requiring the use of chemicals, production of very little sludge, and in most cases (depending on the industry) the retained substance is reused in the process. Also, the membrane treatment plants occupy smaller areas, and the process is easy to control and maintain.

Nanocomposite membranes composed of a polymer matrix and an inorganic additive with at least one dimension in the nanoscale range, have received particular attention over the last decades. The role of nanomaterials in the polymer matrix is to improve the membrane properties. Permeation, anti-fouling, retention, and mechanical resistance are among the properties of interest in membrane technology. Due to intense research especially in nanotechnology, by discovering new methods or materials, membrane technology is constantly developing.

In this context, the motivation to achieve this thesis in the field of mechanical engineering can be explained by highlighting the main goals of understanding the parameters of interest and filling the gaps in the existing research.

The thesis entitled *The influence of nanoparticle type and size on the composite polymeric membranes used in wastewater treatment* aimed to obtain nanocomposite membranes with better properties compared to pure membranes. The research in this thesis was divided into 3 independent studies on membrane optimization, namely: the influence of crystalline structure of titanium dioxide nanoparticles; the influence of zinc oxide nanomaterial shape and the influence of zinc oxide nanoparticle size. The review and experimental research sections are structured on 6 chapters, 112 figures and 23 tables.

In Chapter 1, called *Membranes used in wastewater treatment*, a detailed description of the membrane technology currently in use is provided. This chapter presents membranes classifications in terms of operation, materials, structure and membrane fabrication methods. The most used membranes are porous polymeric materials obtained by the phase inversion method and subsequently, the immersion precipitation technique. With the advent of nanotechnology, a new type of membrane has been developed with superior properties to the previous ones, namely the nanocomposite membranes.

In Chapter 2 entitled *Nanocomposite membranes. State of the art*, some of the current research in the field are presented, especially with respect to the modified membranes by the blending method of nanomaterials of different types, sizes and shapes in the polymeric matrix. Following the bibliographic study on membrane optimization techniques, I have noticed that the role of crystalline structure of nanoparticle was not debated in literature. Also, I did not find studies that compare the influence of nanowires and nanoparticles (with at least one equal dimension) on the polymeric membranes. Regarding the role of zinc oxide nanoparticles size in the membrane matrix, I consider that it has not been approached enough, especially from the mechanical properties point of view. In addition, I highlighted the mechanical testing methods used in the literature to determine the mechanical properties of nanocomposite membranes.



Although the membranes modified by incorporating nanomaterials are studied for nearly two decades, there are still differences in the results obtained by the authors. The authors' common opinion is that the influence of nanomaterials is positive up to a certain concentration.

In Chapter 3, entitled *Materials, methods and experimental procedures*, the materials of interest in this thesis, membrane manufacturing methods as well as methods for investigating the properties of membranes and their performances are presented.

In the structure of Chapter 4 entitled *Morphological, topographic and structural characterizations of the obtained nanocomposite membranes*, the main characteristics of the membranes resulted from the addition of different types of nanomaterials in the polymeric matrix are analyzed. These studies focused on SEM-EDX surface and sectional analyzes, roughness (by atomic force microscopy), hydrophilicity (through contact angle method), porosity properties and chemical compositions of membranes and nanomaterials (through Raman spectroscopy).

In Chapter 5 entitled *Experimental results on the influence of nanoparticles on membrane performance*, the experimental results of nanocomposite membranes are presented, in terms of permeation and Congo Red dye tests, analysis of anti-fouling and mechanical properties, such as elongation at break, tensile strength, and modulus of elasticity. Also, the optimal membranes for each study (crystalline structure, shape and size of nanomaterials) were determined in this chapter by calculating the performance indices obtained from all the tests.

Chapter 6 entitled *General conclusions, own contributions and future research directions* the final conclusions of the thesis, personal contributions and the future research directions are brought to attention.

## CHAPTER I

### MEMBRANES USED IN WASTEWATER TREATMENT

#### 1.1. Membrane technologies. General notions

The notion of membrane filtration is known since the early XXth century [11]. A membrane is a structure with the lengths greater than its thickness, through which transfer occurs under a variety of driving forces [12], its role being to act as a selective barrier between two phases, allowing a preferential passage of a substance or a component of a particular mixture (Figure 1.1) [13].

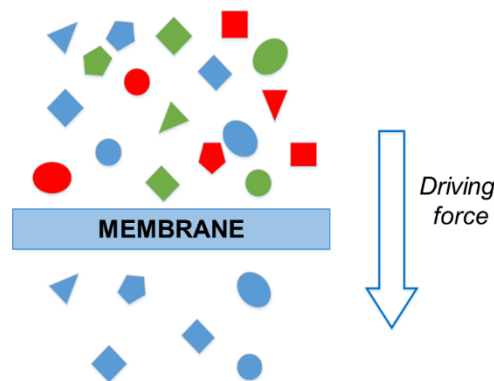


Figure 1.1. Principle of membrane separation

Membrane separation processes have many advantages over conventional processes: energy saving, superior selectivity, separation of thermo-sensitive compounds, simplicity in operation, season-independent process, no phase changes (solid, liquid, gaseous) and the addition of certain chemicals (coagulants and flocculants) is in most cases unnecessary [15].

Nowadays, the main concerns in optimizing membrane separation processes are to avoid loss of performance due to membrane fouling as well as the costs of cleaning and replacing these filters. However, the deposition of material on the surface and within the membrane structure is not easily removed by increasing the pressure or backwash.

#### 1.2. Mass transfer models through membranes

Depending on the size of the pores, the porous materials can be divided into three categories, established by the International Union of Pure and Applied Chemistry (IUPAC), as follows:

- microporous materials: 0,2-2nm;
- mesoporous materials: 2-50nm;
- macroporous materials: 50-1000nm [22].

Depending on the type of permeate transport and the type of membrane, the membrane manufacturing technology can cover all three categories.

#### 1.3. Membranes classifications according to the driving force used

Processes membrane applications in water treatment may be grouped according to the driving forces applied: (1) processes driven by pressure ( $\Delta p$ ), (2) processes driven by concentration ( $\Delta C$ ), (3) processes driven by electric potential ( $\Delta E$ ) and finally (4) processes driven by partial pressure and vapor pressure ( $\Delta T$ ) [28, 29].

##### 1.3.4. Membrane processes based on pressure gradient

Separation with baromembranes has seen a substantial increase in discoveries and advances over the past decades. Many materials and membrane processes have been

developed and proven high performance for separation applications in academia and in industry since the late 1970s.

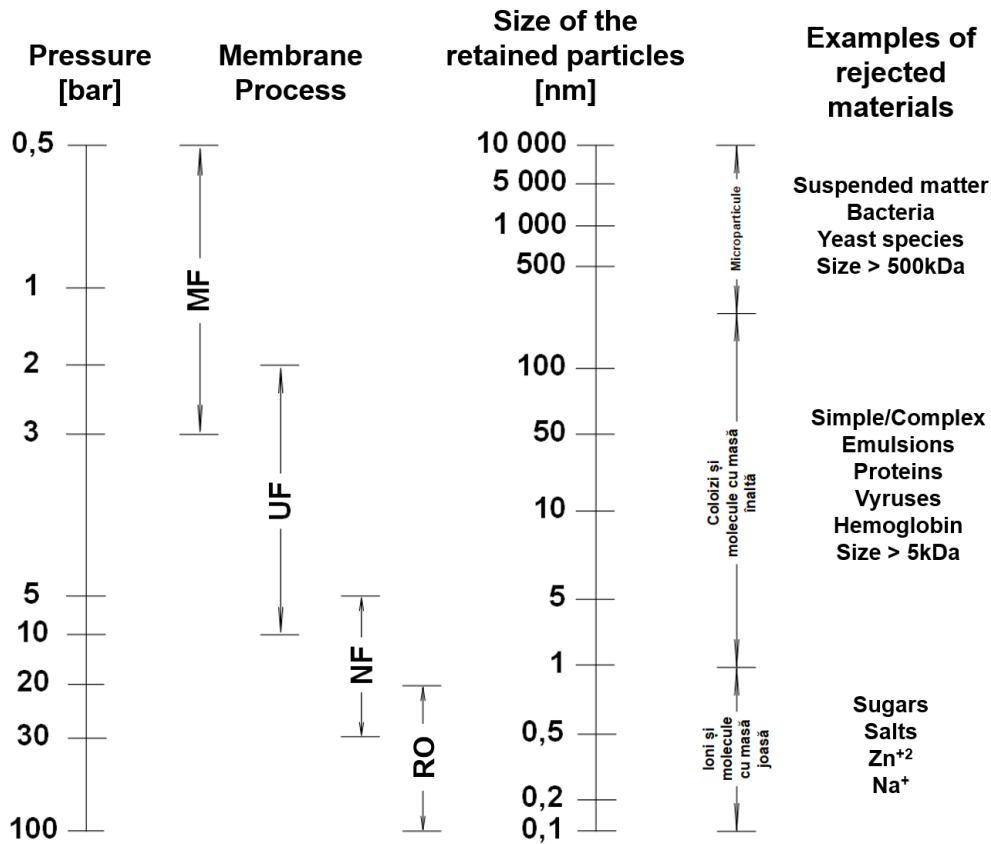


Figure 1.9. The main processes of membrane separation (adaptation after [9] and [15])

An important aspect that is considered essential for the pressure driven membrane processes, is the size of the pores, because many separation processes involve the principle of dimensional exclusion [15].

Figure 1.9 shows the main membrane separation processes involving transmembrane pressure as a driving force. It can be seen the ranges of pressure driven processes for microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), and the size of the dissolved or suspended substances chosen for each process with examples of retained materials.

### 1.4. Membrane Operating Modes

Liquid filtration membrane processes using the pressure gradient can be operated in two ways, direct filtration where there is no secondary stream of the concentrate, and tangential filtration where the feed stream has a constant permeate flow rate, parallel or tangential.

#### 1.4.1. Direct flux

Direct flow filtration, often called *Dead-End filtration*, is the simplest configuration for membrane separation processes. The feed solution is completely forced through a membrane with a perpendicular direction and constant pressure across its surface. The retained matter accumulating on the surface of the membrane is directly proportional to the volume of the filtrate. When the flow reaches a critical value, filtration should be interrupted due to very high material accumulation (*cake formation*), often requiring the membrane surface to be cleaned or replaced. [75, 104].

### 1.4.2. Tangential flux

According to International Union of Pure and Applied Chemistry (IUPAC), the term tangential flow filtration is defined as a method of operating a filtration device in which the retained fluid is driven parallel or tangential to the membrane surface, preventing the undesirable accumulation of filtered material on the membrane [107]. Although in tangential flow filtration systems the rapid accumulation of matter on the surface of the membrane is avoided in most cases, there is another phenomenon of moderate fouling called concentration polarization [91]. Compared with Dead-End filtration, where the permeability decrease is directly proportional to the solids concentration until the membrane cleaning stage, the tangential filtration is continued until the adhesion forces that form the accumulation layer on the surface of the membrane reach a steady state due to the erosion induced by the flowing fluid coming into contact with the membrane [108].

## 1.5. Membrane classification according to the used materials

The selection of appropriate materials to fabricate the membranes for a specific application is an important parameter in membrane science. Choosing the right material provides control over the nature and interaction between the permeate and the membrane [20].

### 1.5.1. Organic membranes

Most of the membranes used are organic polymers, which covers about 90% [23, 44]. In addition to their stable long-term separation properties, these materials are used to manufacture membranes with high mechanical strength, thermal stability and chemical resistance [112].

Most membranes are asymmetric, consisting of a thin top layer followed by a thick pore layer, the retention and permeability being governed only by the top layer [116].

### 1.5.2. Inorganic membranes

Inorganic membranes are mainly made of ceramic materials. Since ceramic membranes are highly resistant to high temperature and have a good chemical stability differences in aggressive environments [20], they are easy to clean and the lifetime is longer than that of polymeric membranes [117].

Ceramic membranes presents some drawbacks, one example being the sealing problem due to different thermal expansion of the ceramic membrane and the module material. Also, the fragility of the ceramic membranes always requires careful handling [122]. Other disadvantages limiting the use of ceramic membranes are: reduced ability to retain ions or molecules with low mass, very high manufacturing costs and limited surface per module due to higher rigidity compared to polymeric membranes [15, 45].

### 1.5.3. Organic-inorganic composite membranes

In the past decade, interest in development of composite membranes increased with the ability to create new products with superior properties, and high applicability. The composite membranes may be obtained from an inorganic support layer and a polymeric active layer [123, 124]. Also, the composite membranes may be formed from a polymer base material with incorporation of micrometric inorganic material [127, 128]. Recently, nanocomposite membranes have gained attention in the membrane industry development, being composed of a polymeric matrix with nanoparticle inclusions [132, 133].

## 1.6. Types of membrane morphologies

A proper selection of the material is an important step for the successful use of membrane filtration. The membranes are divided into two general categories: porous and dense. Dense membranes show a higher retention than the porous membranes, the main drawback being the very low permeate production, while the porous membranes exhibit superior flow. Dense membranes are influenced by their thickness, therefore the thickness must be minimal for a satisfactory flux [23]. Most commercially available membranes are fully porous or consist of a dense top layer on a porous support layer, called anisotropic membranes [42, 58].

## **1.7. Methods for obtaining polymeric membranes**

### **1.7.3. Phase inversion method**

Phase inversion membranes were first developed by Loeb and Sourirajan from cellulose acetate for desalting water [17].

Phase inversion can be described as a separation process where the polymer solution is transformed in a controlled manner from a liquid into a solid state [148].

Immersion precipitation is a process in which a polymer solution is cast on a suitable support and then immersed in a non-solvent coagulation bath where the exchange between solvent and non-solvent produces the final membrane [116].

The most used polymers in the phase inversion membrane manufacture are polysulfone, polyethersulfone, Polyvinylidene fluoride, cellulose acetate and polyamide [29].

These membranes can be used in all membrane pressure processes, namely microfiltration, ultrafiltration, nanofiltration and reverse osmosis, as well as other processes such as membrane distillation, pervaporation, etc. [152].

## **1.8. Partial conclusions**

Membrane separation is a mature technology, being commercially available for a wide range of applications, from domestic water filtration to industrial water purification, to pollution prevention or to the decontamination of natural water sources, up to supporting life in space stations. Membrane technology can be used to separate different mixtures of liquid or gaseous substances for a wide range of applications. Also, in most cases, all substances produced after filtration (permeate, retentate and concentrate) are considered valuable resources.

The most popular membrane processes are divided according pore sizes, in which microfiltration membranes have the largest pores, ultrafiltration and nanofiltration membranes have intermediate pores, and the membranes used in reverse osmosis have pores of the smallest size.

## CHAPTER II

## NANOCOMPOSITE MEMBRANES. STATE OF THE ART

## 2.1. Nanomaterials and nanocomposites. General notions

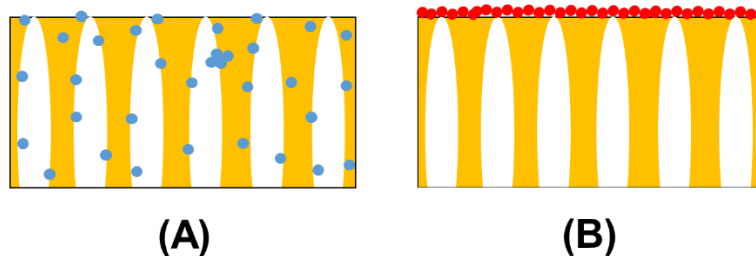
Nanomaterials have different physical, mechanical and chemical properties from the bulk material, due in particular to the structure and very high active surface to volume ratio [20]. These nanomaterials, with unique properties, have high efficiency in water and wastewater treatment with applications such as absorption of contaminants resistant to biological degradation, membrane processes, photocatalysis in disinfection and microbial control systems, sensors, monitoring and others [163].

Polymeric nanocomposites containing functional organic or inorganic nanoparticles in the polymer matrix have attracted a particular interest due to their superior thermo-mechanical properties compared with micro-composite materials, maintaining the same loading and testing conditions [165].

## 2.2. Nanocomposite membranes

In general, nanocomposite membranes are prepared by blending nanomaterials (the additive) into the polymer solution or membrane matrix. The nanoparticles can be used as coatings on the membrane surface or dispersed in the polymer solution before the membrane formation process. Membranes having nanoparticles blended in the polymer matrix are also referred to as Mixed Matrix Membranes (MMM) [133, 169].

Among the most commonly used techniques for membrane modification by nanoparticles are ultraviolet irradiation, blending in the polymer solution / matrix (**Figure 2.2.A**), graft polymerization, plasma grafting, as well as others [180, 181], the latter being considered surface modification techniques (**Figure 2.2.B**).



**Figure 2.2.** The schematic diagram of the nanocomposite membrane modification techniques by nanoparticles: a) blending in a polymer matrix, and b) depositing on the membrane surface

Among these membrane modification methods, the blending of nanoparticles into the polymer solution or membrane matrix is the most commonly used [183] and of technical interest due to simplicity as well as moderate manufacturing conditions [184]. Additionally, although the modifications made only at the surface of the membranes show considerable improvements in hydrophilicity, retention and low fouling, they do not contribute to the optimization of the membranes from a mechanical point of view, and under certain conditions of preparation they can contribute to the decrease of permeability due to blocking pores with deposited nanomaterials [185]. Membranes with nanoparticles embedded in their matrix exhibit surface enhancements (hydrophilicity, anti-fouling, roughness) as well as tensile strength, elongation at break, flux, thermal and chemical resistance [14, 186].

The study of the influence of nanomaterials on membrane performance has to be divided into 4 stages: analysis of type, concentration, size and shape of nanoparticles, all contributing to the selection of optimal parameters in membrane manufacture.

### **2.3. Influence of nanoparticle type and concentration on membrane properties**

The most used nanomaterials in the field of water treatment are zinc oxide (ZnO) and titanium dioxide (TiO<sub>2</sub>) due to high photocatalytic activity in degradation of organic pollutants, stability, superior selectivity and low cost [187].

#### **2.3.1. Titanium dioxide nanoparticles**

Among the metal oxide nanoparticles, TiO<sub>2</sub> has received special attention due to its stability and availability in applications such as dyeing, catalysis and photocatalysis, batteries, cosmetics, etc. In order to accelerate the degradation of organic contaminants, TiO<sub>2</sub> is often used as a photocatalyst in water and wastewater treatment. When dispersed in the membrane, TiO<sub>2</sub> nanoparticles not only can improve membrane hydrophilicity to enhance flux but destroy bacteria, which mitigates membrane fouling and membrane bioreactor systems [188, 189] and reduces biological fouling in reverse osmosis membranes.

#### **2.3.2. Zinc oxide nanoparticles**

Incorporation of zinc oxide nanomaterials into the membrane matrix is a promising approach to solving membrane fouling problems [222]. Due to the high catalytic activity, high chemical and mechanical stability, as well as bactericidal potential [223], the ZnO-nanocomposite membranes ensures the development of a stable filtration system with improved physical and chemical properties [226].

### **2.4. Influence of nanoparticle size on membrane properties**

Choosing the optimal nanoparticles size for nanocomposite membranes manufacturing is an important process in trying to determine their maximum efficiency. The active surface of the nanoparticles is inversely proportional to their size, but the main disadvantage is that with the decrease in nanoparticle size increases, the tendency to agglomerate, contributing to a decrease in performance in the treatment of water and wastewater through membrane processes. Starting from the aforementioned statements, this study is still researched in membrane technology to determine the optimum size of nanoparticles with a high active surface and a minimal agglomeration tendency.

### **2.5. Influence of nanoparticle shape on membrane properties**

The most used nanomaterials in membrane technology are nanoparticles [245] and nanotubes with single-walls [246] or multiple walls [249], and in recent years, increased interest for nanowires [251, 252] and nanoplatelets [256]. The materials of these nano-objects cover an extended sector, from non-metallic chemical elements (allotropes of carbon) [259] and nonmetallic oxides (graphene oxide) [260], metals (silver, copper, etc.) [262, 263] and metal oxides (ZnO, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CuO, etc.) [63, 214] to materials with complex structures such as clay minerals (halloysite, kaolinite, montmorillonite, etc.) [267, 268], metal-organic structures (generally named metal organic frameworks - MOF) [270] and polymeric [273].

### **2.6. Review on mechanical properties of membranes used in water treatment**

Mechanical resistance is one of the important baromembrane specifications that help ensure membranes with stable and long lasting performance in the separation process [138].

Generally, when membranes are subjected to high pressures, they are exposed to the risk of physical compaction, resulting in irreversible loss of water flux. This leads to the need to analyze the membranes under real load conditions, and from the perspective of the mechanical properties studies, also.

Among the most commonly used techniques of analyzes to determine the mechanical properties of membranes are: bursting test [171, 197], nano-indentation [281, 282], bending test (for ceramic membranes) [283, 284], dynamic mechanical test [285] and uniaxial traction test [186, 206, 223].

The uniaxial traction test is one of the fundamental and most commonly used test methods for investigating mechanical behavior of materials. The sample to be analyzed is elongated at a constant rate of controlled stretching until deformation or rupture occurs. The mechanical properties reported by this method are elongation at break, tensile strength, Young modulus, among others [290].

## **2.7. Partial conclusions**

Progress in the development of nanocomposite polymer membranes for water treatment has increased considerably in recent years. Supplementary, the control of physicochemical properties by incorporating nanomaterials can provide the nanocomposite membranes unique properties and can also induce new features and functions based on their synergistic effects between the matrix and the filler. Potential applications of nanocomposite membranes could cover the entire separation spectrum, including MF, UF, NF and RO.

In this chapter several aspects of the process of obtaining membranes with the addition of nanomaterials used in water purification processes have been described. The two major categories of membrane optimizations, highlighted here, are membrane surface changes by nanoparticle coating and those in which nanoparticles are embedded in the polymer matrix, often called blending method. From the efficiency point of view and the possibility of increasing the performance of other properties, the blending method has captured the attention of researchers in the last decades and is still a topical subject.



## CHAPTER III

## MATERIALS, METHODS AND EXPERIMENTAL PROCEDURES

## 3.2. Membrane fabrication process

The parameters of interest for the study of membrane influence in this thesis were the comparison of optimizations produced by membranes after incorporation of nanomaterials with different crystalline structures, different forms, as well as different sizes and concentrations.

## 3.2.1. Polymer solution preparation

In this research, the following materials have been used: polysulfone (PSf, Mw ~ 35,000), n-methylpyrrolidone (NMP, C<sub>5</sub>H<sub>9</sub>NO, 99%), nanoparticles and nanowires of zinc oxide (ZnO) of different sizes and nanoparticles of titanium dioxide (TiO<sub>2</sub>). These were provided by two manufacturers (**Table 3.5**) and used without further modifications. The nonwoven polyester support layer (Novatexx 2471) was delivered from Freudenberg (Winheim, Germany).

**Table 3.5.** Details of labeling, crystalline structure, shape and the size of the nanomaterials used in the thesis

No.	Material	Crystalline structure****	Shape*/ Size	Manufacturer
1	Polysulfone	Amorphous	granules	
2	N- methylpyrrolidone	-	liquid	
3	Titanium dioxide	Rutile***	NP, <100nm	Sigma Aldrich (U.S.A.)
4	Titanium dioxide	Anatase/Rutile mixture**	NP, <100nm	
5	Zinc oxide	Not mentioned	NW, D:50nm, L:300nm	
6	Zinc oxide	Not mentioned	NP, <100nm	
7	Zinc oxide	Not mentioned	NP, <50nm	
8	Zinc oxide	Not mentioned	NP, <25nm	EMFUTUR
9	Zinc oxide	Not mentioned	NP, <14nm	(Spain)

\*NP - nanoparticles; NW - nanowires;

\*\* The Anatase/Rutile mixture of TiO<sub>2</sub> nanoparticles has a ratio of 87.5/12.5, determined by XRD analysis (ANNEX 1);

\*\*\* The detected composition of TiO<sub>2</sub> Rutile nanoparticles is 86.3 / 13.7 (Rutile/TiO<sub>2</sub>-uncategorised) (ANNEX 2);

\*\*\*\* XRD analyzes were obtained with a diffractometer Dron 3M, molybdenum anticathode.

The nanocomposite membranes were manufactured by incorporating the aforementioned nanomaterials into the polymeric solutions of PSf dissolved in NMP. By adding nanomaterials to the solution, the solvent and polymer concentrations were reduced concurrently to maintain the ratio of the two substances. **Table 3.6** shows the concentrations of polymer and solvent used for the control membrane.

**Table 3.6.** Polysulfone and n-methylpyrrolidone concentrations of the polymer used for the control membrane manufacture

Membrane	Polysulfone [wt.%]	N- methylpyrrolidone [wt.%]
Control	25	75

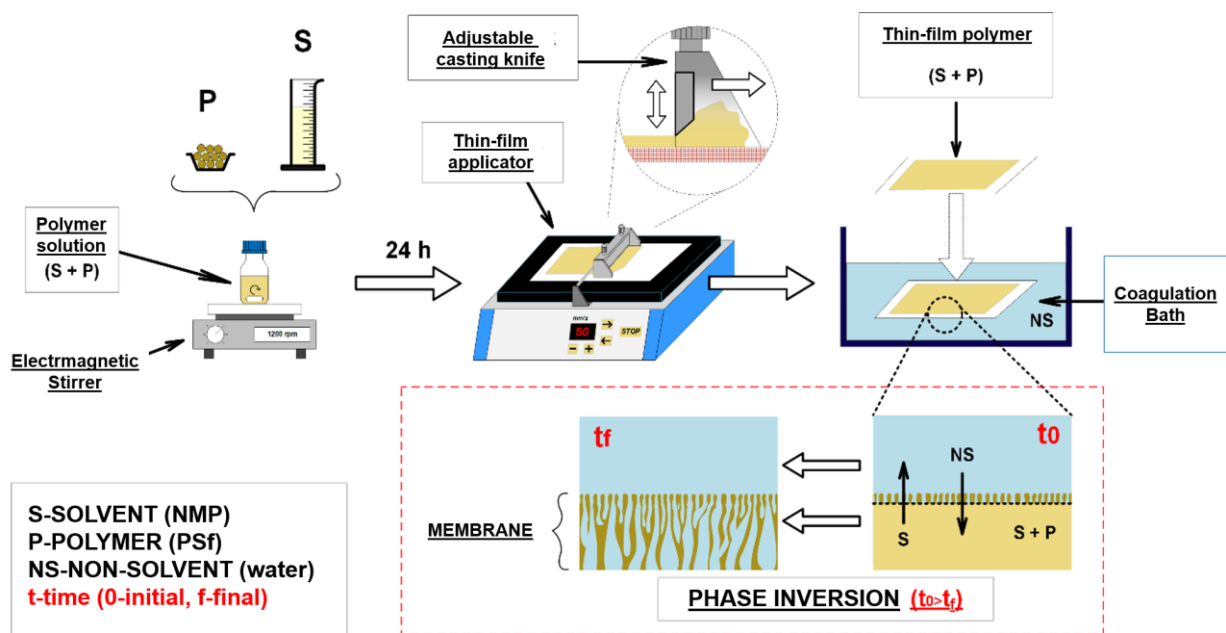
**Table 3.7** presents the nanomaterials used to obtain the nanocomposite membranes as well as their crystalline structure, shape, size and concentrations.

**Table 3.7.** The key details about the nanomaterials added in the polymer solutions for membrane manufacture

		TiO <sub>2</sub> nanoparticles	
I. Influence of TiO <sub>2</sub> NP type	Concentration [wt.%]	Structură cristalină	
	0.1	Rutile	
	0.5	/	
	1	Anatase	
		ZnO nanomaterials	
II. Influence of ZnO nanomaterial shape	Concentration [wt.%]	Shape	
	0.5	Nanowires	
		Nanoparticles	
		ZnO Nanoparticles	
III. Influence of ZnO nanoparticle size	Concentration [wt.%]	Size [nm]	
	0.1	100	
		50	
	0.5	25	
	1	14	

**3.2.2. Membrane formation by phase inversion method**

Figure 3.2 shows the manufacturing steps of the membranes obtained in AN 011 laboratory. Once the polymer-solvent or polymer-solvent-nanomaterial blend has been homogenized for 24 hours, the polymer solutions will be casted in thin films.



**Figure 3.2.** Presentation of the steps in manufacturing the polymer solution and the membrane through phase inversion process

Prior to the casting step, the support layer is attached to a glass support, then wetted with N-methylpyrrolidone solvent to prevent the polymer from penetrating the pores of the support layer. After the excess solvent has been removed, an amount of polymer solution was poured onto the wetted support layer. Afterwards, a thin film polymer solution is casted in a 250 $\mu$ m thin polymer film using a casting knife. After a short time, the thin film solution is immersed in the coagulation bath containing non-solvent (distilled water). At this stage, the phase inversion occurs, where, after the exchange between solvent and non-solvent, a porous polymer film is formed, which represent the final membrane. After 15 minutes the phase inversion is complete and the membrane is transferred and stored in a container containing distilled water to ensure that the solvent residue is completely removed.

For the fabrication of nanocomposite membranes, firstly the solvent solution is stirred with the known nanomaterial for one hour, followed by the normal procedure.

The manufacture of membranes by the phase inversion method is still used in research and production on an industrial scale, also [318].

### 3.3. Membrane characterization

Since the membranes are different in several aspects, such as the materials used to obtain the polymer solution, membrane morphology, separation mechanism and domains of applications, a great number of different techniques are needed for their characterizations [75].

#### 3.3.1. Scanning Electron Microscopy (SEM) and Elemental Analysis with X-ray Dispersive Spectrometry (EDX)

Sample morphology was investigated using the FEI Quanta 200 scanning microscope equipped with an EDX elemental composition analyzer at an acceleration voltage of 15 kV and 25 kV. All samples were sputtered with gold prior to observation in order to obtain conductivity during analysis for better image quality. The presence of nanoparticles with different concentrations was confirmed by the EDX spectra.

#### 3.3.2. UV-VIS spectrophotometry analysis

In the present study, the spectrophotometer was used to determine the concentration of the solution contaminated with a Congo Red dye (696.7 g/mol) before and after membrane filtration.

#### 3.3.4. Atomic force microscopy (AFM) analysis

The membrane roughness analysis obtained in this thesis was performed with the NanoSurf EasyScan 2 roughness measuring instrument with a scanned surface of 5 x 5  $\mu$ m.

#### 3.4.1 Contact angle analysis

The surface hydrophilicity of the prepared PSf nanocomposite membranes was evaluated by measuring the contact angle between the polymer surface and a drop of water using a contact angle goniometer (OCA 15EC, DataPhysics). The dropping was repeated several times and the mean value was reported for the contact angle of each sample [352].

### 3.5. Permeation tests

The prepared membranes were characterized for pure water flux and permeability in a stirred cell (Sterlitech HP4750) with a total volume of 300 mL and a membrane surface area 14.6cm<sup>2</sup>. The cell was fitted with a pressure gauge and pressurized with nitrogen gas to force the liquid to pass through the membrane [352].

*Distilled water flux* (Lm<sup>-2</sup>h<sup>-1</sup>) was measured using the gravimetric method and determined by applying the following equation:

$$J_{AD} = \frac{V}{A \cdot t} \quad (3.2)$$

where  $V$  is the volume of the collected permeate (L),  $A$  - the effective area of the tested membrane ( $m^2$ ) and  $t$  is the duration of the permeation process (h) [63].

The slope of the linear regression of the pure water flow on  $\Delta P$  was determined as the permeability of pure water ( $Lm^{-2}h^{-1}bar^{-1}$ ) which was calculated using the following expression:

$$Permeability = \frac{\text{distilled water flux}}{\Delta p} \quad (3.3)$$

where  $\Delta p$  is the operating pressure (bar).

In the case of permeability, it was determined by measuring flows at different working pressures (10, 12, 14, 16, 18 and 20bar).

### 3.6. Retention tests

The chosen dye is Congo red with a molecular weight of 696.665 g/mol, insoluble in water. The dye concentration is determined spectroscopically using a HACH DR 5000 UV-Vis spectrophotometer (Hach Lange GmbH, Germany) [356].

### 3.7. Degree of fouling analysis

The fouling resistance of the control and modified membranes is characterized by the relative flux,  $RF$ , and is calculated as follows:

$$RF = \frac{J_{RC}}{J_{AD}} \quad (3.6)$$

where  $J_{RC}$  is the retention flux of Congo red Dye solution (10ppm).

Relative flux reduction,  $RFR$  [%], is calculated as follows [356]:

$$RFR = \left(1 - \frac{J_{RC}}{J_{AD}}\right) \times 100 \quad (3.7)$$

Relative flux reduction represents the total membrane fouling, which includes both reversible fouling (it is easily removed by backflushing) and irreversible fouling (cannot be removed).

#### 3.8.1. Elongation-at-break

By measuring the deformation of the sample, the elongation of the membrane subjected to tensile tests performed with the specific instrument for testing the mechanical properties (Instron 8850) was used. This was calculated by the ratio of the length variation  $\Delta L$  of the material and the initial length  $L_0$  [359]:

$$\varepsilon = \Delta L / L_0 = (l - L_0) / L_0 \quad (3.9)$$

The total sample size tested was 2cm wide and 17cm long, and the length of the deformed sample is 10cm, in accordance with ISO 527-1.

#### 3.8.2. Tensile strength

The tensile strength, denoted  $\sigma_r$  [MPa], represents the ratio between the maximum breaking force  $F_{max}$  and the initial cross sectional area of the sample ( $A_0$ ) [360].

$$\sigma_r = F_{max} / A_0 \quad (3.10)$$

In this case, the modulus of elasticity was manually determined by applying the ISO 527-1 standard, where it was calculated according to equation:

$$E_t = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} \quad (3.11)$$

where  $E_t$  is the modulus of elasticity [MPa],  $\sigma_1$  represents de force [MPa] measured at strain  $\varepsilon_1 = 0.0005$  and  $\sigma_2$  represents de force [MPa] at strain  $\varepsilon_2 = 0.0025$  [291].

### 3.9. Partial conclusions

Polysulfone polymer, N-methylpyrrolidone solvent and nanomaterials of different types, shapes and sizes were used in this research as follows: TiO<sub>2</sub> nanoparticles of similar size (100nm) with Rutile and Anatase crystalline structures, ZnO nanowires with diameter of 50nm and 100nm length, and ZnO nanoparticles with four different sizes (14, 25, 50 and 100nm).

To obtain the polymeric membranes, the phase inversion method was used by immersing the polymer film solution in the coagulation bath (distilled water). The membranes so obtained were physically, structurally, chemically and mechanically characterized by advanced analysis methods, namely:

- surface roughness by atomic force microscopy (AFM);
- surface and cross-sectional structure analyzed by electronic scanning microscopy (SEM);
- chemical composition of membranes by X-ray dispersion spectroscopy (EDX) and Raman specroscopy;
- porosity by gravimetric method;
- membrane hydrophilicity by contact angle method.

In order to understand the performance of the membranes in wastewater treatment processes, their permeation properties were determined by studying the distilled water flux, permeability, relative flux and retention capacity of 10 ppm Red Congo dye solution in the *Dead-end* filtration cell.

## CHAPTER IV

## MORPHOLOGICAL, TOPOGRAPHIC AND STRUCTURAL CHARACTERIZATIONS OF THE STUDIED NANOCOMPOSITE MEMBRANES

## 4.1. Influence of the crystalline structure of titanium dioxide nanoparticles on membrane properties

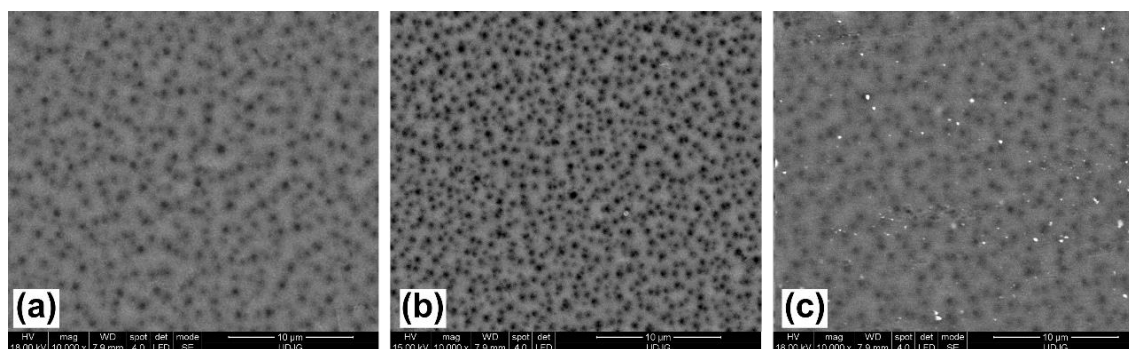
For this study on the influence of the nanoparticle crystalline structure on the membrane properties, two types of titanium dioxide nanoparticles were chosen. Both types of nanoparticles are smaller than 100nm, the major difference being the crystalline structure. The first type of nanoparticles has a Rutile structure and the second type is a mixture of Anatase and Rutile, the Anatase structure being the majority. The membranes are noted after the nanoparticle concentration added to the polymer solution, expressed as weight percent (wt.%), and the majority crystalline structure for each type of nanoparticle (Rutile or Anatase).

Since the first implementation of titanium dioxide nanoparticles in the optimization of membrane separation processes (2005), numerous studies of their influence have been conducted [65, 200, 237]. However, according to my knowledge gained from literature studies, the role of crystalline structure of nanoparticles on the membrane properties has not been discussed.

## 4.1.1. SEM and EDX analysis of the studied membranes

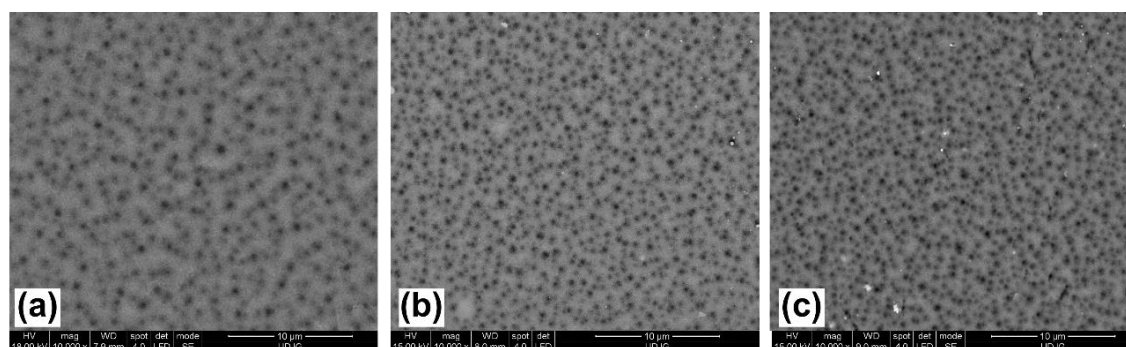
## 4.1.1.1. Membrane surface analysis by SEM-EDX method

Blending a small concentration of nanoparticles can considerably influence the surface properties of the membranes. The number, size and distribution of pores at the surface of the membrane can provide important details on the filtration capacity in terms of water flux and retention of contaminants. In the case of the nanocomposite membranes with 0.1 wt.% TiO<sub>2</sub> Rutile nanoparticles (**Figure 4.1.b**), the number of pores on the surface increases, while the size distribution remains unchanged, similar to the control membrane.



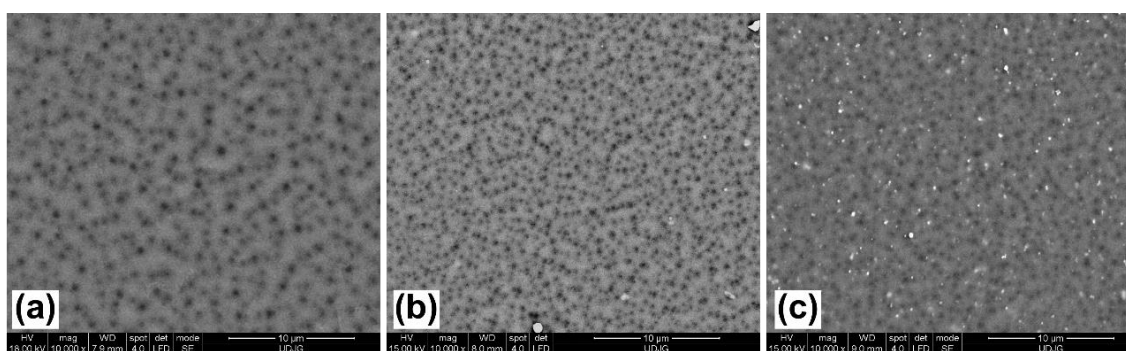
**Figure 4.1.** Surface SEM images of the control membrane (a) and membranes with 0.1wt.% TiO<sub>2</sub> with crystalline structure Rutile (b) and 0.1wt.% TiO<sub>2</sub> with crystalline structure Anatase (c)

The TiO<sub>2</sub> Anatase nanoparticles are influencing the morphology of polymeric membranes in a different manner. **Figure 4.1.c** shows that nanocomposite membranes modified with 0.1wt.% TiO<sub>2</sub> Anatase did not increase the number of pores yet their size decreased compared to the control and 0.1wt.% TiO<sub>2</sub> Rutile membranes.



**Figure 4.2.** Surface SEM images of control membrane (a) and membranes with 0.5wt.%  $\text{TiO}_2$  crystalline structure Rutile (b) and 0.5wt.%  $\text{TiO}_2$  crystalline structure Anatase (c)

Agglomerations are more pronounced in the case of membranes blended with nanoparticles of Anatase crystalline structure (**Figure 4.3.c**).



**Figure 4.3.** Surface SEM images of control membrane (a) and membranes with 1wt.%  $\text{TiO}_2$  with crystalline structure Rutile (b) and with addition of 1wt.%  $\text{TiO}_2$  with crystalline structure Anatase (c)

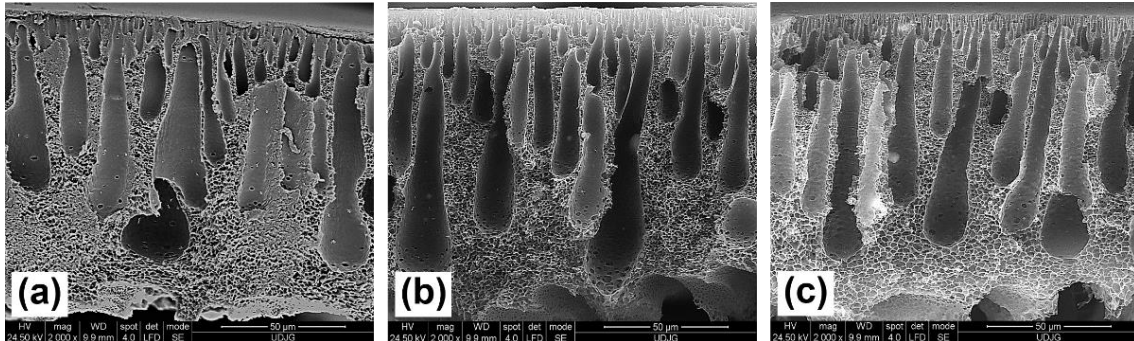
The nanoparticle agglomeration tendency on the surface of the studied membranes is higher for membranes blended with  $\text{TiO}_2$  Anatase nanoparticles. Elemental analysis confirms that the membranes with  $\text{TiO}_2$  Anatase nanoparticles exhibit a higher percentage of nanoparticles on its surface while membranes blended with  $\text{TiO}_2$  Rutile nanoparticles respect to a more precise extent the nanoparticle mass percentage initially incorporated in the polymer solution.

**Table 4.1.** Surface elemental analysis by the EDX method of control membrane and membranes with the addition of titanium dioxide nanoparticles

Membrane	Carbon [%]	Oxygen [%]	Sulphur [%]	Titanium [%]
Control	89.67	6.71	3.62	-
0.1wt.% $\text{TiO}_2$ Rutile	89.17	6.93	3.86	0.04
0.5wt.% $\text{TiO}_2$ Rutile	89.11	7.42	3.80	0.11
1wt.% $\text{TiO}_2$ Rutile	87.75	8.09	3.64	0.52
0.1wt.% $\text{TiO}_2$ Anatase	88.86	7.08	3.92	0.14
0.5wt.% $\text{TiO}_2$ Anatase	88.61	7.46	3.73	0.20
1wt.% $\text{TiO}_2$ Anatase	86.87	8.68	3.57	0.88

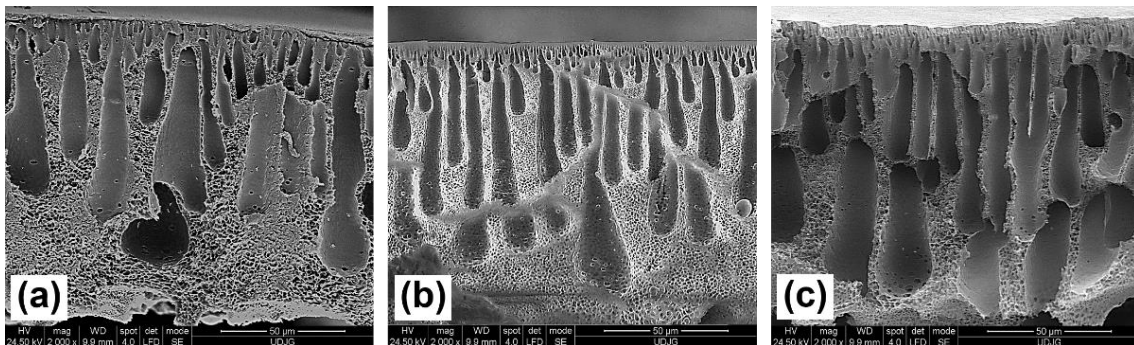
#### 4.1.1.2. Cross-section SEM and EDX analysis of the studied membranes

Membrane morphology indicates that their modification by incorporating 0.1wt.% nanoparticles does not result in noticeable differences compared with the control membrane (**Figure 4.5**).



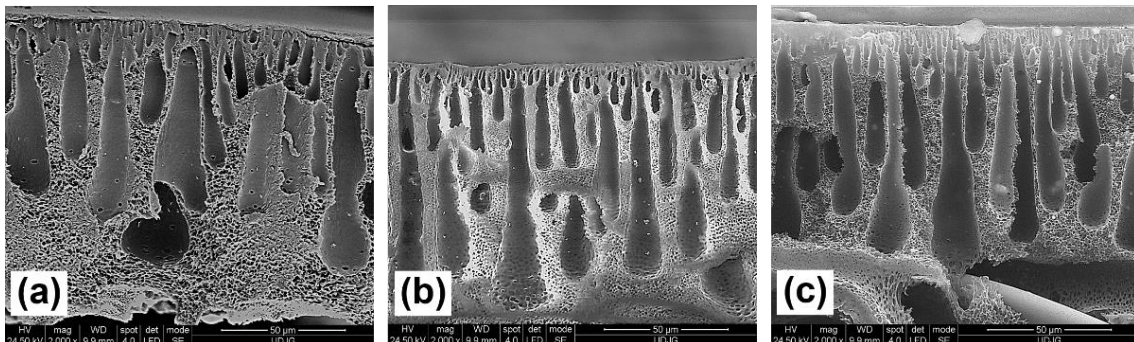
**Figure 4.5.** Cross-section SEM images with the control membrane (a) and membranes with the addition of 0.1wt.% Rutile (b) and 0.1wt.% Anatase (c)

When blending an amount of 0.5wt% nanoparticles into the studied membranes (**Figure 4.6**), the length of the pores increases, so the base is narrower with finger-like shape [204]. The active top layer is thinner and denser, which can lead to superior permeation properties.



**Figure 4.6.** Cross-section SEM images with the control membrane (a) and membranes with the addition of 0.5wt.% Rutile (b) and 0.5wt.% Anatase (c)

In the SEM sectional view of the modified membranes to 1wt.% nanoparticles (**Figure 4.7**), more uniform and elongated finger-like pores were observed, compared to the membranes of lower concentration of the nanoparticles.



**Figure 4.7.** Cross-section SEM images with the control membrane (a) and membranes with the addition of 1wt.% Rutile (b) and 1wt.% Anatase (c)

In the cross-section elemental analysis of the membranes modified with TiO<sub>2</sub> nanoparticles of different concentrations and crystalline structures, **Table 4.2**, it can be seen that



the percentage of the oxygen element increased compared to the control membrane due to the presence of this specific element in the polysulfone's chemical composition, but also present in the composition of the titanium dioxide nanoparticles. The increased percentage of nanoparticles detected by the EDX method (titanium element), relative to the initial nanoparticle amount added to the polymer solutions, denotes their agglomeration behavior.

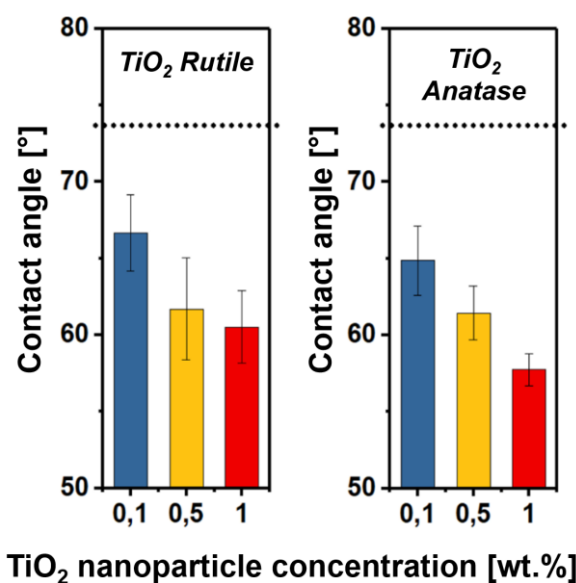
**Table 4.2.** Cross-section elemental analysis by the EDX method of the control membranes and those with addition of titanium dioxide nanoparticles

Membrane	Carbon [%]	Oxygen [%]	Sulphur [%]	Titanium [%]
Control	90.34	7.06	2.60	-
0.1wt.% TiO <sub>2</sub> Rutile	89.88	8.21	1.88	0.03
0.5wt.% TiO <sub>2</sub> Rutile	89.18	8.23	2.24	0.35
1wt.% TiO <sub>2</sub> Rutile	88.89	8.30	2.26	0.55
0.1wt.% TiO <sub>2</sub> Anatase	89.87	7.87	2.10	0.16
0.5wt.% TiO <sub>2</sub> Anatase	89.23	8.17	2.33	0.27
1wt.% TiO <sub>2</sub> Anatase	87.33	10.34	1.90	0.43

From the correlation of Table 4.1 with Table 4.2, it is observed that the presence of TiO<sub>2</sub> Anatase nanoparticles at the surface of the membranes is higher than the percentage found in the cross-section of the membrane. These differences between the surface and the membrane's section can confirm the high degree of migration of the nanoparticles to the surface of the membranes.

#### 4.1.3. Analysis of membrane hydrophilicity by contact angle method

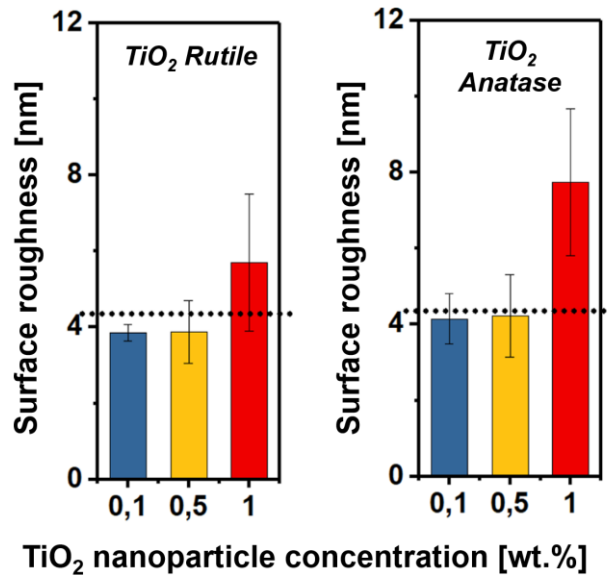
Due to the high hydrophilicity of the nanoparticles, it is observed that at the time of their incorporation, regardless of the chosen weight percentage, the contact angle decreases, improving the hydrophilic character of the membranes. From the crystalline structure of the nanoparticles point of view, it is noticeable that the TiO<sub>2</sub> Anatase-containing membranes have lower contact angles, as observed in **Figure 4.10**.



**Figure 4.10.** Contact angle values of control membranes and those with addition of nanoparticles with different concentrations and crystalline structures. The dotted line represents the contact angle of the control membrane. Standard deviation of control membrane is  $\pm 3,674$

#### 4.1.5. Atomic force microscopy (AFM) results

The average surface roughness (Ra) values of the studied membranes are shown in **Figure 4.16**. These confirm the superior hydrophilic nature of the TiO<sub>2</sub> Anatase-added membranes due to the greater roughness produced by the higher amount of Anatase nanoparticles, compared to membranes containing TiO<sub>2</sub> Rutile nanoparticles.



**Figure 4.16** The roughnesses of control membranes and those with addition of nanoparticles with different concentrations and crystalline structures. The dotted line represents the mean surface roughness of the reference membrane with a standard deviation of  $\pm 0,599$

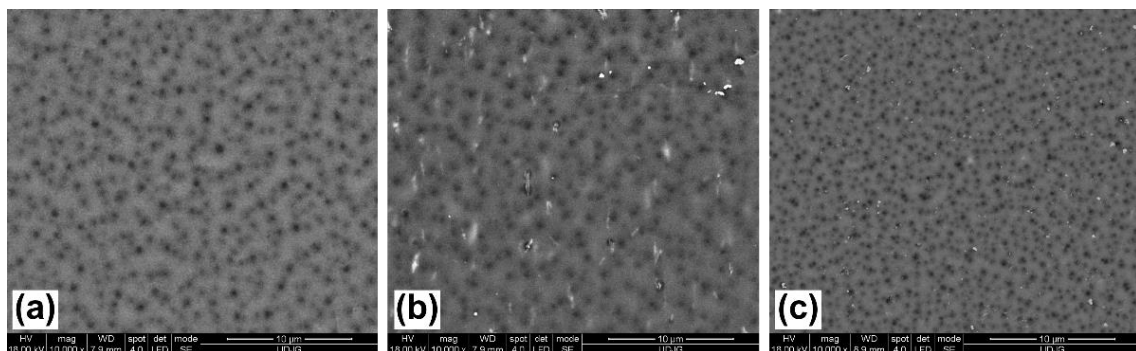
#### 4.2. Influence of zinc oxide nanomaterial shape on membrane properties

Of all the knowledge gained from the dissemination of topical scientific papers, the comparison of zinc oxide nanowires and zinc oxide nanoparticles to their influence on the polysulfone membranes properties has not been discussed so far, especially from a mechanical point of view.

##### 4.2.1. SEM and EDX analysis of the studied membranes

##### 4.2.2.1. Membrane surface analysis by SEM-EDX method

The nanocomposite membranes exhibit a higher number of pores at surface compared to the control membrane (**Figure 4.17.a**).



**Figure 4.17.** Surface SEM images of control membrane (a) and the membranes modified with 0.5 wt% zinc oxide nanowires (b) and nanoparticles (c)

However, there are obvious differences between the nanocomposite membranes, namely that the membrane with the addition of ZnO nanoparticles (**Figure 4.17.c**) has a pore density superior to the nanowire-blended membrane. This phenomenon is closely linked to the differences in the active surfaces of the nanomaterials.

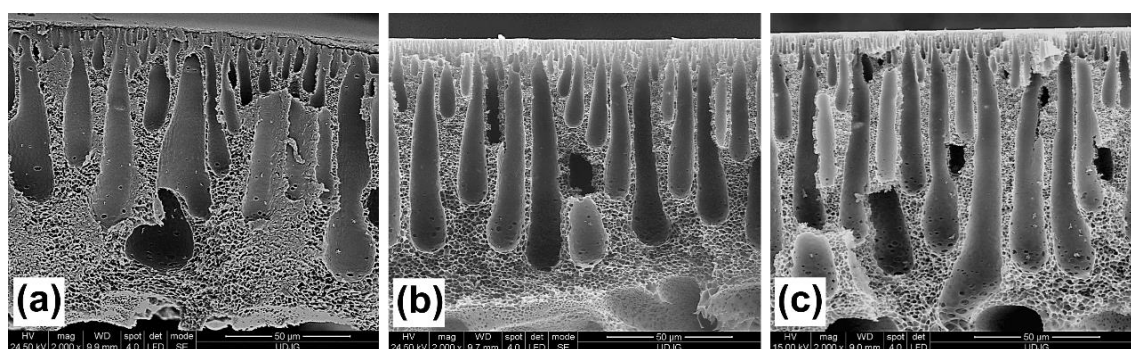
According to EDX results in **Table 4.4**, the presence of nanoparticles on the surface of the membrane is lower than the modified membrane with 0.5wt.% ZnO nanowires, meaning that a certain quantity of nanoparticles has been washed into the coagulation bath during the phase inversion process.

**Table 4.4.** The percentages of the characteristic elements of control membrane and those with addition of zinc oxide nanomaterials detected at the surface by the EDX method

Membrane	Carbon [%]	Oxygen [%]	Sulphur [%]	Zinc [%]
Control	89.67	6.71	3.62	-
0.5wt.% ZnO nanowires	88.68	7.17	3.38	0.77
0.5wt.% ZnO nanoparticles	89.60	6.76	3.06	0.58

#### 4.2.2.2. Cross-section SEM and EDX analysis of the studied membranes

In the case of the nanowire embedded membrane, the pores have a finger-like shape, all of which have similar elongated structures where the upper part does not have a visible connection to the bottom of the membrane, which can condition a high water flux.



**Figure 4.19.** Cross-section SEM images of control membrane (a) and the membranes modified with 0.5 wt% zinc oxide nanowires (b) and nanoparticles (c)

The cross-section structure of the modified membrane by adding 0.5wt% ZnO nanoparticles (**Figure 4.19.c**) show narrower and higher number of pores that assure a direct connection between the upper and lower membrane areas. This type of structure facilitates the transport of water through the membrane, which determines a high flux.

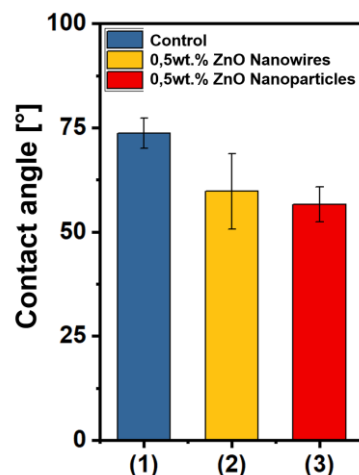
**Table 4.5.** The percentages of the elements present in cross-section structures of the control membrane and those modified with nanowires and nanoparticles of zinc oxide

Membrane	Carbon [%]	Oxygen [%]	Sulphur [%]	Zinc [%]
Control	90.34	7.06	2.60	-
0.5wt.% ZnO nanowire	89.40	7.60	2.51	0.49
0.5wt.% ZnO nanoparticles	88.34	8.77	2.59	0.31

The percentage of zinc element in cross-sections of nanocomposite membranes modified with nanowires is approximately equal to the weight percentage of ZnO nanoparticles-blended membranes.

#### 4.2.3. Analysis of hydrophilic character by contact angle method

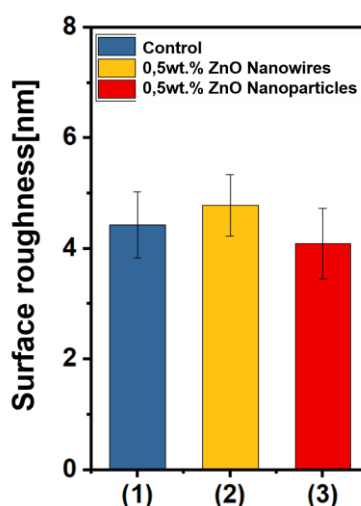
Due to the hydrophilic character of ZnO nanomaterials, it is observed in **Figure 4.22**, that the contact angles of the nanocomposite membranes are lower than that of the membrane without added nanoparticles.



**Figure 4.22.** The contact angles of the control membrane and the membranes with addition of zinc oxide nanoparticles and nanowires

#### 4.2.5. Topographic characterization of membranes by atomic force microscopy (AFM)

**Figure 4.26** shows the surface roughness values of membranes without nanoparticles and those with the addition of ZnO nanowires and nanoparticles. In the study of the roughness profiles the presence of agglomerations on the surface of the membranes with addition of ZnO nanoparticles was observed, but this did not lead to the increase of the final roughness above the value of the control membrane roughness.



**Figure 4.26.** Surface roughness ( $S_a$ ) values and standard deviation of control membrane and membranes modified by addition of 0.5wt.% ZnO nanowires and 0.5wt% ZnO nanoparticles

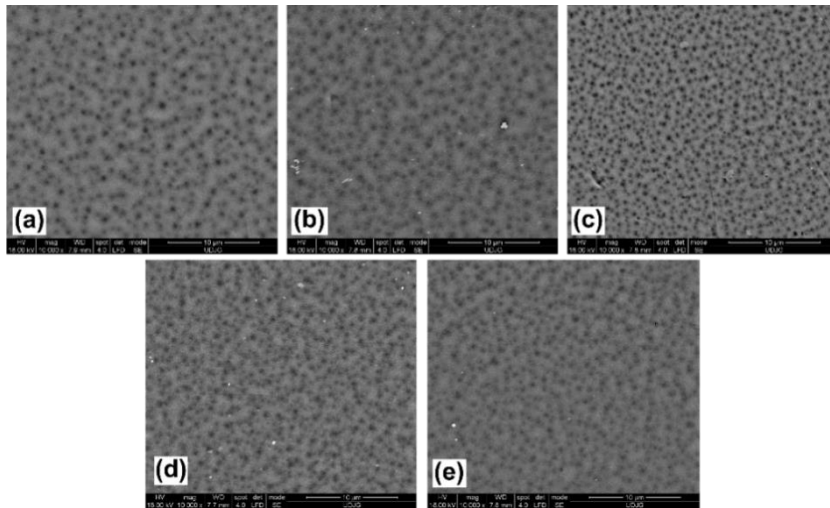
#### 4.3. Influence of zinc oxide nanoparticle size on membrane properties

The effect of size (100nm, 50nm, 25nm and 14nm) and concentration (0.1wt%, 0.5wt% and 1wt.%) of ZnO nanoparticles over the polysulfone membranes obtained by the phase inversion method was of interest in this study.

### 4.3.1. Electronic scanning microscopy (SEM) and EDX analysis on studied membranes

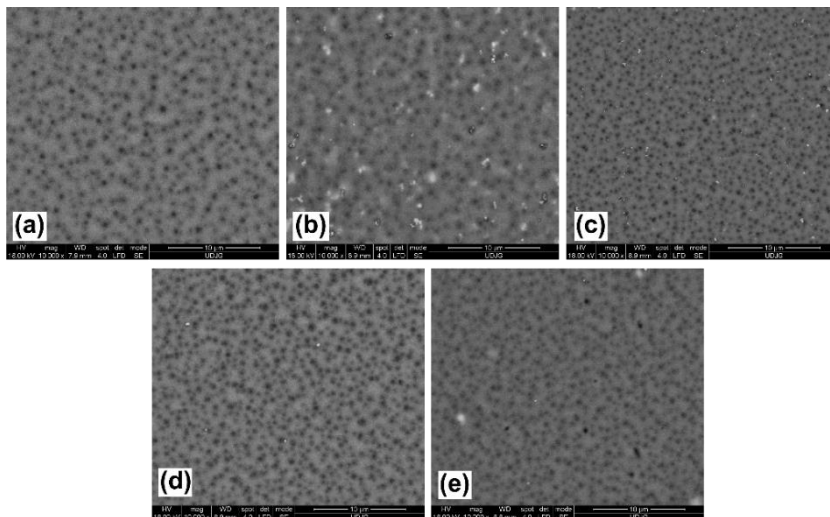
#### 4.3.1.1. Membrane surface analysis by SEM-EDX method

Figure 4.27 shows SEM surface images for membranes with a concentration of 0.1wt.% ZnO nanoparticles. Blending ZnO nanoparticles with sizes of 50nm (Figure 4.27.c), 25nm (Figure 4.27.d) and 14nm (Figure 4.27.e) produced an increase in the number of pores and also their decrease, the most pronounced changes in morphology being for membranes blended with nanoparticles of 25nm and 14nm in size.



**Figure 4.27.** Surface SEM micrographs of the control membrane (a) and the modified membranes by the addition of 0.1wt.% zinc oxide nanoparticles with dimensions of 100nm (b), 50nm (c), 25nm (d) and 14nm (e)

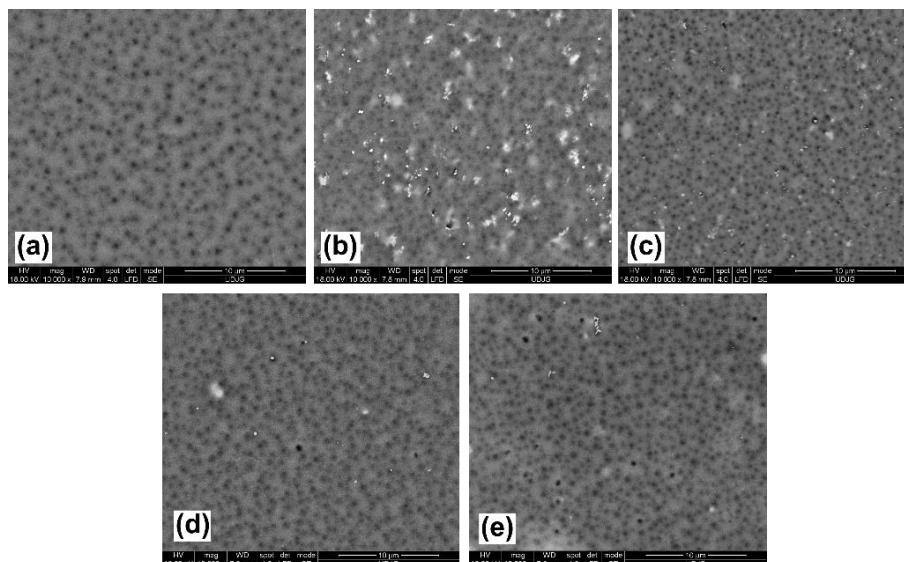
Regarding the influence of nanoparticles with the size of 100nm (Figure 4.27.b) over the surface porosity, there are no differences compared with the control membrane (Figure 4.27.a).



**Figure 4.28.** Surface SEM micrographs of the control membrane (a) and the modified membranes by the addition of 0.5wt.% zinc oxide nanoparticles with dimensions of 100nm (b), 50nm (c), 25nm (d) and 14nm (e)

For the membranes with a mass percentage of 0.5wt.% ZnO (Figure 4.28) it is observed that, for all nanoparticle sizes, there are substantial changes at surface compared with the control membrane (Figure 4.28.a).

The morphology of nanocomposite membrane surface can be analyzed in **Figure 4.29**, where a mass percentage of 1wt.% ZnO nanoparticles of different sizes were added to the polymer solutions of the studied membranes. At this concentration of nanoparticles, it can easily be observed their high agglomeration tendency regardless of size.



**Figure 4.29.** Surface SEM micrographs of the control membrane (a) and the modified membranes by the addition of 1wt.% zinc oxide nanoparticles with dimensions of 100nm (b), 50nm (c), 25nm (d) and 14nm (e)

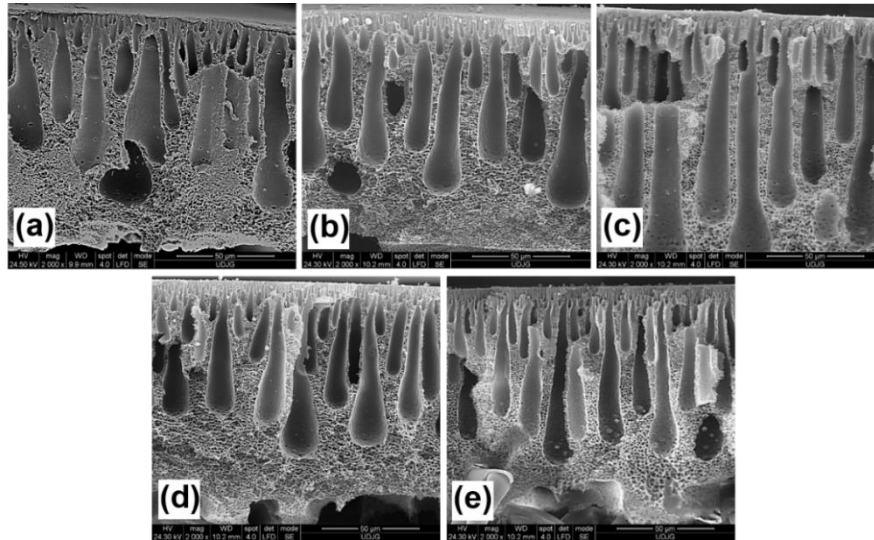
The agglomeration tendency of the nanoparticles on the membrane surfaces can be confirmed by the high values reported by EDX elemental analysis, values shown in **Table 4.6**. The highest percentages of the Zn element are for membranes with nanoparticles with a size of 100nm. The presence of Zn on the surface of the membranes decreases directly in proportion with the decrease in nanoparticle size.

**Table 4.6.** The elemental composition detected by EDX analysis at the surface for the membranes with addition of ZnO nanoparticles of different sizes and concentrations

Membrane	Carbon [%]	Oxygen [%]	Sulphur [%]	Zinc [%]
Control	89.67	6.71	3.62	-
0.1wt.% ZnO 100nm	86.99	7.46	5.22	0.32
0.5wt.% ZnO 100nm	88.26	7.33	3.75	0.67
1wt.% ZnO 100nm	88.23	7.81	2.97	0.99
0.1wt.% ZnO 50nm	89.53	7.38	2.81	0.29
0.5wt.% ZnO 50nm	89.60	6.76	3.06	0.58
1wt.% ZnO 50nm	88.64	7.40	3.13	0.83
0.1wt.% ZnO 25nm	88.34	6.87	4.64	0.15
0.5wt.% ZnO 25nm	89.28	6.89	3.51	0.32
1wt.% ZnO 25nm	88.80	6.94	3.62	0.63
0.1wt.% ZnO 14nm	88.41	7.19	4.30	0.11
0.5wt.% ZnO 14nm	89.40	7.00	3.48	0.12
1wt.% ZnO 14nm	89.43	6.51	3.59	0.47

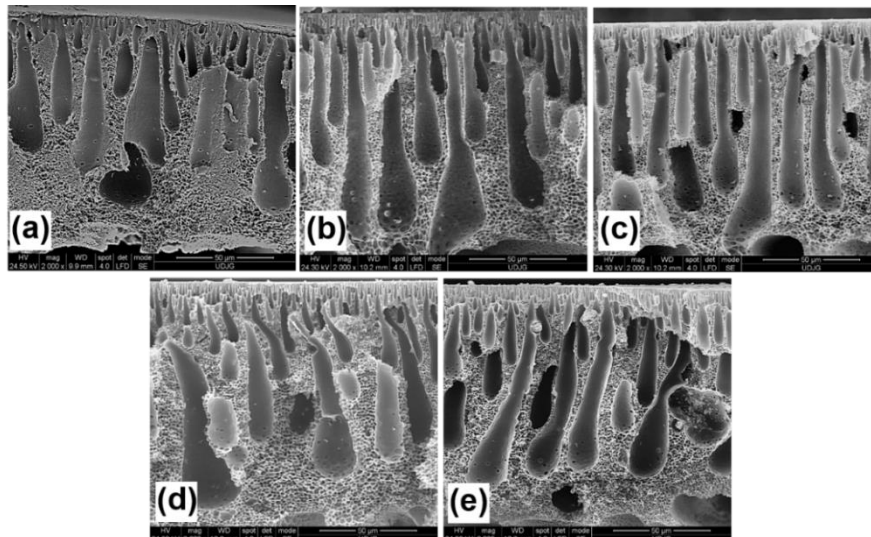
#### 4.3.1.2. Cross-section SEM and EDX analysis of the studied membranes

In the study of the influence of 0.1wt.% nanoparticles on the membrane section morphology (**Figure 4.31**), there are no big differences between the control membrane and the nanocomposite membranes, the asserted structures being affirmed by the porosity values.



**Figure 4.31.** Cross-sectional SEM micrographs of control membranes (a) and with addition of 0.1wt.% ZnO nanoparticles with sizes of 100nm (b), 50nm (c), 25nm (d) and 14nm (e)

At the concentration of 0.5wt.% ZnO added to the polymer solution, the section morphology produced after phase inversion resulted in elongated pores with a denser top-layer than the control membrane. The membranes with blended nanoparticles of 100nm ZnO (**Figure 4.32.b**) and 50nm (**Figure 4.32.c**) showed pores connecting the extremities of membranes, and for membranes with ZnO 25nm (**Figure 4.32.d**) and 14nm ZnO nanoparticles such morphology was not present.

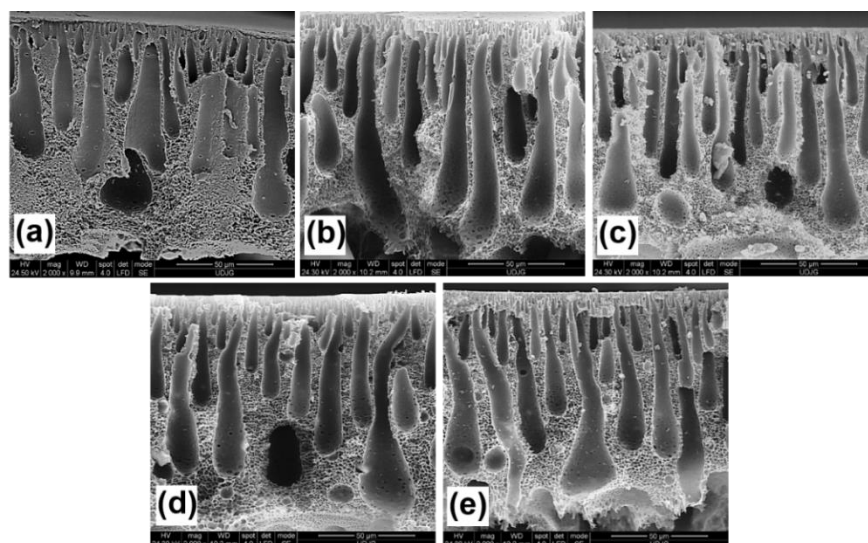


**Figure 4.32.** Cross-sectional SEM micrographs of control membranes (a) and with addition of 0.5wt.% ZnO nanoparticles with sizes of 100nm (b), 50nm (c), 25nm (d) and 14nm (e)

The membranes obtained by the addition of 1wt.% ZnO nanoparticles have an asymmetric structure similar to those obtained previously, according to **Figure 4.33**. By comparing the cross-sections of the membrane structures of different ZnO concentrations, it is observed that by increasing nanoparticle concentration from 0.1 to 1 wt.%, the porosity of the



membranes differs as the pores are smaller but much denser at higher nanoparticle concentrations.



**Figure 4.33.** Cross-sectional SEM micrographs of control membranes (a) and with addition of 1wt.% ZnO nanoparticles with sizes of 100nm (b), 50nm (c), 25nm (d) and 14nm (e)

As for the mass percentage of the Zn element detected in the membrane cross-sections (**Table 4.7**), these values differ from the membrane surfaces (Table 4.6). Here, the concentration increases with the decrease of nanoparticle size.

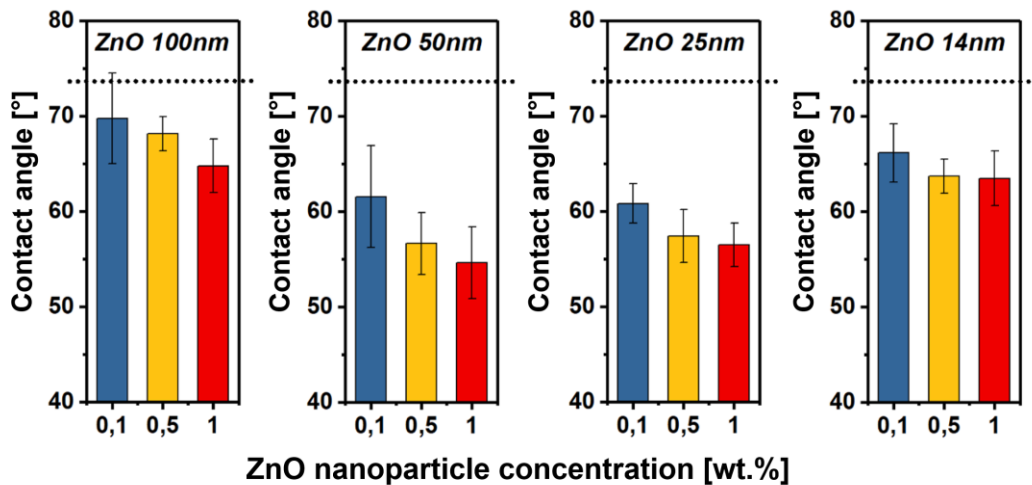
**Table 4.7.** Cross-section elemental EDX analysis of control membranes and with the addition of ZnO nanoparticles of different sizes and concentrations

Membrane	Carbon [%]	Oxygen [%]	Sulphur [%]	Zinc [%]
Control	90.34	7.06	2.60	-
0.1wt.% ZnO 100nm	88.85	8.40	2.50	0.25
0.5wt.% ZnO 100nm	88.68	8.68	2.34	0.30
1wt.% ZnO 100nm	88.62	8.79	2.21	0.38
0.1wt.% ZnO 50nm	88.81	8.63	2.46	0.10
0.5wt.% ZnO 50nm	88.34	8.77	2.58	0.31
1wt.% ZnO 50nm	87.05	9.74	2.41	0.80
0.1wt.% ZnO 25nm	88.49	9.01	2.41	0.09
0.5wt.% ZnO 25nm	88.59	8.53	2.37	0.51
1wt.% ZnO 25nm	88.01	9.02	2.19	0.78
0.1wt.% ZnO 14nm	88.66	8.66	2.57	0.11
0.5wt.% ZnO 14nm	88.12	9.05	2.56	0.27
1wt.% ZnO 14nm	87.46	9.09	2.88	0.57

#### 4.3.3. Analysis of membrane hydrophilicity by contact angle method

The highest contact angle value is characteristic for the control membrane (73°). From the nanoparticles concentration point of view, it is noted that the contact angle is inversely proportional to the nanoparticle weight percent. In terms of nanoparticle size, the downward trend in contact angle is not linear.



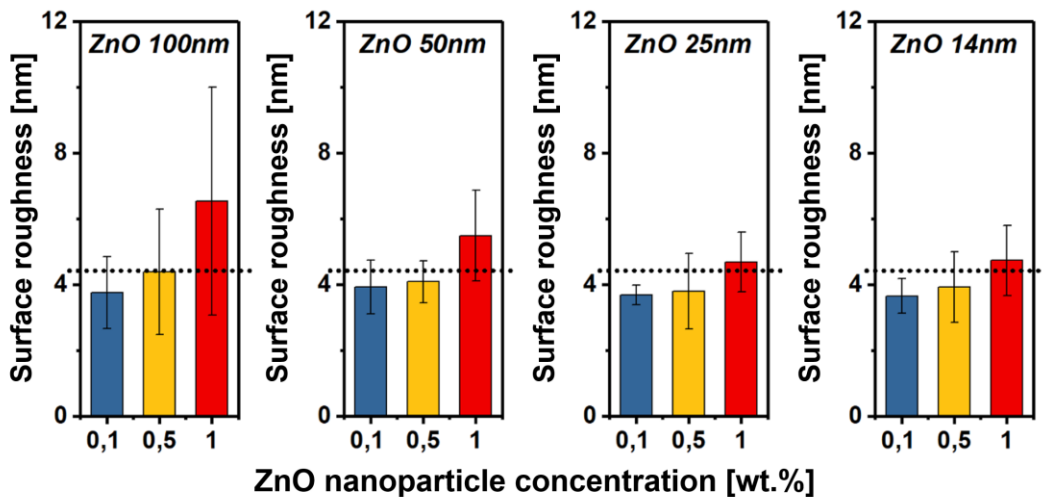


**Figure 4.36.** Hydrophilicity of membranes according to the concentration and size of ZnO nanoparticles. The dotted line represents the contact angle of control membrane. Standard deviation of control membrane is  $\pm 3,674$

#### 4.3.5. Atomic force microscopy (AFM) results

It can be seen that the control membrane exhibits a greater roughness than the 0.1wt% and 0.5wt% ZnO membranes. These results reveal that the presence of nanoparticles leads, up to a certain load, to a smoother membrane surface.

Adding a concentration of zinc oxide nanoparticles greater than 0.5wt.% produces an increase in roughness compared to the control membrane but also to the lower nanoparticle concentration-membranes.



**Figure 4.44.** The average surface roughness values of the control membranes and the addition of zinc oxide nanoparticles of different sizes. The dotted line represents the mean surface roughness of the reference membrane with a standard deviation of  $\pm 0,599$

#### 4.4. Partial conclusions

I. In the investigation of the influence of crystalline structure on the properties of the studied membranes by the addition of TiO<sub>2</sub> Rutile and TiO<sub>2</sub> Anatase nanoparticles in the membrane matrix, the following conclusions can be highlighted:

In the surface SEM analysis, an increase in the number of pores but also a decrease in their size since the incorporation of a small amount of nanoparticles (0.1wt.%) was observed,

these changes being directly proportional to the concentration of the nanoparticles added. These changes lead to an increase in flux as well as an increase in retention degree;

Increasing the amount of nanoparticles leads to the appearance of agglomerations on the surface of the membranes. The SEM images, elemental analyzes and the roughness of the studied membranes confirmed a higher tendency of TiO<sub>2</sub> Anatase nanoparticles to produce agglomerations on the surface of the membranes compared to the modified membranes with addition of TiO<sub>2</sub> Rutile nanoparticles;

Compared to the control membrane, the nanocomposite membranes exhibit improved or similar properties in the case of the membranes modified with 0.1 wt.% titanium dioxide nanoparticles.

II. In the study of the influence of nanomaterial shape on membrane properties, the following partial conclusions were drawn:

The membranes resulted from nanoparticle and nanowire embedding exhibit asymmetric cross-sectional structures and elongated pores where the most notable difference is that membranes blended with 0.5 wt.% nanoparticle have larger pores that are connecting the top with the bottom parts of the membrane;

The surface pores, produced by blending nanowires in the membranes, are larger with a lower density than the nanoparticle blended-membranes, which means a lower flux;

The hydrophilicity of the nanoparticle-added membranes is the highest, whereas the control membrane has a hydrophobic tendency;

As a result of the AFM analysis, an increase in roughness of the nanowire blended-membranes can be observed, while the membrane modified by nanoparticles has reached the lowest roughness.

III. After the inclusion of zinc oxide nanoparticles of various sizes in the membrane matrix, the following results have been observed:

The membrane pore size decreased when small nanoparticles were embedded;

All membranes exhibit an asymmetric structure, the most notable changes being observed for membranes with 50 nm nanoparticle addition and concentrations of 0.5 wt.% and 1 wt.%;

The minimum contact angle was obtained by the membrane with 1 wt.% ZnO 50 nm, and the diminution of the nanoparticle size leads to an increase of the contact angle. The most hydrophobic membrane was the one without the addition of nanoparticles;

Decreasing the size of nanoparticles in the membrane leads to a decrease in surface roughness;

All analyzes of this chapter are closely related to membrane performance in terms of permeation, retention, fouling degree, and mechanical properties.

## CHAPTER V

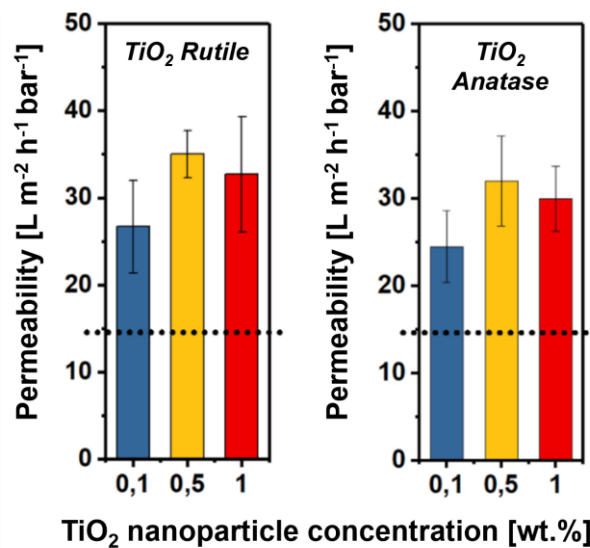
## EXPERIMENTAL RESULTS ON THE INFLUENCE OF NANOPARTICLES ON MEMBRANE PERFORMANCE

## 5.1. Study of membrane properties on the influence of the crystalline structure of titanium dioxide nanoparticles

## 5.1.1. Determination of permeation properties

## 5.1.1.2. The permeability of the studied membranes

After stabilizing the membrane flux at 10bar, the membranes were gradually subjected to higher filtration pressures, up to 20bar, to study permeability. The permeability values are shown in **Figure 5.2**. The most important difference on these nanocomposite membranes, taking into account both crystalline structure and nanoparticle concentration, is produced between the membranes with 0.5wt.%  $\text{TiO}_2$ , the Rutile membrane producing permeability of 9.36% higher than the membranes modified with Anatase. However, compared to the control membrane, inclusion of 0.5wt.%  $\text{TiO}_2$  Rutile and Anatase nanoparticles in the polymer solution resulted in an increase in permeability of 139.73% and 119.18%.

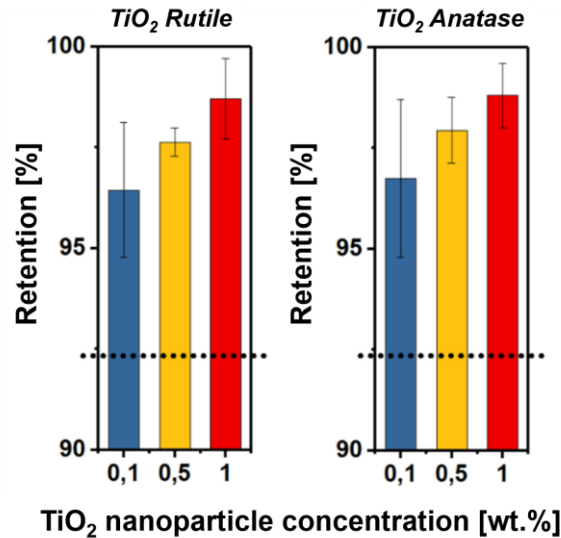


**Figure 5.2.** Permeability of the control membrane and those modified with the addition of Rutile and Anatase nanoparticles at concentrations of 0.1wt.%, 0.5wt.% and 1wt.%. The dotted line represents the permeability of the control membrane with a standard deviation of  $\pm 3.387$

## 5.1.2. The retention capacity of the studied membranes

In membrane retention tests, a Congo Red concentration solution of 10 ppm was used. The Red Congo retention increases directly proportional with the weight percentage of nanoparticles in the membranes. The highest retention rates were obtained at 1wt.%  $\text{TiO}_2$  membranes, with 98.71% and 98.80% for Rutile nanoparticles and Anatase nanoparticles, respectively.

Although the addition of 1 wt.% nanoparticles has led to a decrease in water flux due to the tendency of nanoparticles to block the pores, there has been no decrease in separation performance in the Congo Red retention tests. Good retention means ensuring increased water quality in a membrane process.



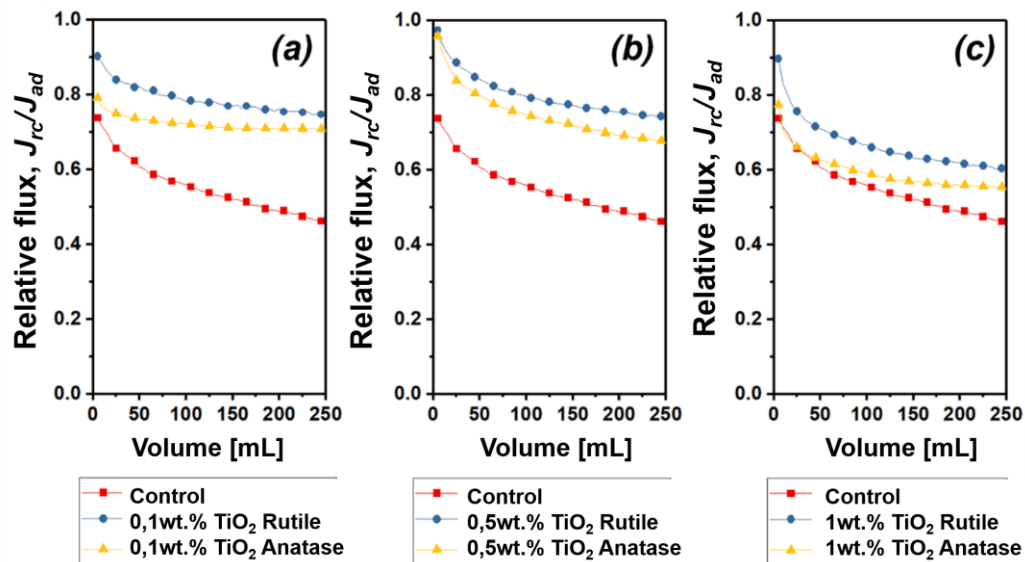
**Figure 5.3.** Retention values of Congo Red dye (10ppm) for control and modified membranes with TiO<sub>2</sub> Rutile and Anatase nanoparticles and different concentrations. The dotted line represents the control membrane dye retention value with a standard deviation of  $\pm 2,877$

### 5.1.3. Fouling studies of the resulted membranes

The membrane's ability to withstand fouling is dependent on surface chemistry, roughness and hydrophilicity [185].

#### 5.1.3.1. Relative flux

The filtration of the dye solution revealed that the reference membrane had the lowest value of relative flux.



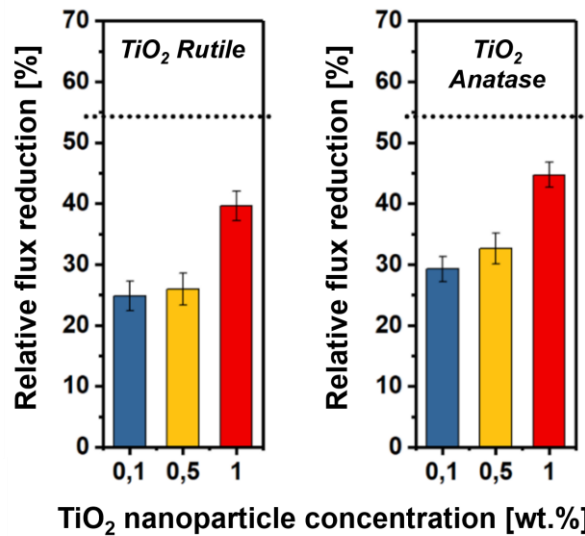
**Figure 5.4.** The membrane fouling study by relative flux method of the control membrane and TiO<sub>2</sub> Rutile and Anatase modified membranes at concentrations of 0.1wt.% (a), 0.5wt.% (b) and 1wt.% (c)

The relative flux of nanocomposite membranes increased for nanoparticle concentrations of 0.1wt% and 0.5wt% (**Figure 5.4.a** and **b**), then decreased considerably at concentrations of 1wt.% TiO<sub>2</sub> both Rutile and Anatase (**Figure 5.4.c**). This trend was also observed by other authors [382, 411].

The 0.5wt.% TiO<sub>2</sub> membranes offered similar values of the relative flux with the membranes with lower quantity of nanoparticles, but their stability over time is lower than the membranes with 0.1wt% nanoparticle. This aspect can be caused by relatively higher roughness values of 0.5wt.% TiO<sub>2</sub> membranes than membranes with 0.1wt.% TiO<sub>2</sub>. For membranes with 1wt.% TiO<sub>2</sub>, the relative flux decline is the most pronounced, mainly due to the increase in roughness produced by high nanoparticle agglomerates on the surface of the membranes.

### 5.1.3.2. Relative flux reduction

The lowest relative flux reduction was obtained by the membrane with the addition of 0.1wt.% TiO<sub>2</sub> Rutile with a value of 24.91%. It can be seen that membranes with nanoparticle concentrations of 0.1wt% and 0.5wt% have similar values, which means they have favorable anti-fouling properties.



**Figure 5.5.** Study of fouling degree for membranes with TiO<sub>2</sub> rutile and anatase nanoparticles. The dotted line represents the relative flux reduction of the control membrane. The standard deviation of the control membrane is  $\pm 1.968$

The increase in the relative flux reduction by membranes with 1wt.% TiO<sub>2</sub> nanoparticle addition means that they have suffered a higher fouling degree.

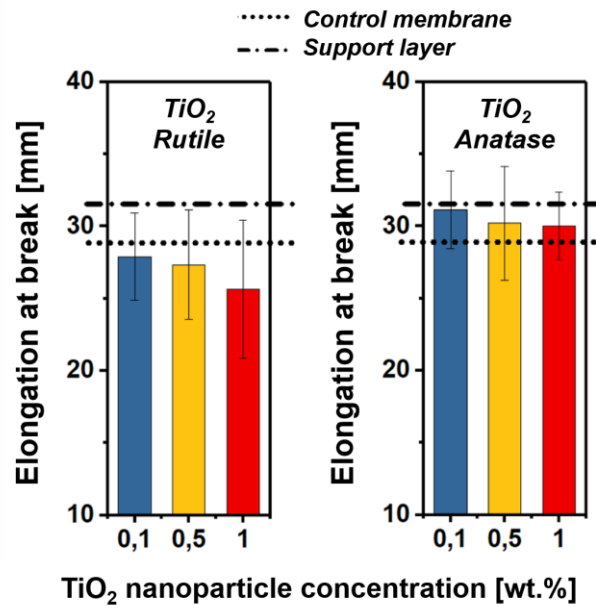
### 5.1.4. Mechanical properties of the studied membranes

An appropriate concentration of titanium dioxide nanoparticles can optimize mechanical properties such as tensile strength, elongation at break and modulus of elasticity. These efficiencies are necessary to prevent possible defects caused by high pressures from water filtration in engineering applications.

#### 5.1.4.2. Elongation at break

**Figure 5.7** shows the details of the elongation of the membranes resulting from the sample break. The decrease in elongation at break is directly proportional to the increase in nanoparticle concentration. The lower elongation of TiO<sub>2</sub> Rutile blended membranes can be explained by the higher nanoparticle stiffness, which limits the free movement of polymer chains.

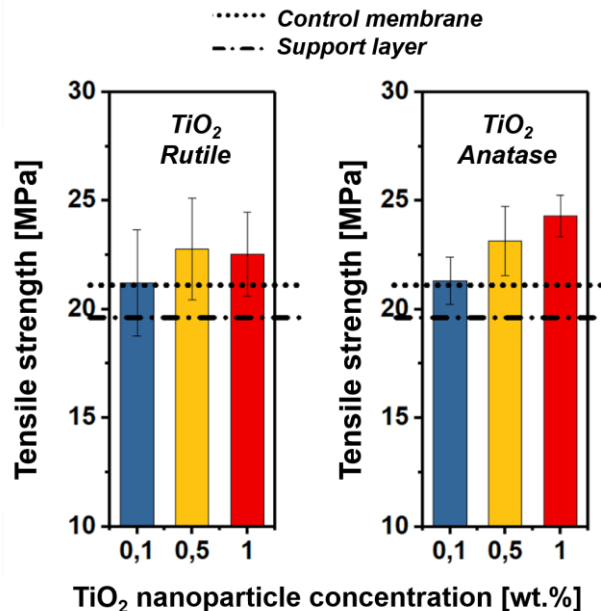
Higher elongation at break values for TiO<sub>2</sub> Anatase membranes are explained by the presence of higher nanoparticles in the membrane structure confirmed by EDX analysis as well as their uniform distribution in membrane matrices.



**Figure 5.7.** Elongation at break of TiO<sub>2</sub> Rutile and Anatase blended membranes. The dotted line represents the elongation at break of the control membrane with a standard deviation of  $\pm 3,961$ . The dash-dotted line is the elongation at break of the support layer with a standard deviation of  $\pm 1.258$

#### 5.1.4.3. Tensile strength

The incorporation of low concentration TiO<sub>2</sub> nanoparticles does not affect nanocomposite membranes in terms of breaking strength, as can be seen in **Figure 5.8**. However, increasing the concentration of nanoparticles in the PSf polymer matrix results in improved breaking strength of nanocomposite membranes compared to the control membrane.



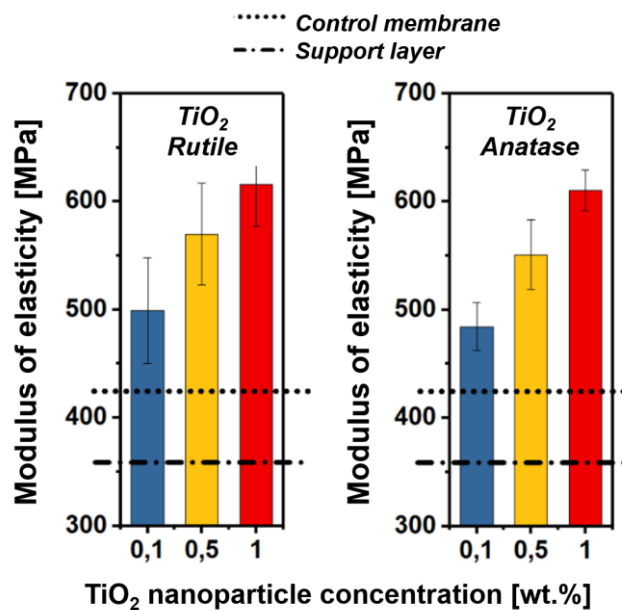
**Figure 5.8.** Tensile strength of TiO<sub>2</sub> Rutile and Anatase blended membranes. The dotted line represents the tensile strength of control membrane with a standard deviation of  $\pm 1.601$ . The dash-dotted line is the tensile strength of support layer with a standard deviation of  $\pm 1.789$

By increasing the TiO<sub>2</sub> content from 0.1wt.% to 0.5wt.%, the tensile strength increases from 21.207MPa to 22.766MPa for Rutile-modified membranes, and in the case of Anatase-

modified membrane an increase from 21.313MPa at 23.153MPa is observed. Further increase of nanoparticle concentrations up to 1wt.% produced different behaviors between Rutile and Anatase blended membranes. The 1wt.% TiO<sub>2</sub> Anatase membrane achieved the highest value of tensile strength up to 24.298MPa, a 23.88% increase relative to control membrane. For membrane with 1wt.% TiO<sub>2</sub> Rutile, the tensile strength value decreased to 22.534MPa.

#### 5.1.4.4. Modulus of elasticity

The modulus of elasticity of the control membrane has a value of 424.565MPa, which is the lowest value among the tested membranes. The most notable increases in the modulus of elasticity compared to the control membrane were obtained by 1wt% TiO<sub>2</sub> Rutile and 1wt% TiO<sub>2</sub> Anatase membranes with higher increases of 45,053% and 43,726%, respectively. The values of the modulus of elasticity resulting from the uniaxial mechanical tests of the membranes are directly proportional to the percentage of nanoparticles added to the polymer solutions.



**Figure 5.9.** Modulus of elasticity of membranes with TiO<sub>2</sub> Rutile and Anatase. The dotted line represents the modulus of elasticity of the control membrane with a standard deviation of  $\pm 32.201$ . The dash-dotted line represents the modulus of elasticity of the support layer with a standard deviation of  $\pm 46.169$ .

#### 5.1.5. Determination of total membrane performance

For a comparison of the obtained results on the studied membrane performance, six properties of interest were selected: permeability [Lm<sup>2</sup>h<sup>-1</sup>bar<sup>-1</sup>], relative flux reduction [%], retention [%], modulus of elasticity [MPa], tensile strength [MPa] and elongation at break [mm].

Due to the fact that the differences between the two types of nanoparticles are not very high, it is quite difficult to find the optimum membrane. We consider that there is an ideal membrane with all the parameters of the highest mark (10). Thus, the ideal area of performance of this simulated membrane would be the total area of the hexagon. By establishing the ratio between the real area produced by membrane performances with the ideal area, we can quantify them in performance indices, values shown in **Table 5.2**.

It can be seen that the best membrane is the one modified with 0.5wt.% TiO<sub>2</sub> Rutile, the next being obtained by the membrane with 0.5wt.% TiO<sub>2</sub> Anatase. The difference between the two membranes is relatively small, with the Rutile membrane recording only 6.682% higher performance compared to the Anatase membrane. However, we can conclude that a concentration of 0.5wt.% nanoparticles of titanium dioxide, regardless of the crystalline structure, provides the best performance for the nanocomposite membranes.



**Table 5.2.** Analysis of total membrane performance resulting from incorporation of titanium dioxide nanoparticles

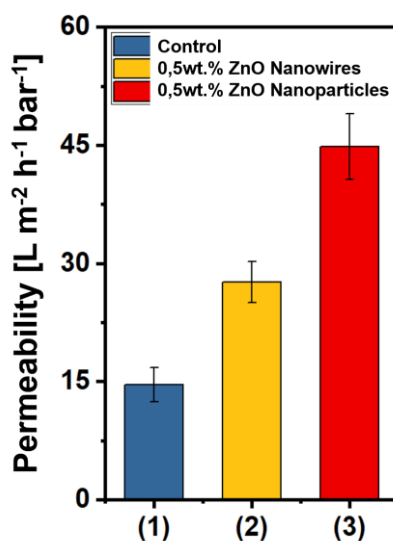
Membrane	Performance indice
Control	0.528
0.1wt.% TiO <sub>2</sub> Rutile	0.765
<b>0.5wt.% TiO<sub>2</sub> Rutile</b>	<b>0.926</b>
1wt.% TiO <sub>2</sub> Rutile	0.850
0.1wt.% TiO <sub>2</sub> Anatase	0.725
<b>0.5wt.% TiO<sub>2</sub> Anatase</b>	<b>0.868</b>
1wt.% TiO <sub>2</sub> Anatase	0.833

## 5.2. Determination of membrane properties resulting from blending of zinc oxide nanomaterials of different forms

### 5.2.1. Permeation tests

#### 5.2.1.2. The permeability of the studied membranes

As can be seen, the lowest permeability is obtained by the control membrane, with a value of  $14.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . Membranes blended with zinc oxide nanowires produces an increase in permeability of 89.16%, while nanoparticle-modified membranes exert an increase in permeability by 207.19% higher than the control membrane.

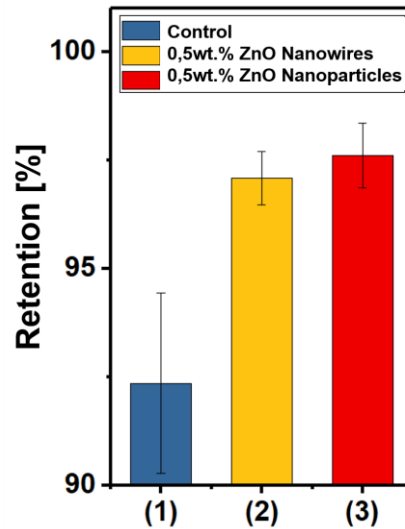


**Figure 5.12.** Permeability of control membrane and membranes blended with zinc oxide nanoparticles and nanowires

### 5.2.2. The retention capacity of the studied membranes

Modification of the membrane by addition of nanowires produced an increase in retention of 5.11% and in the case of ZnO nanoparticle blended membrane, an increase in retention of 5.68% was achieved compared to the control membrane.



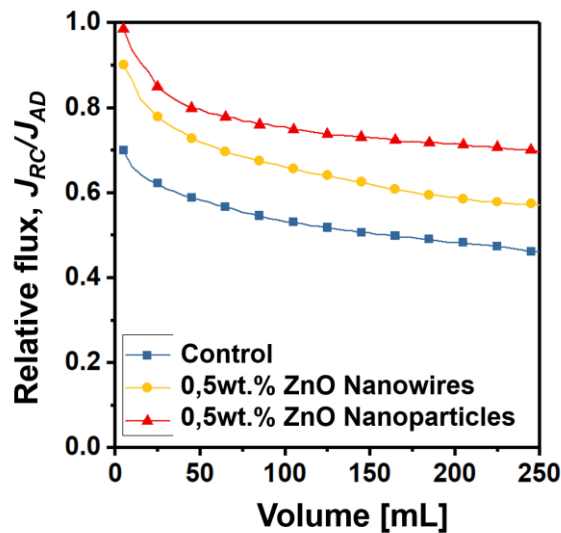


**Figure 5.13.** Congo Red dye retention of control and nanocomposite membranes modified with zinc oxide nanowires and nanoparticles

### 5.2.3. Fouling studies of the resulted membranes

#### 5.2.3.1. Relative flux

In **Figure 5.14**, it can be seen that the control membrane is more prone to fouling compared to nanocomposite membranes. Due to the hydrophobic character of the control membrane, it is easy to understand that during the Congo Red dye filtration, the contaminant creates a dye-polymer hydrophobic bond. Increasing the hydrophilicity of nanocomposite membranes, as well as changes in roughness, have led to an improvement in their fouling resistance.

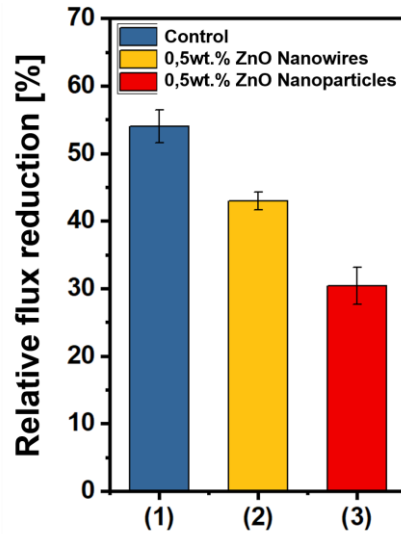


**Figure 5.14.** Fouling studies by calculating the relative fluxes of the control and nanocomposite membranes with 0.5 wt% zinc oxide nanowires and nanoparticles

#### 5.2.3.2. Relative flux reduction

It can be noticed that due to the less hydrophilic nature, the control membrane exhibits the highest fouling, whereas the tendency to fouling decreases due to the presence of nanomaterials on the surface of the membranes.

These nanomaterials that were added to the polymer solution produced two major changes following the phase inversion: it reduced the contact angle and the surface roughness of the membranes. These are considered important factors in the attempt to minimize membrane fouling.

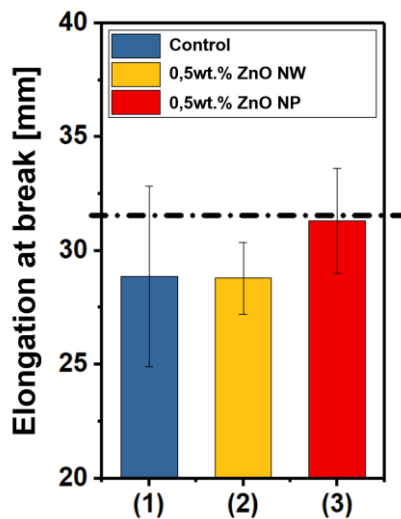


**Figure 5.15.** Relative flux reductions of control membrane and nanocomposite membranes with addition of zinc oxide nanowires and nanoparticles after Congo Red dye retention tests

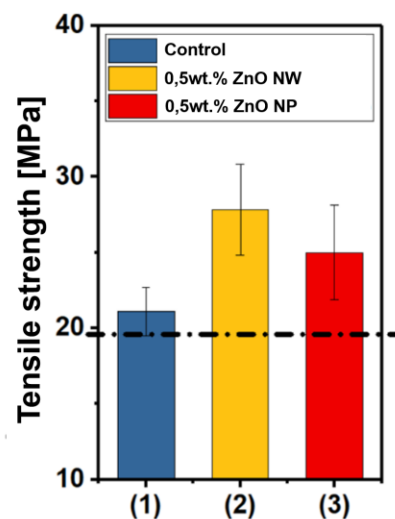
## 5.2.4. Mechanical properties of the studied membranes

### 5.2.4.2. Elongation at break and tensile strength

As can be seen in **Figure 5.17**, the elongation at break of the nanoparticle modified-membranes produced an increase from 28.879mm (control membrane) to 31.318mm.



**Figure 5.17.** Elongation at break of the control and zinc oxide nanoparticles and nanowires modified membranes. The dotted line is the elongation at break of the support layer with a standard deviation of  $\pm 1.258$



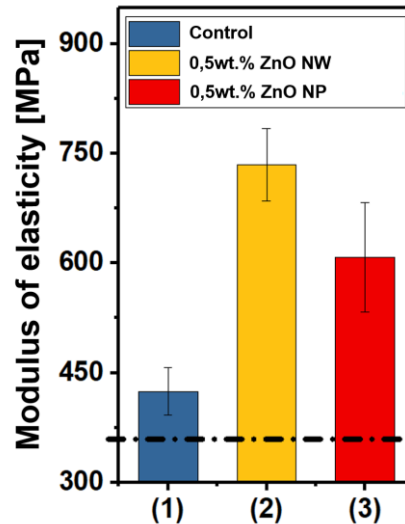
**Figure 5.18.** The tensile strength of the control and zinc oxide nanoparticles and nanowires modified membranes. The dotted line is the tensile strength of the support layer with a standard deviation of:  $\pm 1,789$

The dimension differences (especially in length) between nanoparticles and nanowires are responsible for the distinct results in mechanical properties of the formed membranes. Larger lengths of nanowires provide greater linkages between nanowire and polymer chains, meaning that the transfer of energy from the polymer to nanowires is higher and the elongation is unchanged. In the case of nanoparticles, the associated membranes exhibit a higher elongation, which means they absorb the energy produced by mechanical traction but also produce a larger plastic deformation without breaking the sample. Increasing the tensile strength (**Figure 5.18**) of the 0.5wt.% ZnO nanowire addition membranes can be explained by a good transfer of mechanical stress from the polymer matrix to nanowires, and due to their high length (300nm),

these can lead to a distribution of much more uniform stress, which can minimize the emergence of high stress areas [279]. The balance between breaking strength and elongation at break is achieved by the addition of zinc oxide nanoparticles.

#### 5.2.4.3. Modulus of elasticity

The good compatibility between the nanowire and the polymeric matrix resulted in the formation of a membrane with the best mechanical properties.



**Figure 5.19.** The modulus of elasticity of the control membrane and those with addition of zinc oxide nanowires and nanoparticles. The dotted line represents the modulus of elasticity of the support layer with a standard deviation of  $\pm 46.169$

The highest modulus of elasticity was obtained by the membrane with addition of 0.5wt.% ZnO nanowire, with a 68.85% increase over the control membrane and 22.02% higher relative to the membrane with the addition of zinc oxide nanoparticles.

#### 5.2.5. Determination of total membrane performance

**Table 5.4** shows the ratios between the real areas produced by membrane performances and the ideal performance area. The calculated indices confirmed that the addition of 0.5wt.% of ZnO nanoparticles in the polymer solution produced the highest performance membrane, showing an increase of 84.689% than the pure membrane and 29.133% compared to the membrane by 0.5wt% ZnO nanowires. Due to the smaller size and the larger active surface, the zinc oxide nanoparticles have positively influenced the overall properties of the membranes.

**Table 5.4.** Membrane performance index of control membranes and modified membranes by addition of zinc oxide nanowires and nanoparticles

Membrane	Performance indice
Control	0.516
0.5wt.% ZnO Nanowires	0.738
0.5wt.% ZnO Nanoparticles	0.953

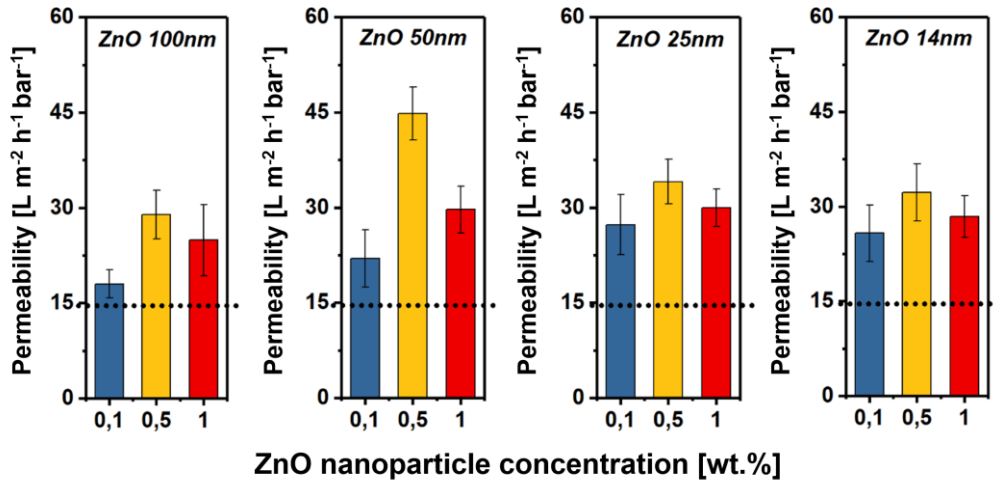
### 5.3. Analysis of the influence of zinc oxide nanoparticle size on membrane properties

#### 5.3.1. Permeation tests of the studied membranes

##### 5.3.1.2. The permeability of the studied membranes

**Figure 5.22** shows the permeability values of the studied membranes. The lowest value was obtained by the control membrane,  $14.6 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . The lowest influence on nanocomposite membranes was induced by 100nm zinc oxide nanoparticles, recording a maximum increase of

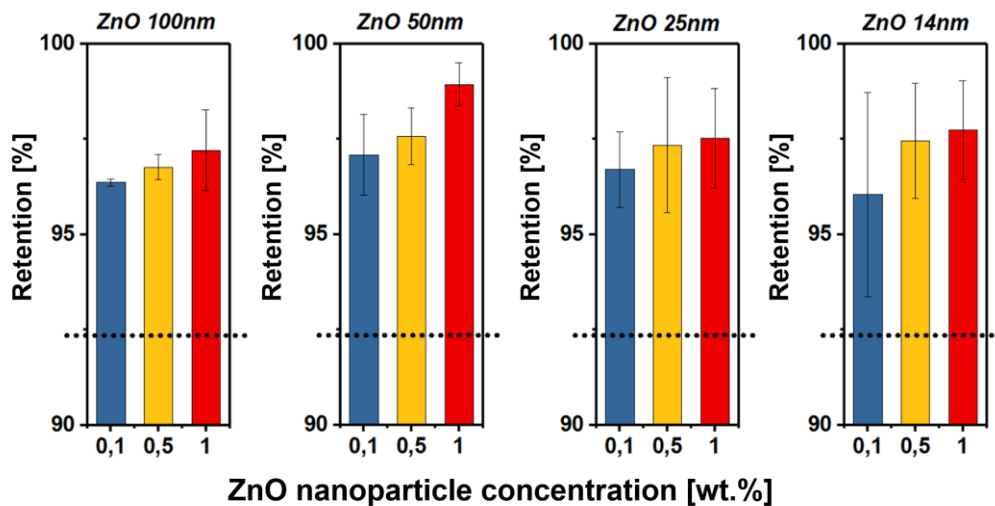
97.95% for membranes with 0.5wt.% ZnO 100nm. The membrane with 0.5wt.% ZnO 50nm achieved the highest increase of approximately 207% compared to the control membrane. Decrease in nanoparticle size from 50nm to 14nm resulted in lower permeability, membranes with 25nm and 14nm ZnO nanoparticles showed an increase in permeability of only 133.56% and 120.55%, respectively.



**Figure 5.22.** Permeabilities of the control membrane and membranes with the addition of nanoparticles of different sizes and concentrations. The dotted line represents the permeability of the control membrane with a standard deviation of  $\pm 3.387$

### 5.3.2. Congo Red dye degree of retention

The control membrane recorded a retention of 92.34%, being the lowest value among the membranes studied.



**Figure 5.23.** Congo Red dye retention of the control membrane and membranes with the addition of nanoparticles of different sizes and concentrations. The dotted line represents the degree of retention achieved by the control membrane with a standard deviation of  $\pm 2.877$

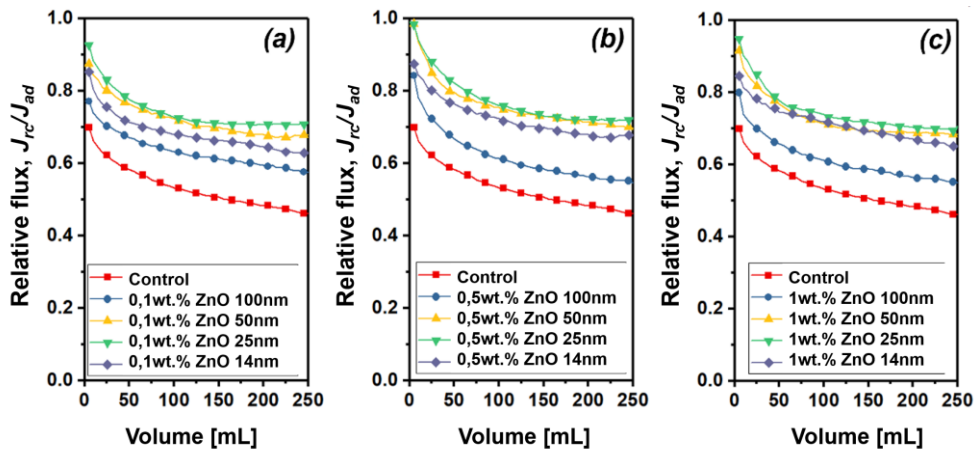
The degree of retention increases with the concentration of zinc oxide nanoparticles. Although inclusion of a 1wt.% ZnO nanoparticle concentration resulted in a decrease in permeability and distilled water flux compared to 0.5wt.% ZnO modified membranes, in Congo Red Dye retention tests, higher concentration nanoparticles show the highest values. The 1wt% ZnO 50nm membrane produced a 98.93% retention, which is classified as the highest retention membrane. The 25nm and 14nm ZnO membranes showed a lower retention rate than ZnO 50nm modified membranes.

### 5.3.3. Study on the degree of membrane fouling

The degree of fouling of the membranes can be studied by the relative flux and relative flux reduction methods. The first method provides information on the fouling behavior during the Red Congo solution retention, while the second method analyzes the percentage of the fouling produced at the end of the dye filtration.

#### 5.3.3.1. Relative flux

A high relative flux can be understood as the ability of the membrane to better resist fouling. Decrease in relative flux is an increase in membrane fouling. The control membrane exhibited the lowest resistance to fouling due to the high absorption of the contaminant on the polymer. The presence of nanoparticles has led to better control of the fouling. Considering the investigation of the influence of zinc oxide nanoparticle concentrations, relative flux increases up to 0.5wt.% ZnO (**Figure 5.24.b**) is observed. An increase in fouling at the concentration of 1% by weight of the nanoparticles added to the membranes (**Figure 5.24.c**) is governed by the increase in surface roughness even if contact angles were lower than the membranes with concentrations of 0.1wt% and 0.5wt%.

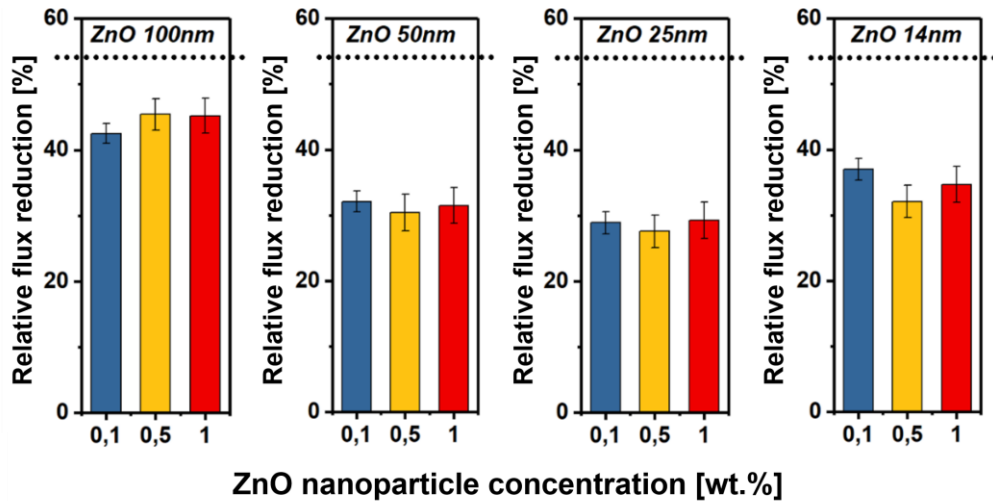


**Figure 5.24.** Membrane fouling study by the relative flow method of the control membrane and nanoparticle blended membranes of different sizes and concentrations of 0.1wt.% (a), 0.5wt.% (b) and 1wt.% (c)

In the analysis of the fouling trend according to the nanoparticle size, it can be noticed that the lowest fouling resistance is related to 100nm ZnO membranes, regardless of the concentration. The nanoparticle membranes with 50nm and 25nm nanoparticles have obtained the best results of the relative flux. The hierarchy of nanoparticles depending on the positive influence of their size on the membranes is the order of 0nm (control membrane) <100nm <14nm <50nm <25nm.

#### 5.3.3.2. Relative flux reduction

Membranes with the addition of 100nm nanoparticles showed the highest degree of fouling, with a relative flux reduction of 45.445%, these values are shown in **Figure 5.25**. Decreasing the size of the nanoparticles led to a decrease in the fouling trend, the smallest value being recorded by the membrane with addition of 0.5wt.% ZnO 25nm, ie 27.631%. Relative flux reduction is higher for membranes with 1wt.% addition and can be correlated with increased surface roughness.



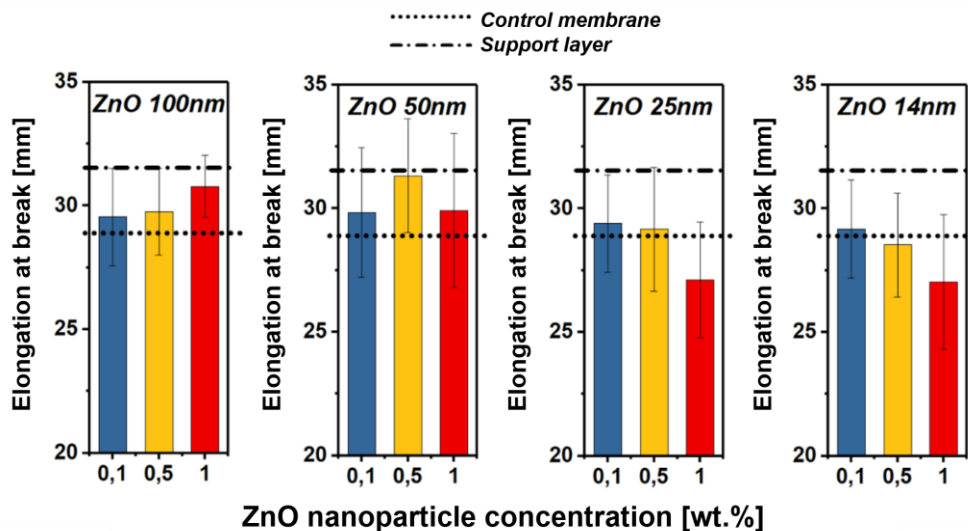
**Figure 5.25.** Study of the fouling degree by relative flux reduction method of membranes with addition of ZnO nanoparticles of different sizes and concentrations. The dotted line represents the relative flux reduction for the control membrane with deviation standard of  $\pm 1.968$

### 5.3.4. Mechanical properties of the studied membranes

Mechanical parameters such as tensile strength, elongation at break and modulus of elasticity provide useful predictions on membrane capabilities to withstand tensile stresses, plastic deformations and resistance to dimensional changes that will occur in industrial applications under harsh operating conditions [138]. Although these parameters are not directly correlated with permeate flux or retention, they have proven to be of valuable over long membrane stresses [422].

#### 5.3.4.2. Elongation at break

The largest elongation is attributed to the membrane with 0.5wt.% ZnO 50nm.



**Figure 5.27.** Elongation at break of membranes with the addition of ZnO nanoparticles of different sizes and concentrations. The dotted line represents the elongation at break of the control membrane with a standard deviation of  $\pm 3,961$ . The dash-dotted line is the elongation at break of the support layer with a standard deviation of  $\pm 1.258$

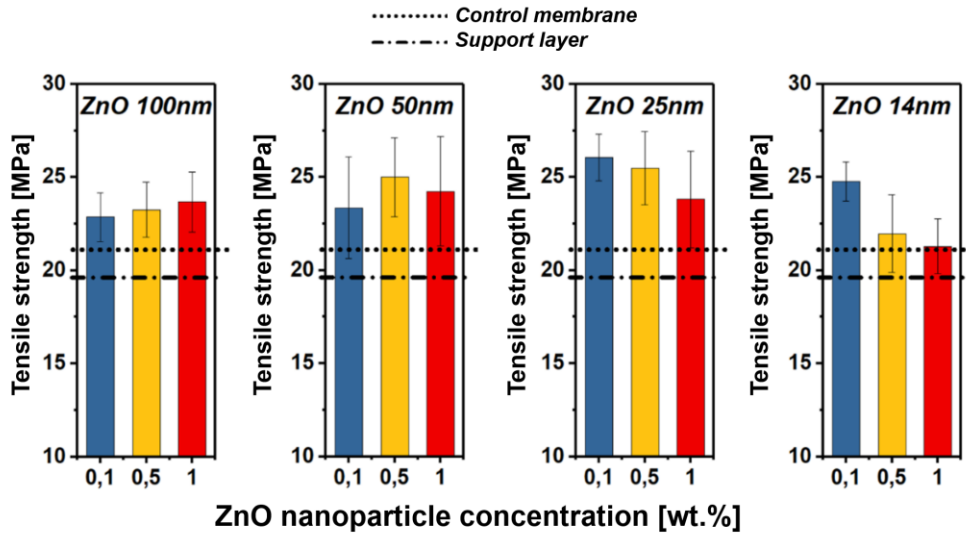
The elongation at break produced by 0.1 wt% and 0.5 wt% zinc oxide nanoparticles and sizes of 25nm and 14nm differs from the control membrane, these behaviors being interdependent with the relatively weak bond between the polymer matrix and nanoparticles. Addition of 1 wt% ZnO 25nm and 14nm in the polymeric matrix resulted in elongation below that characteristic of the control



membrane. This decline can be caused by the appearance of defects in the membrane structure produced by nanoparticle agglomerations observed in SEM surface images.

**5.3.4.3. Tensile strength**

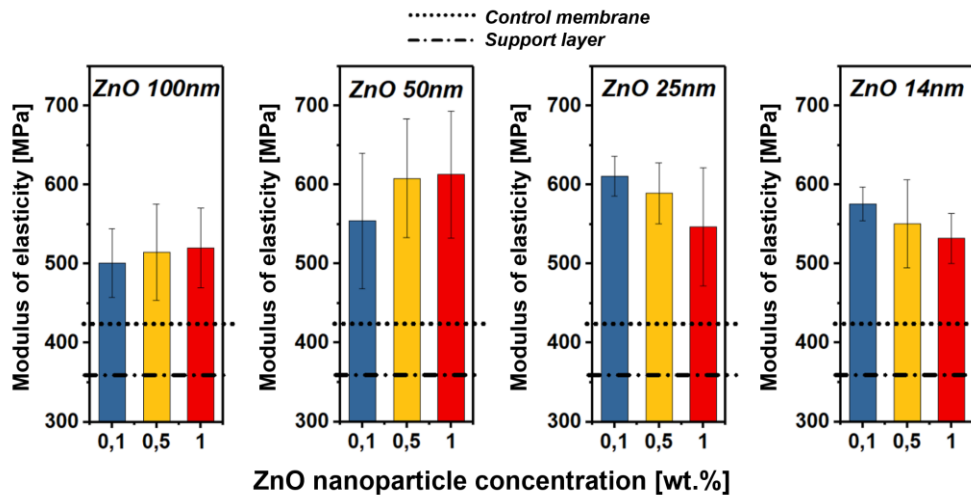
Higher compatibility between 50nm and 25nm nanoparticles with the polymeric matrix has led to a strong link, resulting in the need for more energy to break the bonds between ZnO and PSf, leading to improved mechanical properties. For membranes with 50nm ZnO addition, the tensile strength increases for nanocomposite membranes to a concentration of 0.5wt.%, followed by a decrease in membrane rupture resistance by 1wt% ZnO. Also, the most pronounced decline in breaking strength was for membranes with 14nm ZnO and 1wt% concentration.



**Figure 5.28.** The tensile strengths of membranes with the addition of zinc oxide nanoparticles of different sizes and concentrations. The dotted line represents the breaking resistance of the control membrane with a standard deviation of  $\pm 1.601$ . The dash-dotted line is the breaking strength of the support layer with a standard deviation of  $\pm 1.789$

**5.3.4.4. Modulus of elasticity**

It can be noticed that in the case of membranes modified by high nanoparticle size (100nm and 50nm), the modulus of elasticity increases with the present concentration in the membrane matrix



**Figure 5.29.** Modulus of elasticity of membranes with the addition of zinc oxide nanoparticles of different sizes and concentrations. The dotted line represents the modulus of elasticity of the control membrane with a standard deviation of  $\pm 32.201$ . The dash-dotted line represents the modulus of elasticity of the support layer with a standard deviation of  $\pm 46.169$

### 5.3.5. Determination of total membrane performance

Analyzing the performance coefficients of the studied membranes, the 0.5 wt.% ZnO 50nm addition membranes show the highest performance index, which means that nanoparticles measuring 50nm have a positive impact on membrane properties.

**Table 5.6.** The membrane performance index based on the concentration and size of the zinc oxide nanoparticles

Membrane	Performance indice
Contrl	0.491
0.1wt.% ZnO 100nm	0.623
0.5wt.% ZnO 100nm	0.702
1wt.% ZnO 100nm	0.689
0.1wt.% ZnO 50nm	0.730
<b>0.5wt.% ZnO 50nm</b>	<b>0.966</b>
1wt.% ZnO 50nm	0.834
0.1wt.% ZnO 25nm	0.831
0.5wt.% ZnO 25nm	0.875
1wt.% ZnO 25nm	0.779
0.1wt.% ZnO 14nm	0.771
0.5wt.% ZnO 14nm	0.775
1wt.% ZnO 14nm	0.709

### 5.4. Partial conclusions

Embedding TiO<sub>2</sub> and ZnO nanoparticles and ZnO nanowires in the polymer solution resulted in the production of nanocomposite membranes with superior pure membrane properties. All studied nanomaterials (Nanoparticles of TiO<sub>2</sub> Rutile and Anatase, Zinc Oxide Nanowires and Nanoparticles, 100nm, 50nm, 25nm and 14nm zinc oxide nanoparticles) have shown maximum potential at a concentration of 0.5wt% added to the solution polymer for membrane formation. Increasing the concentration to 1wt.% In the membrane matrix led to a decrease in performance, the unitary agreement in the membrane domain of this phenomenon being attributed to the blocking of pores with nanomaterials or clusters of nanomaterials.

From the general performance analyzes performed in this study on the influence of inclusions of 0.1wt.%, 0.5wt.% And 1wt.% TiO<sub>2</sub> Rutile and Anatase, it was determined that the 0.5 wt.% TiO<sub>2</sub> Rutile addition membrane showed an improvement superior to the rest of the membranes. Although the membranes with nanoparticles with Rutile crystalline structure showed high performance, the difference is still very small, ie about 6% higher than the modified membranes by the addition of TiO<sub>2</sub> Anatase nanoparticles.

The best-performing membrane was the nanoparticle addition, showing a higher optimization of 84.689% than the pure membrane and 29.133% higher compared to the membrane with 0.5wt% ZnO nanofire.

The most important parameter in the study of the influence of nanoparticles on membrane property is the choice of the optimum size of ZnO. After incorporation of nanoparticles of different sizes (100nm, 50nm, 25nm and 14nm) membranes with different structural and performance properties were formed compared to the reference membrane. Following the determination of the best membrane in terms of concentration and size of the embedded nanoparticles, by calculating the performance index, it was found that a concentration of 0.5wt.% and nanoparticle size of 50nm resulted in the formation of a nanocomposite membrane with the best performance compared to the rest of the studied membranes.



## CHAPTER VI

### FINAL CONCLUSIONS, PERSONAL CONTRIBUTIONS AND NEW RESEARCH DIRECTION

#### 6.1. Final conclusions

In this research thesis I studied the influence of some parameters of fabrication of nanocomposite membranes destined for wastewater treatment, membrane characterization from morphological and structural point of view, as well as determination of permeation properties, fouling control and study of mechanical properties.

The membranes of this study were obtained by the phase inversion technique by immersion of thin films of polymeric solutions into the coagulation bath composed of distilled water. The polymeric solutions consisted of 1:3 ratios of PSF:NMP mixture. The parameters of interest of this study used to modify the membranes were the addition of TiO<sub>2</sub> nanoparticles with different crystalline structures (Rutile, Anatase) and concentrations (0.1wt%, 0.5wt% and 1wt%), shape of ZnO nanomaterial (nanowires, nanoparticles) and variation in the size of the zinc oxide nanoparticles (100nm, 50nm, 25nm and 14nm) with different concentrations (0.1wt%, 0.5wt% and 1wt%).

As a general conclusion, the performance of nanocomposite membranes was dependent on the nanoparticle concentration that was incorporated in the polymeric matrices. In the case of permeability, distilled water flux and fouling rate, it was experimentally determined that their value increased to a concentration of 0.5wt.% nanoparticles, and at concentrations of 1wt.%, their tendencies were decreasing.

I. Following the modification of the membranes by the addition of titanium dioxide nanoparticles with the crystalline structures of Rutile and Anatase, the following conclusions can be drawn:

1. Substantial structural changes were observed, most notably the increase in pore number and decrease in their size, and increased porosity in the modified membrane section, also. These characteristics were correlated with increasing permeability and water flux of nanocomposite membranes compared to the control membrane.

2. The retention percentage of Congo Red dye reached by nanocomposite membranes was over 95%, its value being directly proportional to the mass percentage of the nanoparticles blended in the membranes, as confirmed by the SEM micrographs. Differences in nanoparticle crystalline structures in membrane performance were not significant.

3. Mechanical tests have shown a positive impact of nanoparticles on membrane integrity. All nanocomposite membranes showed superior mechanical properties than the control membrane. From the nanoparticle crystalline structure point of view, TiO<sub>2</sub> Anatase membranes have been found to have the highest tensile strength and elongation at break. The modulus of elasticity and compaction degree did not show pronounced differences between the nanocomposite membranes.

4. From the total performance calculated for each membrane it was found that the difference between the crystalline forms of the TiO<sub>2</sub> nanoparticles was not pronounced, the improvement of the membranes after inclusion of 0.5wt% TiO<sub>2</sub> Rutile being 6% higher than the membrane with 0.5wt.% TiO<sub>2</sub> Anatase.

5. It can be concluded that the role of the crystal structure in obtaining a membrane with optimal properties can not be taken in consideration, at least when discussing about the crystalline structures of titanium dioxide.

II. In the study of the influence of the ZnO nanomaterial type according to its shape, the following conclusions are highlighted:

1. The addition of zinc oxide nanoparticles and nanowires to the polymer solution resulted in increased surface porosity of the membranes, the most pronounced being produced by nanoparticles. The proof of these characteristics is confirmed by high water flux and permeability values, where the nanoparticle membrane recorded a 207% flux increase compared

to the control membrane, and about 55% greater than the ZnO nanowire-modified membrane. These results are also confirmed by the calculated porosities, where porosity is directly proportional to the flux and permeability of distilled water.

2. Dye retention increases due to the presence of nanomaterials in the membrane structure, the most obvious being the membrane with the addition of nanoparticles.

3. From mechanical behavior analysis, it emerged that zinc oxide nanowires, used as a membrane modification agent, resulted in the best tensile properties with superior values compared to control membranes and the nanoparticle blended membranes.

4. The best-performing membrane was resulted from nanoparticle addition, showing an optimization of 84.689% higher than the pure membrane and 29.133% higher compared to the membrane with 0.5wt% ZnO nanowire.

5. Due to the large interaction between the nanoparticles and the membrane polymer matrix we can conclude that the ideal choice for optimizing the membrane processes is by introducing the nanoparticle form into the membrane structure.

III. From the study of nanoparticle size influence on nanocomposite membranes, the following conclusions were drawn:

1. The highest permeability and flux of distilled water values were obtained by the membrane with the addition of nanoparticles with the size of 50nm and concentration of 0.5wt.%.

2. The retention percentage exceeded the 95% threshold, regardless of the concentration or size of the nanoparticles added to membrane fabrication.

3. From the mechanical properties of the membranes, the results showed that the values of elongation at break, breaking strength and modulus of elasticity increased in the case of the 100nm and 50nm ZnO nanoparticle blended membranes, and further decrease in nanoparticle size led to the decline of these parameters.

4. Following the determination of the best membrane in terms of concentration and size of the embedded nanoparticles, by calculating the performance index, it was found that a nanoparticle concentration of 0.5wt.% and size of 50nm resulted in the formation of a membrane nanocomposites with the best performance of the studied membranes.

## **6.2. Personal contributions**

The analysis of the current trends regarding the evolution of research in the technology of manufacturing nanocomposite water treatment membranes by elaborating a detailed bibliographic study.

The approach of the present research topic was carried out within a research domain still in development in Romania regarding the obtaining and characterization of the mixed matrix polymeric membranes used in wastewater purification.

The main purpose of the research is to study the influence of the type and size of nanoparticles on membranes with high concentration of polysulfone (25wt.%).

Confirmation of the role of crystalline structure of titanium dioxide nanoparticles in the optimization of membrane processes. The similarities of the resulting performances from the inclusion of titanium dioxide nanoparticles with different crystalline structures in the membrane matrix is large enough to be disregarded in membrane manufacture.

The identification of the optimal ZnO nanomaterial shape for positive modification of membranes and analyzing their mechanical properties.

Determination of the optimal size and concentration of zinc oxide nanoparticles required for efficiency increase of membranes with 25 wt.% polysulfone.

Choosing the range of nanoparticle concentrations to study their influence on the overall membrane properties resulted in the identification of both the increase and the decline in membrane performance, desirable in the rapid identification of the positive and negative fingerprints of the nanoparticles in the polymer matrix.

The properties resulting from the carried out experiments, such as permeation, retention, fouling and mechanical strength, were correlated with the membrane morphological, structural and compositional characterizations.

The use of the performance index concept provides value to the studied membranes. This membrane classification tool based on the observed performance is a precise method for

finding the optimum membrane as well as observing the progress compared to the reference membrane.

### 6.3. New research directions

The study presented in the current thesis will be directed to the next research directions:

1. Determination of membrane performance in real cases of wastewater treatment and natural water purification;
2. Analysis permeation properties of the obtained membrane with a cross-flow filtration cell;
3. Study of the influence of other types of nanomaterials, especially the nanoparticles that comprise the -OH group, to increase the hydrophilic character of the membrane;
4. Study of the influence of nanometric biopolymers (eg Nanocellulose) on membrane property;
5. Determination of the influence of the studied nanomaterials in this thesis on the properties of other polymers (eg PVDF, CA etc.) under the same manufacturing conditions;
6. Studying the influence of various special chemical cleaning solutions (NaOH, HCl, NaOCl, Acetone, etc.) but also physical cleaning on the long-term performance of membranes used in wastewater filtration;
7. Study of several methods of modifying nanomaterials to provide them with higher stability in the polymer solution;
8. Study of the influence of coagulation bath composition on the membrane formation process by using water with more degrees of purity (tap, deionized, distilled, ultra-pure);
9. Fabrication of polymeric membranes used in wastewater treatment with 3D printing technology.

**BIBLIOGRAPHY**

- [9] Singh R., *Hybrid Membrane Systems for Water Purification: Technology, Systems Design and Operations*, Elsevier B.V., 2006, Netherland, ISBN: 978-1-85617-442-8, DOI: 10.1016/B978-1-85617-442-8.X5000-3.
- [11] Crittenden J.C., Trussell R.R., Hand D.W., Howe K., Tchobanoglous G., *MWH's Water Treatment*, John Wiley & Sons, 2012, United States of America, ISBN: 978-1-118-10375-3.
- [12] Koros W.J., Ma Y.H., Shimidzu T., *Terminology for membranes and membrane processes*, IUPAC, *Pure and Applied Chemistr*, Volume 68, 1996, Issue 7, Pages 1479-1489, DOI: 10.1351/pac199668071479.
- [13] Balta S., *Materiale nanostructurate cu aplicații în obținerea membranelor pentru purificarea apelor*, Galati University Press, 2015, Romania, ISBN 978-606-696-036-6.
- [14] Grumezescu A., *Water Purification*, Academic Press, 2017, United States of America, ISBN: 9780128043714.
- [15] Biron D.S., Santos V., Zeni M., *Ceramic Membranes Applied in Separation Processes*, Springer, 2018, Germany, ISBN-13: 978-3319586038.
- [17] Loeb S., Sourirajan S., *Sea Water Demineralization by Means of an Osmotic Membrane*, *Advances in Chemistry*, Volume 38, 1963, Chapter 9, Pages 117-132, ISBN13: 9780841200395, DOI: 10.1021/ba-1963-0038.ch009.
- [20] Saleh T.A., Gupta V.K., *Nanomaterial and Polymer Membranes, Synthesis, Characterization, and Applications*, Elsevier, 2016, Netherland, ISBN: 978-0-12-804703-3.
- [22] Horie K., Barón M., Fox R. B., He J., Hess M., Kahovec J., Kitayama T., Kubisa P., Maréchal E., Mormann W., Stepto R. F. T., Tabak D., Vohlídal J., Wilks E. S., Work W. J., *Definitions of terms relating to reactions of polymers and to functional polymeric materials*, *Pure and Applied Chemistry*, Volume 76, 2004, No.4, pages 889-906, doi:10.1351/pac200476040889.
- [23] Somasundaran P., *Encyclopedia of Surface and Colloid Science*, CRC Press, Volume 7, 2006, United States of America, ISBN 978-0-8493-9603-8.
- [28] Wibisono Y., *Two-phase flow for fouling control in membranes*, Enschede: Universiteit Twente, 2014, Netherland, DOI: 10.3990/1.9789036537179.
- [29] Baker R.W., *Membrane Technology and Applications*, Second Edition, John Wiley & Sons, Ltd, 2004, United States of America, ISBN:9780470854457.
- [42] Nunes S.P., Peinemann K.V., *Membrane Technology: in the Chemical Industry*, Wiley-VCH, 2006, Germany, ISBN: 978-3-527-31316-7.
- [44] Mulder J., *Basic Principles of Membrane Technology*, Springer Netherlands, 1996, Netherland, ISBN 978-0-7923-4247-2.
- [45] <http://www.lenntech.com/microfiltration.htm>, Water Treatment Solutions. 1998, Lenntech.
- [58] Ladewig B., Al-Shaeli M.N.Z., *Fundamentals of Membrane Bioreactors*, Springer Singapore, 2017, Singapore, ISBN 978-981-10-2013-1.
- [63] Nasrollahi N., Vatanpour V., Aber S., Mahmoodi N.M., *Preparation and characterization of a novel polyethersulfone (PES) ultrafiltration membrane modified with a CuO/ZnO nanocomposite to improve permeability and antifouling properties*, *Separation and Purification Technology*, Volume 192, 2018, Pages 369-382, DOI: 10.1016/j.seppur.2017.10.034.
- [65] Enache D.F., Popa G.A., Vasile E., Razvan A., Oprea O., Voicila E., Dumitru F., *Preparation and Characterization of Ultrafiltration TiO<sub>2</sub> Nanoparticles-Polysulfone Membranes*, *Revista de Chimie*, Volume 68, 2017, Issue 11, Pages 2635-2640, ISSN: 0034-7752.
- [75] Jye L.W., Ismail A.F., *Nanofiltration Membranes: Synthesis, Characterization, and Applications*, CRC Press, 2016, United States of America, ISBN 9781498751377.
- [91] Liu S.X., *Food and Agricultural Wastewater Utilization and Treatment*, John Wiley & Sons, Ltd, 2014, United States of America, ISBN:9781118353974.
- [104] Vogel H.C., Todaro C.M., *Fermentation and Biochemical Engineering Handbook: Principles, Process Design and Equipment*, William Andrew Publishing, 2007, United States of America, ISBN-13: 978-0815514077.

- [107] Nagel B., Dellweg H., Gierasch L.M., Glossary for Chemists of Terms Used in Biotechnology (IUPAC Recommendations 1992), Pure and Applied Chemistry, Volume 64, 1992, Issue 1, Pages 143-168, DOI: 10.1351/pac199264010143.
- [108] Judd S., The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment, Elsevier Science, 2006, United States of America, ISBN: 9781856174817.
- [112] Manawi Y., Kochkodan V., Mahmoudi E., Johnson D.J., Mohammad A.W., Atieh M., Characterization and Separation Performance of a Novel Polyethersulfone Membrane Blended with Acacia Gum, Scientific Reports, Volume 7, 2017, Pages 1-12, DOI:10.1038/s41598-017-14735-9.
- [116] Lalia B.S., Kochkodan V., Hashaikh R., Hilal N., A review on membrane fabrication: Structure, properties and performance relationship, Desalination, Volume 326, 2013, Pages 77-95, DOI: 10.1016/j.desal.2013.06.016.
- [117] Warsinger D.M., Chakraborty S., Tow E.W., Plumlee M.H., Bellona C., Loutatidou S., Karimi L., Mikelonis A.M., Achilli A., Ghassemi A., Padhye L.P., Snyder S.A., Curcio S., Vecitis C.D., Arafat H.A., Lienhard J.H.V., A review of polymeric membranes and processes for potable water reuse, Progress in Polymer Science, Volume 81, 2018, Pages 209-237, DOI:10.1016/j.progpolymsci.2018.01.004.
- [122] Abadi S.R.H., Sebzari M.R., Hemati M., Rekabdar F., Mohammadi T., Ceramic membrane performance in microfiltration of oily wastewater, Desalination, Volume 265, 2011, Issues 1-3, Pages 222-228, DOI: 10.1016/j.desal.2010.07.055.
- [123] Liu G., Wei W., Jin W., Xu N., Polymer/Ceramic Composite Membranes and Their Application in Pervaporation Process, Chinese Journal of Chemical Engineering, Volume 20, 2012, Issue 1, Pages 62-70, DOI: 10.1016/S1004-9541(12)60364-4.
- [124] Faibish R.S., Cohen Y., Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions, Journal of Membrane Science, Volume 185, 2001, Issue 2, Pages 129-143, DOI: 10.1016/S0376-7388(00)00595-0.
- [127] Wedel-Grzenda A., Fraczek-Szczypta A., Terrones M., Ellas A.L., Lekka M., Menaszek E., Blazewicz S., Polysulphone composite membranes modified with two types of carbon additives as a potential material for bone tissue regeneration, Bulletin of Materials Science, Volume 40, 2017, Issue 1, Pages 201-212, DOI:10.1007/s12034-017-1360-x.
- [128] Bottino A., Capannelli G., Comite A., Preparation and characterization of novel porous PVDF-ZrO<sub>2</sub> composite membranes, Desalination, Volume 146, 2002, Issues 1-3, Pages 35-40, DOI:10.1016/S0011-9164(02)00469-1.
- [132] Richards H.L., Baker P.G.L., Iwuoha E., Metal Nanoparticle Modified Polysulfone Membranes for Use in Wastewater Treatment: A Critical Review, Journal of Surface Engineered Materials and Advanced Technology, Volume 2, 2012, pages 183-193, DOI:10.4236/jsemat.2012.223029.
- [133] Ursino C., Castro-Muñoz R., Drioli E., Gzara L., Albeirutty M.H., Figoli A., Progress of Nanocomposite Membranes for Water Treatment, Membranes, Volume 8, 2018, Issue 2, DOI:10.3390/membranes8020018.
- [138] Goh P.S., Ng B.C., Lau W.J., Ismail A.F, Inorganic Nanomaterials in Polymeric Ultrafiltration Membranes for Water Treatment, Separation & Purification Reviews, Volume 44, 2015, Issue 3, Pages 216-249, DOI:10.1080/15422119.2014.926274.
- [148] Drioli E., Giorno L., Membrane Operations: Innovative Separations and Transformations, Wiley-VCH, 2009, Germany, ISBN: 978-3-527-32038-7.
- [152] Guillen G.R., Pan Y., Li M., Hoek E.M.V., Preparation and Characterization of Membranes Formed by Nonsolvent Induced Phase Separation: A Review, Industrial & Engineering Chemistry Research, Volume 50, 2011, Issue 7, Pages 3798-3817, DOI:10.1021/ie101928r.
- [163] Qu X., Alvarez P.J.J., Li Q., Applications of nanotechnology in water and wastewater treatment, Water Research, Volume 47, 2013, Pages 3931-3946, DOI:10.1016/j.watres.2012.09.058.
- [165] Liu J., Wu Y., Shen J., Gao Y., Zhang L., Cao D., Polymer-nanoparticle interfacial behavior revisited: a molecular dynamics study, Physical Chemistry Chemical Physics, Volume 13, 2011, Pages 13058-13069, DOI:10.1039/C0CP02952A.
- [169] Kim J., Van der Bruggen B., The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water

- treatment, *Environ Pollut.*, Volume 158, 2010, Issue 7, Pages 2335-2349, doi:10.1016/j.envpol.2010.03.024.
- [171] Wang K., Abdalla A.A., Khaleel M.A., Hilal N., Khraisheh M.K., Mechanical properties of water desalination and wastewater treatment membranes, *Desalination*, Volume 401, 2017, Pages 190-205, DOI:10.1016/j.desal.2016.06.032.
- [180] Wu G., Gan S., Cui L., Xu Y., Preparation and characterization of PES/TiO<sub>2</sub> composite membranes, *Applied Surface Science*, Volume 254, 2008, Issue 21, Pages 7080-7086, DOI:10.1016/j.apsusc.2008.05.221.
- [181] Khan S.B., Asri A.M., Akhtar K., *Nanomaterials for Environmental Applications and their Fascinating Attributes*, Bentham science, 2018, United Arab Emirates, DOI: 10.2174/97816810864531180201, ISBN: 978-1-68108-646-0.
- [183] Yin J., Deng B., Polymer-matrix nanocomposite membranes for water treatment, *Journal of Membrane Science*, Volume 479, 2015, Pages 256-275, DOI:10.1016/j.memsci.2014.11.019.
- [184] Yanan Y., Peng W., Preparation and characterizations of a new PS/TiO<sub>2</sub> hybrid membranes by sol-gel process, *Polymer*, Volume 47, 2006, Pages 2683-2688, DOI:10.1016/j.polymer.2006.01.019.
- [185] Razmjou A., Mansouri J., Chen V., The effects of mechanical and chemical modification of TiO<sub>2</sub> nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes, *Journal of Membrane Science*, Volume 378, 2011, Issues 1-2, Pages 73-84, DOI:10.1016/j.memsci.2010.10.019.
- [186] Shukla A.K., Alam J., Alhoshan M., Dass L.A., Muthumareeswaran M.R., Development of a nanocomposite ultrafiltration membrane based on polyphenylsulfone blended with graphene oxide, *Scientific Reports*, Volume 7, 2017, Pages 12, DOI:10.1038/srep41976.
- [187] Amin M.T., Alazba A.A., Manzoor U., A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials, *Advances in Materials Science and Engineering*, Volume 2014, 2014, Pages 24, DOI:10.1155/2014/825910.
- [188] Kim S.H., Kwak S.Y., Sohn B.H., Park T.H., Design of TiO<sub>2</sub> nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem, *Journal of Membrane Science*, Volume 211, 2003, Issue 1, Pages 157-165, DOI:10.1016/S0376-7388(02)00418-0.
- [189] Bae T.H., Tak T.M., Effect of TiO<sub>2</sub> nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration, *Journal of Membrane Science*, Volume 249, 2005, Pages 1-8, DOI:10.1016/j.memsci.2004.09.008.
- [197] Yang Y., Wang P., Zheng Q., Preparation and properties of polysulfone/TiO<sub>2</sub> composite ultrafiltration membranes, *Journal of Polymer Science: Part B: Polymer Physics*, Volume 44, 2006, Pages 879-887.
- [200] Livari A.E., Aroujalian A., Raisi A., Fathizadeh M., The effect of TiO<sub>2</sub> nanoparticles on PES UF membrane fouling in water-oil emulsion, *Procedia Engineering*, Volume 44, 2012, Pages 1783-1785, doi:10.1016/j.proeng.2012.08.949.
- [204] Dzinun H., Othman M.H.D., Ismail A.F., Puteh M.H., Rahman M.A., Jaafar J., Adrus N., Hashim N.A., Antifouling Behavior and Separation Performance of Immobilized TiO<sub>2</sub> in Dual Layer Hollow Fiber Membranes, *POLYMER ENGINEERING AND SCIENCE*, 2017, DOI:10.1002/pen.24753.
- [206] Li J.B., Zhu J.W., Zheng M.S., Morphologies and Properties of Poly(phthalazinone ether sulfone ketone) Matrix Ultrafiltration Membranes with Entrapped TiO<sub>2</sub> Nanoparticles, *Journal of Applied Polymer Science*, Volume 103, 2007, Pages 3623-3629, DOI:10.1002/app.25428.
- [214] Leo C.P., Lee W.P.C., Ahmad A.L., Mohammad A.W., Polysulfone membranes blended with ZnO nanoparticles for reducing fouling by oleic acid, *Separation and Purification Technologies*, Volume 89, 2012, Pages 51-56, DOI:.
- [222] Zinadini S., Rostami S., Vatanpour V., Jalilian E., Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite, *Journal of Membrane Science*, Volume 529, 2017, Pages 133-141, DOI:10.1016/j.memsci.2017.01.047.

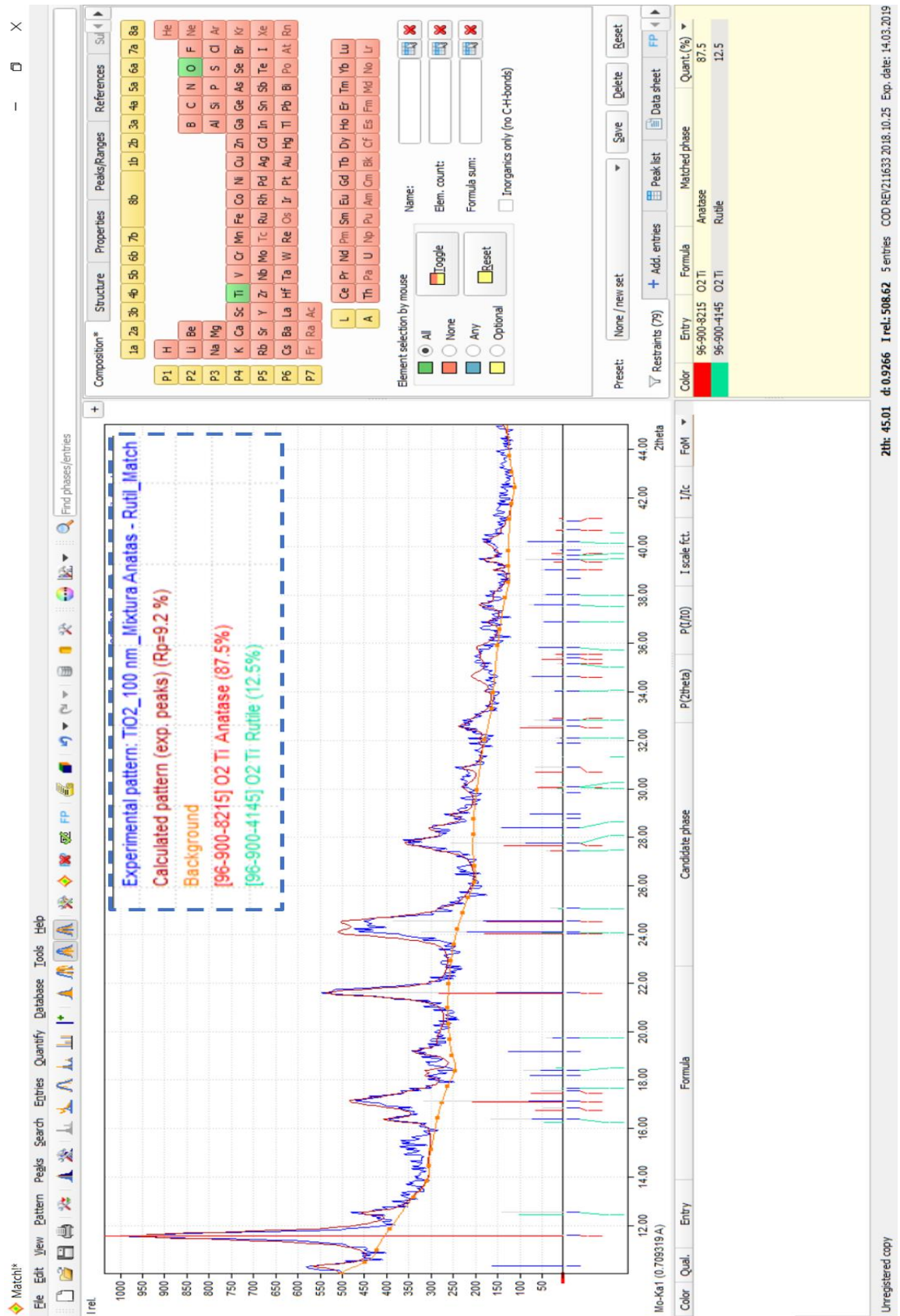
- [223] Hong J., He Y., Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning, *Desalination*, Volume 332, 2014, Issue 1, Pages 67-75, DOI:10.1016/j.desal.2013.10.026.
- [226] Rajabi H., Ghaemi N., Madaeni S.S., Daraei P., Astinchap B., Zinadini S., Razavizadeh S.H., Nano-ZnO embedded mixed matrix polyethersulfone (PES) membrane: Influence of nanofiller shape on characterization and fouling resistance, *Applied Surface Science*, Volume 349, 2015, Pages 66-77, DOI:10.1016/j.apsusc.2015.04.214.
- [237] Cao X., Ma J., Shi X., Ren Z., Effect of TiO<sub>2</sub> nanoparticle size on the performance of PVDF membrane, *Applied Surface Science*, Volume 253, Issue 4, 2006, Pages 2003-2010, DOI:10.1016/j.apsusc.2006.03.090.
- [245] Song H.J., Kim C.K., Fabrication and properties of ultrafiltration membranes composed of polysulfone and poly(1-vinylpyrrolidone) grafted silica nanoparticles, *Journal of Membrane Science*, Volume 444, 2013, Pages 318-326, DOI:10.1016/j.memsci.2013.05.024.
- [246] Zeng G., Ye Z., He Y., Yang X., Ma J., Shi H., Feng Z., Application of dopamine-modified halloysite nanotubes/PVDF blend membranes for direct dyes removal from wastewater, *Chemical Engineering Journal*, Volume 323, 2017, Pages 572-583, DOI:10.1016/j.cej.2017.04.131.
- [249] Vatanpour V., Madaeni S.S., Moradian R., Zinadini S., Astinchap B., Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO<sub>2</sub> coated multiwalled carbon nanotubes, *Separation and Purification Technology*, Volume 90, 2012, Pages 69-82, DOI:10.1016/j.seppur.2012.02.014.
- [251] Zhao X., Chen Y., Xuan H., He C., Investigation of one-dimensional multi-functional zwitterionic Ag nanowires as a novel modifier for PVDF ultrafiltration membranes, *New Journal of Chemistry*, Volume 40, 2016, Issue 1, Pages 441-446, DOI:10.1039/C5NJ02030A.
- [252] Xu Z., Ye S., Zhang G., Li W., Gao C., Shen C., Meng Q., Antimicrobial polysulfone blended ultrafiltration membranes prepared with Ag/Cu<sub>2</sub>O hybrid nanowires, *Journal of Membrane Science*, Volume 509, 2016, Pages 83-93, DOI:10.1016/j.memsci.2016.02.035.
- [256] Mahmoudi E., Ng L.Y., Ba-Abbad M., Mohammad A.W., Novel nanohybrid polysulfone membrane embedded with silver nanoparticles on graphene oxide nanoplates, *Chemical Engineering Journal*, Volume 277, 2015, Pages 1-10, DOI:10.1016/j.cej.2015.04.107.
- [259] Rahimpour A., Jahanshahi M., Khalili S., Mollahosseini A., Zirepour A., Rajaeian B., Novel functionalized carbon nanotubes for improving the surface properties and performance of polyethersulfone (PES) membrane, *Desalination*, Volume 286, 2012, Pages 99-107, DOI:10.1016/j.desal.2011.10.039.
- [260] Wang Z., Yu H., Xia J., Zhang F., Li F., Xia Y., Li Y., Novel GO-blended PVDF ultrafiltration membranes, *Desalination*, Volume 299, 2012, Pages 50-54, DOI:10.1016/j.desal.2012.05.015.
- [262] Zhang M., Zhang K., De Gusseme B., Verstraete W., Biogenic silver nanoparticles (bio-Ag<sub>0</sub>) decrease biofouling of bio-Ag<sub>0</sub>/PES nanocomposite membranes, *Water Research*, Volume 46, 2012, Issue 7, Pages 2077-2087, DOI:10.1016/j.watres.2012.01.015.
- [263] Akar N., Asar B., Dizge N., Koyuncu I., Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles, *Journal of Membrane Science*, Volume 437, 2013, Pages 216-226, DOI:10.1016/j.memsci.2013.02.012.
- [267] Buruga K., Kalathi J.T., Kim K.H., Ok Y.S., Danil B., Polystyrene-halloysite nano tube membranes for water purification, *Journal of Industrial and Engineering Chemistry*, Volume 61, 2018, Pages 169-180, DOI:10.1016/j.jiec.2017.12.014.
- [268] Saranya R., Arthanaresswaran G., Sakthivelu S., Manohar P., Preparation and Performance Evaluation of Nanokaolinite-Particle-Based Polyacrylonitrile Mixed-Matrix Membranes, *Industrial & Engineering Chemistry Research*, Volume 51, 2012, Issue 13, Pages 4942-4951, DOI:10.1021/ie300026s.
- [270] Wei W., Gupta K.M., Liu J., Jiang J., Zeolitic Imidazolate Framework Membranes for Organic Solvent Nanofiltration: A Molecular Simulation Exploration, *ACS Applied Materials & Interfaces*, 2018, DOI:10.1021/acsami.8b08364.
- [273] Fan Z., Wang Z., Sun N., Wang J., Wang S., Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers, *Journal of Membrane Science*, Volume 320, 2008, Issues 1-2, Pages 363-371, DOI:10.1016/j.memsci.2008.04.019.

- [279] Alam J., Shukla A.K., Alhousan M., Dass L.A., Muthumareeswaran M.R., Khan A., Ahmed Ali F.A., Graphene oxide, an effective nanoadditive for a development of hollow fiber nanocomposite membrane with antifouling properties, *Advances in Polymer Technology*, 2017, DOI:10.1002/adv.21935.
- [281] Fan X., Zhao H., Liu Y., Quan X., Yu H., Chen S., Enhanced Permeability, Selectivity, and Antifouling Ability of CNTs/Al<sub>2</sub>O<sub>3</sub> Membrane under Electrochemical Assistance, *Environmental Science and Technology*, Volume 49, 2015, Issue 4, Pages 2293-2300, DOI:10.1021/es5039479.
- [282] Demirel E., Zhang B., Papakyriakou M., Xia S., Chen Y., Fe<sub>2</sub>O<sub>3</sub> nanocomposite PVC membrane with enhanced properties and separation performance, *Journal of Membrane Science*, Volume 529, 2017, Pages 170-184, DOI:10.1016/j.memsci.2017.01.051.
- [283] Kritikaki A., Tsetsekou A., Fabrication of porous alumina ceramics from powder mixtures with sol-gel derived nanometer alumina: Effect of mixing method, *Journal of the European Ceramic Society*, Volume 29, 2009, Issue 9, Pages 1603-1611, DOI:10.1016/j.jeurceramsoc.2008.10.011.
- [284] Qi H., Fan Y., Xing W., Winnubst L., Effect of TiO<sub>2</sub> doping on the characteristics of macroporous Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> membrane supports, *Journal of the European Ceramic Society*, Volume 30, 2010, Issue 6, Pages 1317-1325, DOI:10.1016/j.jeurceramsoc.2009.12.011.
- [285] Singh A.K., Thakur A.K., Shahi V.K., Self-assembled nanofiltration membrane containing antimicrobial organosilica prepared by sol-gel process, *Desalination*, Volume 309, 2013, Pages 275-283, DOI:10.1016/j.desal.2012.10.011.
- [290] Ammar A., Al-Enizi A.M., AlMaadeed M.A., Karim A., Influence of graphene oxide on mechanical, morphological, barrier, and electrical properties of polymer membranes, *Arabian Journal of Chemistry*, Volume 9, 2016, Issue 2, Pages 274-286, DOI:10.1016/j.arabjc.2015.07.006.
- [291] ISO, ISO 527-3:1995, Plastics — Determination of tensile properties — Part 3: Test conditions for films and sheets.
- [318] Garcia-Ivars J., Ilborra-Clar M.I., Alcaina-Miranda M.I., Van der Bruggen B., Comparison between hydrophilic and hydrophobic metal nanoparticles on the phase separation phenomena during formation of asymmetric polyethersulphone membranes, *Journal of Membrane Science*, Volume 493, 2015, Pages 709-722, DOI:10.1016/j.memsci.2015.07.009.
- [352] Pintilie S.C., Tiron L.G., Birsan I.G., Ganea D., Balta S., Influence of ZnO Nanoparticle Size and Concentration on the Polysulfone Membrane Performance, *Materiale Plastice*, Volume 54, 2017, Issue 2, Pages 257-261, [http://www.revmaterialeplastice.ro/article\\_eng.asp?ID=4828](http://www.revmaterialeplastice.ro/article_eng.asp?ID=4828).
- [356] Pintilie S.C., Tiron L.G., Lazar A.L., Vlad M., Birsan I.G., Balta S., The influence of ZnO/TiO<sub>2</sub> nanohybrid blending on the ultrafiltration polysulfone membranes, *Revista de Materiale Plastice*, Volume 55, 2018, Issue 1, Pages 54-62, WOS:000444129500013.
- [359] LeClech P., Development of predictive tools for membrane ageing, IWA Publishing, United Kingdom, 2013, ISBN:978-1-921732-12-6.
- [360] \*\*\*[http://www.sim.utcluj.ro/stm/download/Mat\\_compozite/Inc\\_tractiune.pdf](http://www.sim.utcluj.ro/stm/download/Mat_compozite/Inc_tractiune.pdf), Încercarea la tracțiune a materialelor compozite.
- [382] Ahmad A.L., Abdulkarim A.A., Mohd Shafie Z.M.H., Ooi B.S., Fouling evaluation of PES/ZnO mixed matrix hollow fiber membrane, *Desalination*, Volume 403, 2017, Pages 53-63, DOI:10.1016/j.desal.2016.10.008.
- [411] Celik E., Choi H., Carbon Nanotube/Polyethersulfone Composite Membranes for Water Filtration, Chapter in: *Modern Applications in Membrane Science and Technology*, ACS Symposium Series, Volume 1078, 2011, United States of America, DOI: 10.1021/bk-2011-1078.ch015, ISBN: 9780841226180.
- [422] Zhao S., Wang P., Wang C., Sun X., Zhang L., Thermostable PPESK/TiO<sub>2</sub> nanocomposite ultrafiltration membrane for high temperature condensed water treatment, *Desalination*, Volume 299, 2012, Pages 35-43, DOI:10.1016/j.desal.2012.05.013.



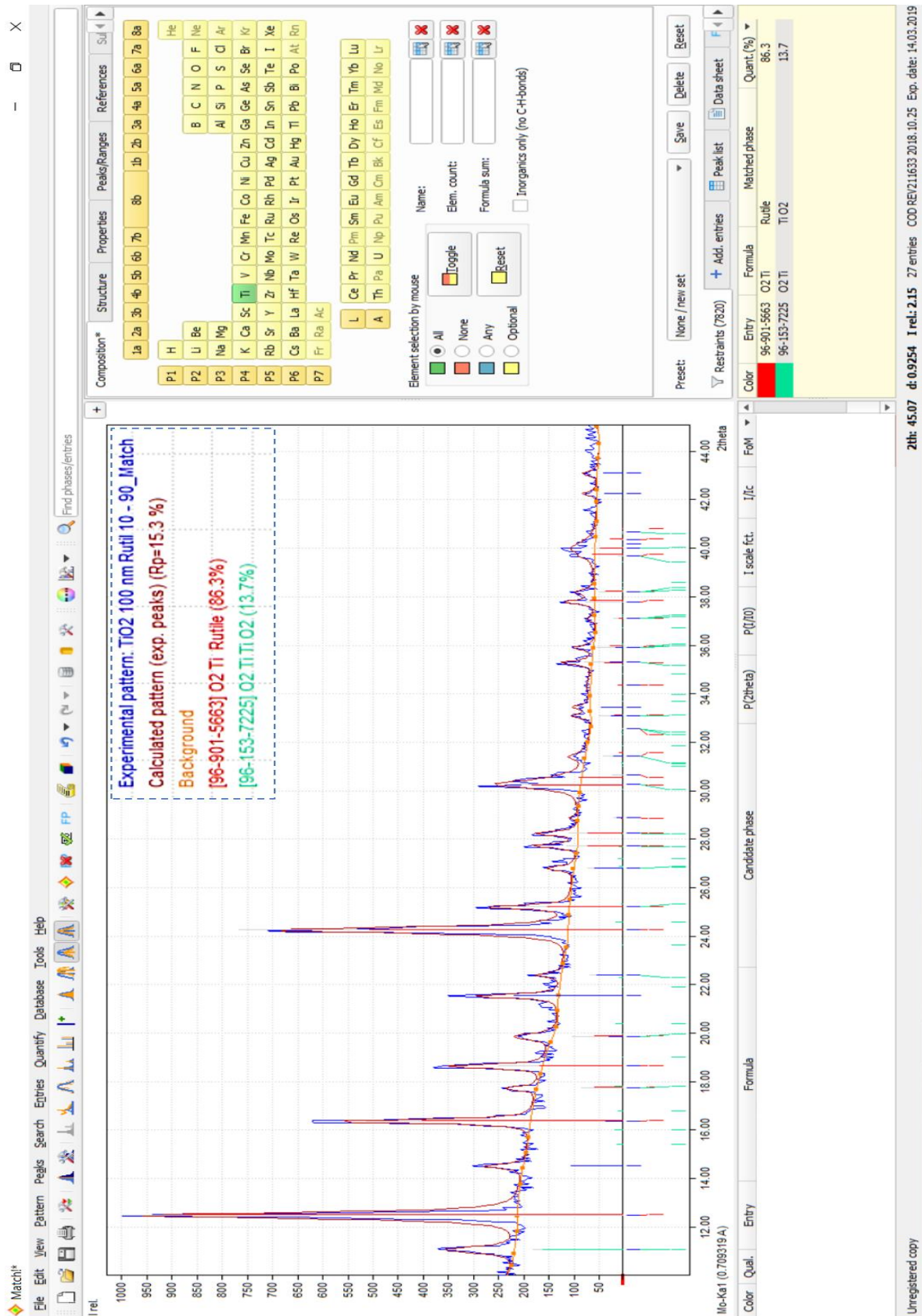
### ANNEX 1

#### Determination of the composition of Anatase titanium dioxide nanoparticles from the XRD spectrum



### ANNEX 2

#### Determination of the composition of Rutile titanium dioxide nanoparticles from the XRD spectrum



## SCIENTIFIC ACHIEVEMENTS

### *Publications in WOS journals*

1. Ștefan Catalin PINTILIE, Laurentia Geanina TIRON, Iulian Gabriel BIRSAN, Daniel GANEA, Ștefan BALTA, **INFLUENCE OF ZnO NANOPARTICLE SIZE AND CONCENTRATION ON THE POLYSULFONE MEMBRANE PERFORMANCE**, Jurnalul de Materiale Plastice Vol.54, No.2 (2017) 257-261, ISSN: 0025-5289, WOS:000408702100013, Factor de impact: 1.248;
2. Ștefan Cătălin PINTILIE, Laurenția Geanina TIRON, Andreea Liliana LAZĂR, Maria VLAD, Iulian Gabriel BIRSAN, Ștefan BALTA, **THE INFLUENCE OF ZnO/TiO<sub>2</sub> NANOHYBRID BLENDING ON THE ULTRAFILTRATION POLYSULFONE MEMBRANES**, Materiale Plastice 55 Issue: 1 (2018) 54-62, ISSN: 0025-5289, WOS:000444129500013, Factor de impact: 1,248;
3. Laurenția Geanina TIRON, Ștefan Cătălin PINTILIE, Andreea Liliana LAZĂR, Maria VLAD, Ștefan BALTA, Marius BODOR, **INFLUENCE OF POLYMER CONCENTRATION ON MEMBRANE PERFORMANCE IN WASTEWATER TREATMENT**, Materiale Plastice 55 Issue: 1 (2018) 95-98, ISSN: 0025-5289, WOS:000444129500021, Factor de impact: 1,248.

### *ISI Proceedings volume publications*

1. Laurenția Geanina TIRON, Marius BODOR, Maria VLAD, Ștefan Cătălin PINTILIE, Ștefan BALTA, **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, ISSN:1314-2704, WOS:000391348700021, doi: 10.5593/SGEM2016/B42/S18.021;
2. Ștefan Catalin PINTILIE, Laurentia Geanina TIRON, Andreea Liliana LAZAR, Iulian Gabriel BIRSAN, Ștefan BALTA, **THE INFLUENCE OF NANOPARTICLE TYPE ON THE COMPOSITE POLYMERIC MEMBRANES**, Ecology, Economics, Education and Legislation Conference Proceedings, SGEM 2016, International Multidisciplinary Scientific GeoConference-SGEM, Vol 2 (2016) 849-855, ISSN: 1314-2704, WOS:000391519600110, doi: 10.5593/SGEM2016/B52/S20.110;
3. Laurenția Geanina TIRON, Ștefan Cătălin PINTILIE, Maria VLAD, Iulian - Gabriel BÎRSAN, Ștefan BALTA, **CHARACTERIZATION OF POLYSULFONE MEMBRANES PREPARED WITH THERMALLY INDUCED PHASE SEPARATION TECHNIQUE**, IOP Conf. Series: Materials Science and Engineering, 209 (2017) Art. No.012013, ISSN: 1757-898, WOS:000423732100013, doi:10.1088/1757-899X/209/1/012013;
4. Laurenția Geanina TIRON, Ștefan Cătălin PINTILIE, Maria VLAD, Ștefan BALTA, 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, ISSN 1314-2704, doi: 10.5593/sgem2017/61/S24.051;
5. Ștefan Cătălin PINTILIE, Laurenția Geanina TIRON, Andreea Liliana LAZĂR, Iulian Gabriel BÎRSAN, Ștefan BALTA, **NANOPARTICLE EMBEDDED MIXED MATRIX PSF MEMBRANES CHARACTERIZATION AND MEMBRANE PERFORMANCE**, Ecology, Economics, Education and Legislation Conference Proceedings, SGEM 2017, International Multidisciplinary Scientific GeoConference-SGEM, Vol 2 (2017) 249-256, ISSN: 13142704, doi: 10.5593/sgem2017/61/S24.033;
6. Ionuț MIHALACHE, Ștefan Cătălin PINTILIE, Iulian Gabriel BÎRSAN, Eliza DĂNĂILĂ, Ștefan BALTA, **RESEARCH REGARDING MEMBRANE FILTRATION CAPACITY OF WATER COLLECTED FROM SIRET RIVER**, IOP Conf. Series: Materials Science and Engineering, 374 (2018) Art. No. 012042, ISSN: 1757-8981, WOS:000446775900042, doi: 10.1088/1757-899X/374/1/012042;
7. Ștefan Cătălin PINTILIE, Marius BODOR, Andreea Liliana LAZĂR, Iulian Gabriel BÎRSAN, Ștefan BALTA, **STUDIES ON DANUBE WATER FILTRATION PERFORMANCE OF NANOCOMPOSITE ULTRAFILTRATION MEMBRANES**, 18th International Multidisciplinary Scientific GeoConference SGEM2018, Micro and Nano Technologies, Vol. 18 (2018) 457-464, ISSN 1314-2704, doi: 10.5593/sgem2018/6.1/S24.061.

**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;

3. Ștefan Cătălin PINTILIE, Laurenția Geanina TIRON (PINTILIE), Ștefan BALTĂ, Iulian Gabriel BÎRSAN, **CERCETĂRI PRIVIND FILTRAREA APEI DE DUNĂRE UTILIZÂND PROCESSE MEMBRANARE**, "Cele mai bune tehnologii pentru protecția mediului și siguranța muncii în ingineria materialelor" (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. Ștefan Cătălin PINTILIE, Laurenția Geanina TIRON, Andreea Liliana LAZĂR, Ștefan BALTĂ, Iulian Gabriel BÎRSAN, Maria VLAD, Vasile BAȘLIU, **INFLUENCE OF ACTIVATED CARBON BLENDED IN POLYSULFONE MATRIX MEMBRANE USED IN WASTEWATER TREATMENT**, Scientific Conference of Doctoral Schools CDS – UDJG 2017, Universitatea „Dunărea de Jos”, Galați (prezentare orală), Iunie 2017;

4. Ștefan Catalin PINTILIE, Laurentia Geanina TIRON, Maria VLAD, Iulian Gabriel BIRSAN, Ștefan BALTA, **LIGHT TRANSMISSION ANALYSIS ON PHASE INVERSION MEMBRANES USING SMARTPHONE LIGHT SENSOR**, Scientific Conference of Doctoral Schools CDS – UDJG 2018, Universitatea „Dunărea de Jos”, Galați (prezentare orală), Iunie 2018.

**Participations at 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, Galați (prezentare orală), 21 -23 Octombrie 2015;

2. Ștefan Cătălin PINTILIE, Ionuț MIHALACHE, Iulian Gabriel BÎRSAN, Ștefan BALTĂ, **THE INFLUENCE OF NANOPARTICLE TYPE AND SIZE ON THE COMPOSITE POLYMERIC MEMBRANES**, International Conference New Trends in Environmental and Materials Engineering TEME, Galați (prezentare orală), 21 -23 Octombrie 2015;

3. 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;

4. Andreea Liliana LAZAR, *Ștefan Catalin PINTILIE*, Laurentia Geanina TIRON; Eliza DANAILA, Ștefan BALTA, **DETERMINING THE DEGREE OF CONTAMINATION OF AGRICULTURAL SOILS IN THE COUNTY OF GALATI**, 16th International Multidisciplinary Scientific GeoConference SGEM 2016, Bulgaria (poster), Iulie 2016;

5. *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;

6. 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;

7. 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;

8. 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;

9. Ștefan Cătălin PINTILIE, Laurenția Geanina TIRON, Andreea Liliana LAZĂR, Iulian Gabriel BÎRSAN, Ștefan BALTĂ, **NANOPARTICLE EMBEDDED MIXED MATRIX PSF MEMBRANES CHARACTERIZATION AND MEMBRANE PERFORMANCE**, 17th International Multidisciplinary Scientific GeoConference SGEM 2017, Bulgaria (poster), Iunie 2017;

10. 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;

11. *Ștefan Cătălin PINTILIE*, Laurenția Geanina TIRON, Andreea Liliana LAZĂR, Ștefan BALTĂ, Iulian Gabriel BÎRSAN, **PERFORMANCE OF [PAC/Psf]-MIXED MATRIX MEMBRANE USED IN DYE WASTEWATER TREATMENT**, 4rd International Conference New Trends in Environmental and Materials Engineering - TEME 2017, Galați (prezentare orală), Octombrie 2017;

12. Ionuț MIHALACHE, *Ștefan Cătălin PINTILIE*, Eliza DĂNĂILĂ, Iulian Gabriel BÎRSAN, Ștefan BALTĂ, **RESEARCH REGARDING MEMBRANE FILTRATION CAPACITY OF WATER COLLECTED FROM SIRET RIVER**, International Conference on Innovative Research – Euroinvent ICIR 2018 Iași (prezentare orală), Mai 2018;

13. *Ștefan Cătălin PINTILIE*, Marius BODOR, Andreea Liliana LAZAR, Iulian Gabriel BÎRSAN, Ștefan BALTĂ, **STUDIES ON DANUBE WATER FILTRATION PERFORMANCE OF NANOCOMPOSITE ULTRAFILTRATION MEMBRANES**, 18th International Multidisciplinary Scientific GeoConference-SGEM 2018, Bulgaria (prezentare orală), Iulie 2018.

14. *Ștefan Cătălin Pintilie*, *Eliza Dănăilă*, *Andreea Liliana Lazăr*, *Iulian-Gabriel Bîrsan*, *Ștefan Baltă*, **SHAPE EFFECT OF ZnO NANOMATERIALS ON PSF MEMBRANE PERFORMANCE IN WASTEWATER TREATMENT**, 7th International Conference on Materials Science and Technologies – RoMat 2018 București (prezentare orală), Noiembrie 2018.