Ministry of Education
University* Politehnica *from Bucureşti
Faculty of *Chemical Engineering and Biotechnologies*
Doctoral Schoool Chemical Engineering and Biotechnologies

PhD Thesis

Decizie Nr. ..... din .....

Membranes and membrane processes in the transport, separation, and synthesis of products with implications in sports medicine/
Membrane şi procese de membrana in transportul, separarea si sinteza de produsi cu implicatii in medicina sportivă

PhD student:
Florentina Mihaela PĂNCESCU

Supervisor:
***Prof.dr.ing.* Gheorghe NECHIFOR**

June

Bucharest 2023

Ministry of Education
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Abstract
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June 2023, București

CONTENT

THANKS

Throughout my professional training, research and doctoral studies within the Doctoral School of Chemical Engineering and Biotechnology, Mr. University Professor Dr. Eng. Nechifor Gheorghe was my permanent guide in the work carried out.

I give all my gratitude to the Professor, scientific coordinator of this doctoral thesis, for the constant guidance, effort and patience he showed for the completion of this study.

Also, I would like to thank the Professors, the members of the commission for their contribution to the evaluation of this doctoral thesis: Ștefan Ioan Voicu, Ioan Mămăligă, Maria Tomoaia-Cotisel, Gabriel Lucian Radu, who contributed to the completion of this doctoral thesis.

I also thank the Professors: Maria Claudia Simionescu, Mihaela Emanuela Crăciun and Aurelia Cristina Nechifor - members of the guidance committee, who trained me in research processes, experiments, publications.

I would like to thank the "Chemical Engineering and Biotechnologies" team: who helped me throughout my studies, with reagents, materials, access to equipment, advice.

I thank all those who directly or indirectly supported me in carrying out the experiments in the thesis.

Thanks to my family for their support and patience throughout my career.

INTRODUCTION

The development of the doctoral thesis **"Membranes and membrane processes in the transport, separation, and synthesis of products with implications in sports medicine"** represents, par excellence, an research applied activity.

The study is part of the national and foreign research concerns for obtaining, characterizing, and applying active products through membranes and membrane processes for sports medicine.

The thesis addresses a subject of practical importance and presents the results obtained in order to obtain new membranes for the separation of products of biological interest with biomedical applications.

The doctoral thesis falls under the broad theme "Obtaining biological products with applications in biotherapy using immunologically active fractions" which provided both the general research framework and the technical-scientific arguments for the development of publications and patent applications.

Novelty

The work presents an original and novel part, the results of which can be used in the pharmaceutical, medical industry for sport medicine support.

The doctoral thesis consists of three parts: part A – literature data synthesis, which includes chapter 1, part B – the experimental part structured in two chapters and part C made up of – elements of originality, general conclusions, and research perspectives.

PERT A, the first chapter "Membranes and membrane processes" represents a study with reference to recent information on the methods of obtaining, characterizing, and applying membrane processes.

PART B. Chapter 2 present the experimental results of the PhD thesis and was divided in two parts:

Chapter 2.1. Transport and separation of the silver ion with *n*–decanol liquid membranes based on 10–undecylenic acid, 10–undecen–1–ol and magnetic nanoparticles

Chapter 2.2. Reactional Processes on Osmium-Polymeric Membranes for 5–Nitro benz imidazole Reduction to 5-Aminobenzimidazole

2.3. Chitosan-polypropylene hollow fibers composite membrane for Ions or Molecules transport OR release

2.3.1. Chitosan-polypropylene hollow fibers composite membrane for ions transport

2.3.2. Chitosan/sEPDM composite membranes for melatonin transport and release

PART C, the paper ends with General Conclusions, Elements of originality and Prospects for research development.

In the last part of the doctoral thesis, the dissemination of the experimental results was carried out by publishing some scientific papers in specialized magazines, by presenting some scientific communications at internal and international symposia and by carrying out some papers within the framework of some invention patents.

A. SYNTHESIS OF LITERATURE DATA

Membrane processes are a viable alternative for analytical, biotechnological, and industrial separations due to process selectivity, low energy consumption, reduction in the number or elimination of chemicals used as auxiliaries, small installations, simple and fully automated operations.

The most developed membrane processes are those governed by the pressure gradient: micro-, ultra-, nano- and hyper-filtration.

Membranes have experienced a special development because they benefit from the enormous progress in the field of obtaining materials: polymeric, composite, hybrid, intelligent and those synthesized at the nano scale.

The preparation of the membranes involved in the processes developed today, on an industrial scale, is mainly carried out by phase inversion, from polymer solutions and melts.

The characterization of membranes is usually carried out by three complementary methods, chosen from the following: electron microscopy, porosimetry with mercury, permporometry, permeation of solvents, filtration of standard solutions.

One of the most attractive membrane separation processes, both for studies in research laboratories and for industrial practice, is liquid membranes.

The advantages of liquid membranes are related to: high and controlled selectivity, constructive versatility, high productivity, low investments, automation and low energy consumption.

Liquid membranes can be used in several constructive and operational variants: volume membranes, immobilized or supported membranes, emulsion membranes.

The contact surfaces between the phases can be increased by the appropriate design of permeators or pertractors with immobilized membranes (lumen fibers, spiral modules) or with emulsion membranes.

Immobilized membranes are, at present, in a special progress, because they ensure low consumption of organic solvents, avoid the loss of organic substances in the environment and can use the benefits of process engineering known by biomedical and biotechnologies developing.

B. EXPERIMENTAL PART

The objectives of the doctoral thesis

The objective of the doctoral thesis "Membranes and membrane processes in the transport, separation and synthesis of products with implications in sports medicine/Membranes and membrane processes in the transport, separation, and synthesis of products with implications in sports medicine" refers to the transport, separation and the synthesis of products of biological interest (chemical species with therapeutic potential) with biomedical implications usable in sports medicine.

Specific objectives

- ***Obtaining*** composite membranes based on dispersions
- Physico-chemical and morpho-structural *characterization* of the new membranes
- ***Transport and separation*** of undecenoic acid and silver ions using dispersion composite membranes
- ***Synthesis*** of 5-amino-benzimidazoles from 5-nitro-benzimidazoles by reducing composite membranes containing osmium nanoparticles
- **Controlled release** of melatonin from composite membranes.

Capitolul 2.1. Transport and separation of the silver ion with *n*–decanol liquid membranes based on 10–undecylenic acid, 10–undecen–1–ol and magnetic nanoparticles

Abstract: This chapter presents a transport and recovery of silver ions through bulk liquid membranes based on *n*–decanol using as carriers 10–undecylenic acid and 10–undecylenyl alcohol. The transport of silver ions across membranes has been studied in the presence of two types of magnetic oxide nanoparticles obtained by the electrochemical method with iron electrodes in the electrolyte with and without silver ions, which act as promoters of turbulence in the membrane. Separation of silver ions by bulk liquid membranes using 10–undecylenic acid and 10–undecylenyl alcohol as carriers was performed by comparison with lead ions. The configuration of the separation module has been specially designed for the chosen separation process. Convective-generating magnetic nanoparticles were characterized in terms of the morphological and structural points of view: scanning electron microscopy (SEM),

high resolution SEM (HR–SEM), energy dispersive spectroscopy analysis (EDAX), Fourier Transform InfraRed (FTIR) spectroscopy, thermal gravimetric analysis (TGA), differential scanning calorimetry and magnetization. The process performance (flux and selectivity) was tested were tested for silver ion transport and separation through *n*–decanol liquid membranes with selected carriers. Under the conditions of the optimized experimental results (pH=7 of the source phase, pH=1 of the receiving phase, flow rate of 30 mL/min for the source phase and 9 mL/min for the receiving phase, 150 rot/min agitation of magnetic nanoparticles) separation efficiencies of silver ions of over 90% were obtained for the transport of undecenoic acid and about 80% for undecylenyl alcohol.

Keywords: bulk liquid membranes; 10-undecilenic acid carrier; 10-undecenol carrier; silver separation; silver transport; magnetic nanoparticles; oxide nanoparticles; turbulence promotors.

2.2. Reactional Processes on Osmium-Polymeric Membranes for 5–Nitrobenzimidazole Reduction to 5-Aminobenzimidazole

Abstract: Membranes are associated with the efficient processes of separation, concentration, and purification, but a very important aspect of them is the realization of a reaction process simultaneously with the separation process. From a practical point of view, chemical reactions have been introduced in most membrane systems: with on liquid membranes, with inorganic membranes or with polymeric and/or composite membranes. This paper presents the obtaining of polymeric membranes containing metallic osmium obtained in situ. Cellulose acetate (CA), polysulfone (PSf) and polypropylene hollow fiber membranes (PPM) were used as support polymer membranes. The metallic osmium is obtained directly onto the considered membranes using a solution of osmium tetroxide (OsO4), dissolved in tert–butyl alcohol (t–Bu–OH) by reduction with molecular hydrogen. The composite osmium–polymer (Os–P) obtained membranes were characterized in terms of the morphological and structural points of view: scanning electron microscopy (SEM), high resolution SEM (HR–SEM), energy dispersive spectroscopy analysis (EDAX), Fourier Transform Infra-Red (FTIR) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The process performance was tested for reduction of 5–nitrobenzimidazole to 5–aminobenzimidazole with molecular hydrogen. The paper presents the main aspects of the possible mechanism of transformation of 5–nitrobenzimidazole to 5–aminobenzimidazole with hydrogen gas in the reaction system with osmium–polymer membrane (Os–P).

Keywords: composite membranes; osmium polymer membrane; nitro derivatives reduction; reactional processes; 5–nitrobenzimidazole; cellulose acetate membranes; polysulfone membranes; polypropylene hollow fiber membranes.

2.3. CHITOSAN-POLYPROPYLENE HOLLOW FIBERS COMPOSITE MEMBRANE FOR IONS OR MOLECULES TRANSPORT OR RELEASE

2.3.1. CHITOSAN-POLYPROPYLENE HOLLOW FIBERS COMPOSITE MEMBRANE FOR IONS TRANSPORT

Abstract: *Composite membranes based on cellulosic derivatives or related natural compounds with ionizing groups represent one of the viable alternatives for separation, concentration and purification of acidic aqueous solutions containing copper and zinc ions. This work presents the preparation and characterization of a chitosan–polypropylene hollow fiber composite membrane. The prepared membrane was tested in the pertraction process of copper and zinc ions from strongly acidic solutions. The obtained results show that this type of membrane achieves both the separation and the concentration of the tested solutions. The contribution of each component of the composite membrane was comparatively evaluated under the same working conditions.*

Keywords: composite membranes; chitosan; polypropylene hollow fiber; pertraction; cupper-zinc separation.

2.3.2. Chitosan/sEPDM composite membranes for melatonin transport and release

Abstract: Melatonin is the hormone that focuses the attention of membrane researchers due to its multiple biomedical implications. The variety of techniques and methods for the controlled release of melatonin is linked to the multitude of applications, among which sports medicine occupies a special place. This chapter presents the preparation and characterization of composite membranes based on chitosan (Chi) and sulfonated ethylene-propylene-diene terpolymer (sEPDM). The membranes were obtained by controlled vacuum evaporation from an 8% sEPDM solution in toluene (w/w) in which chitosan was dispersed in an ultrasonic field (sEPDM:Chi=1:1, w/w). They were morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and infrared analysis, and contact angle measurements, but also from the point of view of performance in the process of transport and release of melatonin in dedicated environments (aqueous solutions with controlled pH and salinity). The prepared membranes can release melatonin in amounts between 0.4 mg/day (M1) and 1.6 mg/day (M2).

Keywords: melatonin; composite membranes; chitosan; sEPDM; melatonin release; melatonin transport.

1. Introduction

The biomedical implications of melatonin, the hormone secreted by the pineal gland, are so diverse and of particular importance that the researchers have devoted extensive studies to it [1-3].

One of the current medical concerns is ensuring the daily amount of melatonin in the body, because the secretion of the pineal gland can be affected by various dysfunctions of the human body [4,5]. Even getting older is a problem in reducing the amount of melatonin generated in the body [6].

The scheme presented in Figure 1 highlights the main medical implications of melatonin [7-11].

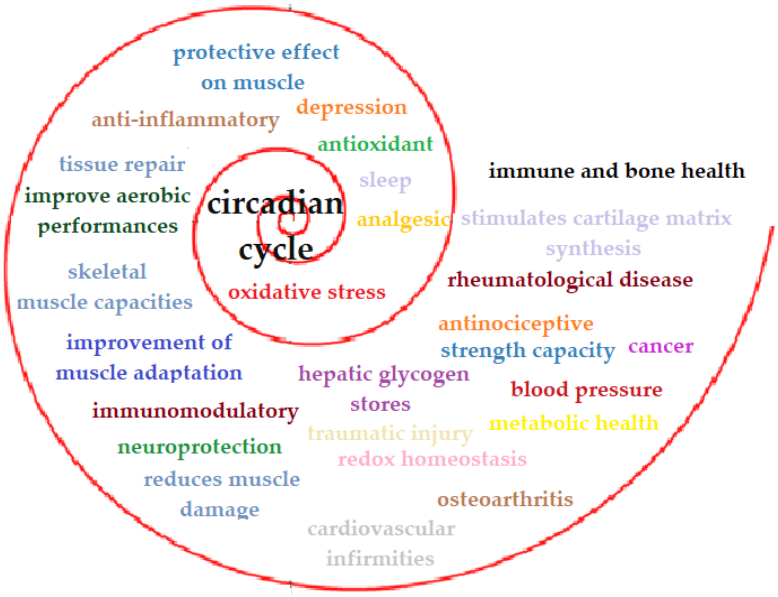


Figure 1. Schematic presentation of the melatonin biomedical implication.

The representative ways of controlled release of the various chemical species of interest, many of which have been studied for melatonin as well, are suggested in Figure 2 [12–14].

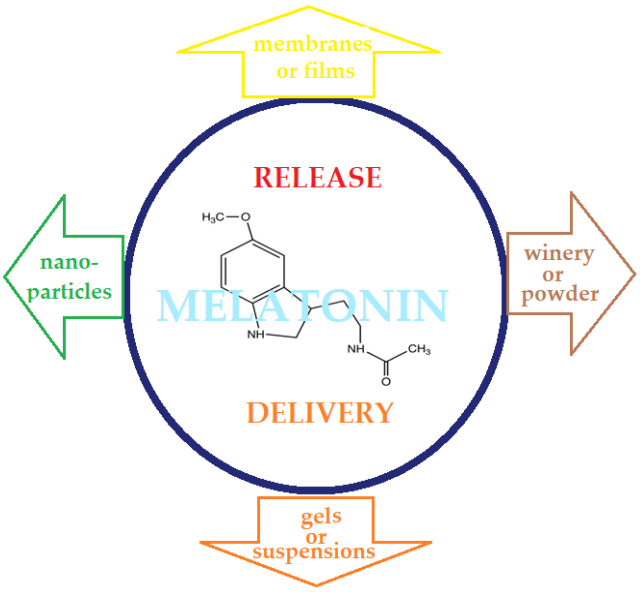


Figure 2. Schematic presentation of interest chemical species release techniques.

Among the recent applications with significant results of melatonin are those in sports medicine, while among the methods of controlled release, the attention given to the involvement of chitosan in various formulations can be highlighted [15].

Chitosan ensures a controlled release of melatonin, especially through ingestion, but for applications in sports medicine, orthopaedics or dentistry, a reduction in the solubility of this biopolymer and an improvement in physical stability are necessary [16]. By embedding in various organic or inorganic nanoparticles, films and membranes from biodegradable polymers, it was possible to reduce the solubility of chitosan [17].

Studies related to improving the performance of fuel cell membranes have shown that an effective means of chitosan reticulation can be done with ionophores with sulfonic groups of the polyether-ether sulfonated ketone type [18].

The study presented in this paper refers to the preparation and characterization of a composite membrane based on chitosan (Chi) and sulfonated ethylene-propylene-diene terpolymer (sEPDM) and its controlled release performance in synthetic aqueous solutions.

2. Materials and Methods

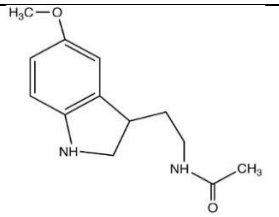
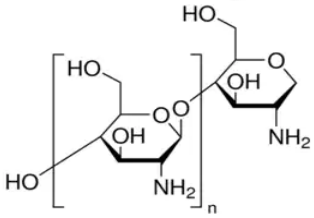
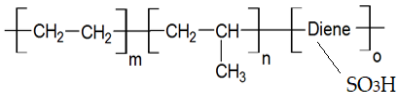
2.1. Reagents and Materials

All reagents and organic compounds used in the presented work were of analytical grade. They were purchased from Merck (Merck KGaA, Darmstadt, Germany): hydrochloric acid, sodium chloride, sodium hydroxide.

Melatonin (Mel-Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) and the basic polymeric materials for making the membranes, i.e. chitosan (Chi) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and sulfonated ethylene-propylene-

diene terpolymer (sEPDM), were recently used in our research group for ionic and molecular separations [19]. Their main characteristics are given in Table 1.

Table 1. The characteristics of the used organic compounds

Organic Compounds	Name and Symbol	Molar mass (g/mol)	Solubility in water (g/L)	pKa
	Melatonin (Mel)	232.28	2g/L; max. $3 \cdot 10^{-3}$ mol/L	5.7 and 10.2
	Chitosan (Chi)	1526.5	soluble in acid media (0.5 M HCl: 50 mg/mL)	6.2 to 7.0
	sulfonated ethylene-propylene-diene terpolymer (sEPDM)	–	soluble in toluene	1.9 to 2.2

The purified water characterized by 18.2 μS/cm conductivity was obtained with a RO Millipore system (MilliQ® Direct 8 RO Water Purification System, Merck, Darmstadt, Germany) [20].

2.2. Obtaining the composite membrane and the procedure for evaluating the transport and release effects

Obtaining the membranes from sEPDM and chitosan with sEPDM was carried out by phase inversion method [21] and by controlled evaporation technique [22]. The polymer solution (sEPDM 8%) in toluene is introduced in a Petri dish and evaporated in a vacuum oven at a temperature of 60 °C, thus obtaining the polymer membrane from sEPDM (M1) (Figure 3). To obtain the chitosan with sEPDM (M2) composite membrane, a dispersion of chitosan in the toluene solution of sEPDM was made, by introducing 1 g of chitosan in 12.5 g of sEPDM solution so that the mass ratio of the two polymers is 1:1.

The obtained membranes have the macroscopic characteristics illustrated in table 2, the thickness and the contact angle with distilled water being determined by the previously presented methods [23,24].

Table 2. The macroscopic characteristics for the obtained membranes.

Material	Membrane Symbols	Thickness *)	View (photo)	Contact angle **) (θ°)

		(µm)		
sEPDM	M1	50 ± 2		73 ± 3
Chi–sEPDM	M2	51 ± 4		42 ± 5

*) The micro-meter measurements on dry membrane [23].
**) The contact angle measurements (with distilled water) [24].

The membranes were cut into approx. 10 cm^2 disks, intended for morphological, structural and transport characterizations. The prepared membranes were morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and analysis in infrared, and contact angle measurements, but also from the point of view of performance in the process of transport and release of melatonin in dedicated environments (aqueous solutions with controlled pH and salinity).

To determine the transport performances of the prepared membranes, a permeation module with two compartments separated by a disk with a free membrane diameter of 3.3 cm was used [25]. Both compartments have a stirring magnetic bar (50 rpm) placed at the base. In one compartment a solution of 2.0 g/L melatonin in ultra-pure water is introduced (the source phase, SP), and in the second compartment, synthetic solutions of imposed pH made with hydrochloric acid or sodium hydroxide are introduced, in a range close to biological pH (the receiving phase, RP).

In another set of experiments, 1-5% NaCl salinity solutions in ultra-pure water were used as the receiving phase. The experiments were carried out in five identical bipartite modules, with a volume of 100 mL melatonin solution and an imposed pH or salinity solution of the same volume, so that the results can be averaged. The five membranes, dedicated to each set of tests, were kept for 48 hours in the 2 g/L melatonin solution, were wiped by gentle pressing between two filter paper discs (Whatman® Filter Paper, Merck KGaA, Darmstadt, Germany) and then were fixed by silicone rubber gaskets in the permeation modules. The spectrophotometric analyses were performed daily, at two wavelengths, 278 nm and 285 nm, for ten days, collecting 1.0 mL of solution from the source phase. The analyses were performed on two different spectrometers, by the same operator and repeated by an independent operator. The analysis laboratory works and respects the specific recommendations and guidelines of

EURACHEM [26]. The validation of the analysis method was carried out by a fast and sensitive electrochemical method, developed and reported previously [27].

The controlled release experiments were carried out according to a previously described procedure [28]. Thus, the membrane discs were placed in the lids of 10 cm^3 glass bottles. Then, 5.0 mL of controlled 2 g/L melatonin aqueous solution was introduced into the glass bottles, and the perforated bottle cap was sealed with a membrane and placed with the cap down in a cup in which 100 bottles could be inserted simultaneously (Figure 3b). The entire assembly is placed in a vessel with controlled pH or salinity solution, which is magnetically stirred bottle (200 rpm). Seven bottles were retrieved daily for analysis so that the results of the melatonin analysis could be averaged, and three bottles were stored as control samples. The validation of the results was performed periodically by electrochemical and/or UV–Vis methods at an independent laboratory [29,30].

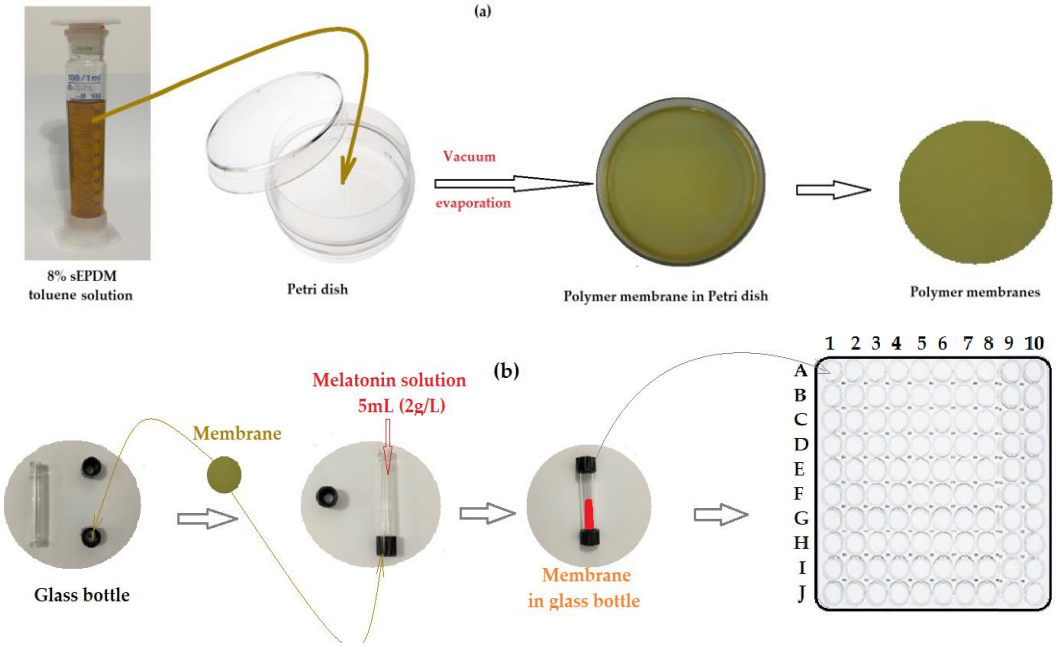


Figure 3. Schematic representation of the procedure for obtaining sEPDM based membranes **(a)**; and release schematic procedure **(b)**.

The flows of the melatonin derivatives from the source phase were determined at specific time intervals, using the relation (1) [31]:

$$J = \frac{M}{S \cdot \Delta t} \text{ (mg/(m}^2 \text{ s)) or mol/(m}^2 \text{ s))}$$

M being the permeate mass (g or mol), *S* being the effective surface of the membrane (m^2), and Δt the time interval (s).

The release efficiency (RE %) for the melatonin derivatives was calculated as follows [32], based on melatonin solution concentration:

$$RE(\%) = \frac{(c_0 - c_f)}{c_0} \cdot 100$$

c_f being the final concentration of the solute (melatonin) and c_0 the initial concentration of solute (melatonin).

The same release efficiency can also be obtained based directly upon the absorbance of the considered solutions (melatonin) [31,32], as in (3):

$$RE(\%) = \frac{(A_0 - A_s)}{A_0} \cdot 100$$

A_0 being the initial absorbance of the sample melatonin solution and A_s the current absorbance of the sample.

2.3. Equipment

The surface and cross-sections characteristics of the membranes were determined with a scanning electron microscopy (SEM) equipped with a probe for energy dispersive spectroscopy analysis (EDX). A Hitachi S4500 system was used (Hitachi High-Technologies Europe GmbH, Krefeld, Germany) [33].

Thermal analysis (TG-DSC) was performed with a STA 449C Jupiter apparatus, from Netzsch (NETZSCH-Gerätebau GmbH, Selb, Germany). Each sample weighed approximatively 10 mg. The samples were placed in an open alumina crucible and heated up to 900 °C with 10 K·min^{-1} rate, under flow of 50 mL·min^{-1} dried air. As reference, we used an empty alumina crucible. The evolved gases were analysed with a FTIR Tensor 27 from Bruker (Bruker Co., Ettlingen, Germany), equipped with a thermostat gas cell [34].

FTIR 2D maps were recorded with a Nicolet iS50R FTIR microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA), with a deuterated triglycine sulfate (DTGS) detector, in the wavenumber range 4000–600 cm^{-1}. The FTIR 2D maps were used to obtain information about the spatial distribution of the components [35].

Determination and monitoring of pH and salinity for every stock solution was achieved using a conductance cell or combined selective electrode (HI 4107, Hanna Instruments Ltd., Leighton Buzzard, UK) and a multi-parameter system (HI 5522, Hanna Instruments Ltd., Leighton Buzzard, UK) [36].

The UV–Vis spectra of the melatonin samples were recorded for a wavelength ranging from 200 to 800 nm, at room temperature, using 10 mm quartz cells on CamSpec M550 spectrometer (Spectronic CamSpec Ltd., Leeds, UK), and for the daily determinations, two wavelengths were chosen, 278 nm and 285 nm [37,38].

Also, the UV–Vis validation analysis of the melatonin solutions was performed on a dual-beam UV equipment–Varian Cary 50 (Agilent Technologies Inc., Santa Clara, CA, USA) at a resolution of 1 nm, spectral bandwidth of 1.5 nm, and a scan rate of 300 nm/s [38,39].

Contact angle measurements for the considered spheres materials (with distilled water, or melatonin derivatives solution) [24], were carried out with a horizontal microscope with video camera (Viola–Shimadzu, Bucharest, Romania).

3. Results and discussion

The controlled release of pharmaceutical preparations is an important aspect that doctors take into account both when prescribing drug doses and when administering food supplements [40–43].

In the case of melatonin, the possibility of oral administration allows its inclusion in powdery materials, tablets or cassettes which, by ingestion, ensure the release of controlled amounts in the body [44]. If a localized administration is desired (injuries, trauma, areas of the oral cavity) as is the case in sports accidents, creams, gels, patches or films (membranes) can be used [45].

In the present study, the controlled transport or release of melatonin through a chitosan (Chi)–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) composite membrane with possible applications in sports medicine were considered.

The membrane prepared by controlled evaporation from a chitosan dispersion in sEPDM solution in toluene was characterized morphologically and structurally by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and infrared analysis, but also from the point of view of melatonin transport to solutions of controlled pH and salinity.

3.1. Morphological and structural membrane characteristics

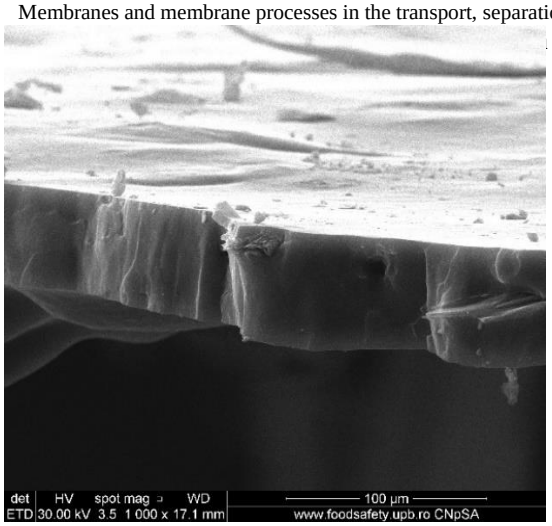
3.1.1. Scanning electron microscopy (SEM)

The membrane samples based on sulfonated ethylene-propylene-diene terpolymer (sEPDM) (M1) and chitosan (Chi)–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) (M2), with a size of 10 cm^2, were fractured in liquid nitrogen and metallized with a superficial layer of gold, to be able to examine the section of the membranes (scanning electron microscopy, SEM) and the elemental distribution on the surface (energy-dispersive spectroscopy analysis, EDAX), analyses available on a Hitachi S4500 system.

Figure 4 shows the images obtained for the two membranes, at a magnification of ×1000; ×2000; and ×10.000, and in Figure 5 the elemental composition is illustrated.

The SEM images show the aspect of film of both prepared membranes (Figures 4a-d), which was expected considering the method of preparation by controlled evaporation [46], but also highlighting the agglomeration of chitosan inside the polymeric film (Figures 4d and 4e).

The elemental analysis on the surface (EDAX) allows highlighting of carbon (C) elements, the majority, but also oxygen (O) and sulfur (S) both in the sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) (Figure 5a) and in the chitosan (Chi)–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) composite membrane (M2) (Figure 5b).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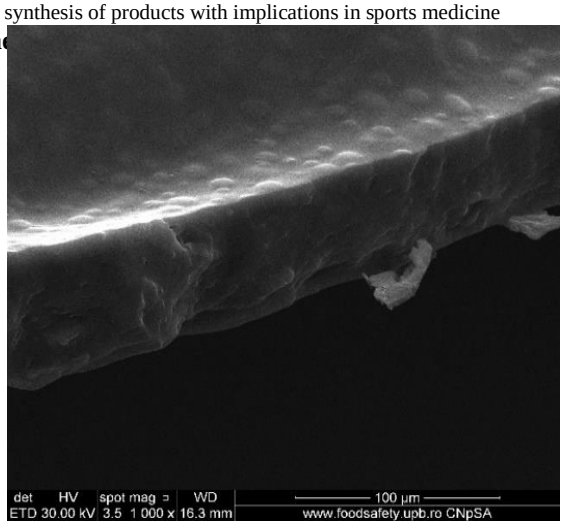
(**a**)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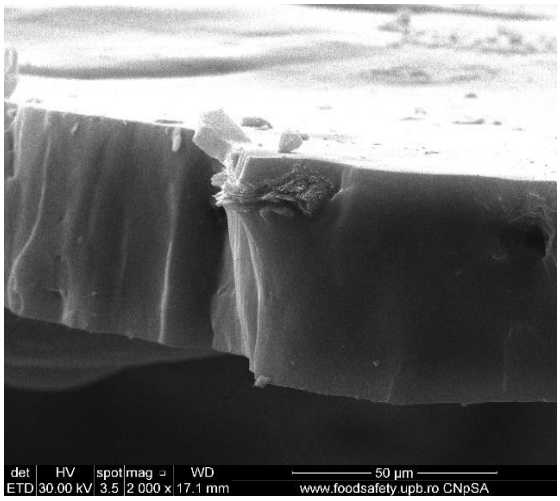
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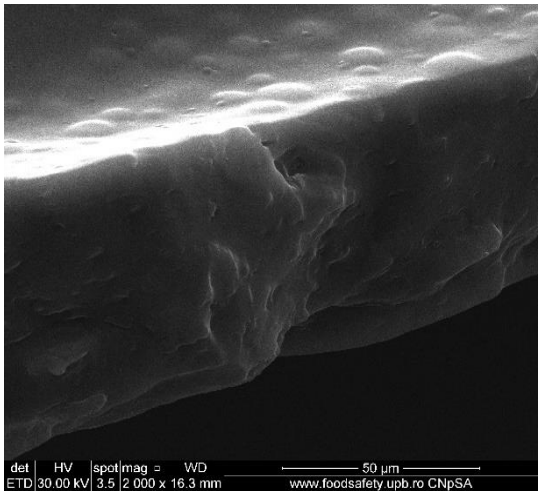
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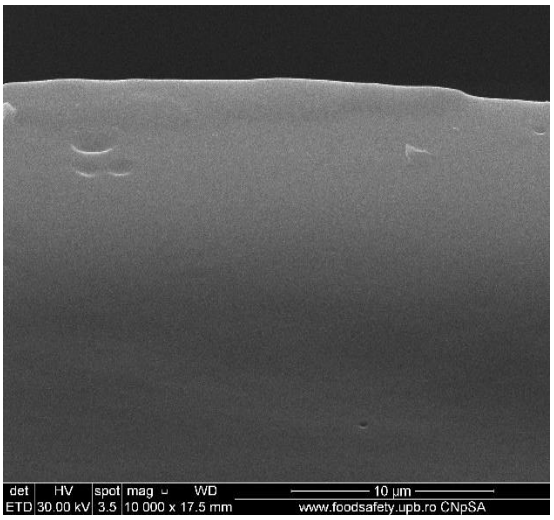
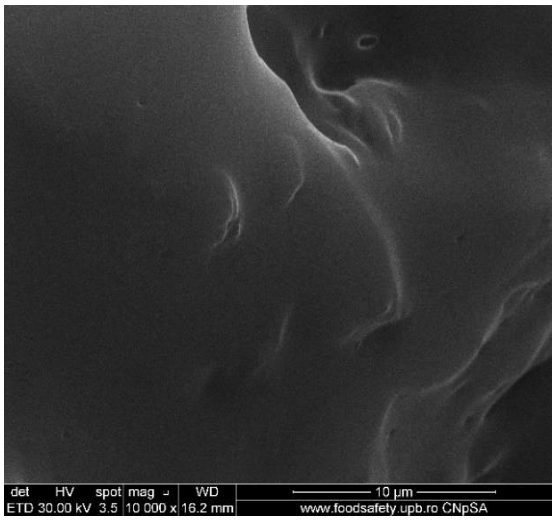
(**d**)



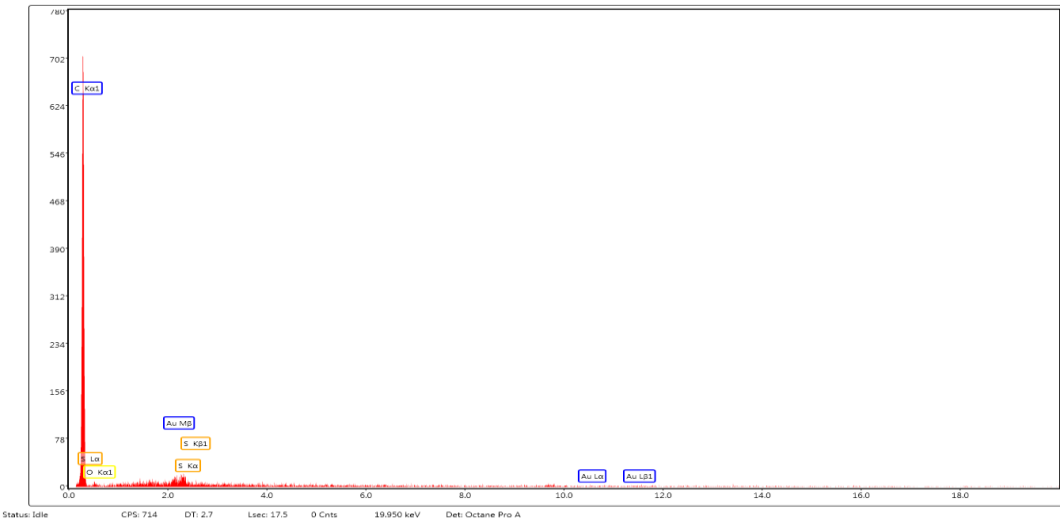
(**e**)



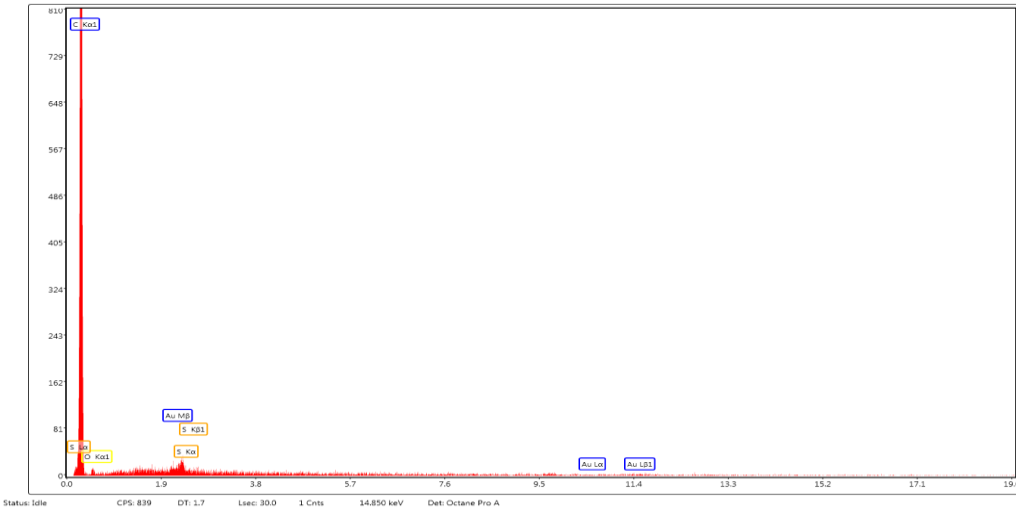
(**f**)

The surface elemental concentration is slightly different for the two membranes (Table 3), with a remarkable reduction by almost a third of the surface concentration of both sulfur and oxygen in the case of Chi–sEPDM membrane (M2), compared to the sEPDM membrane (M1).

Figure 4. Scanning electron microscopy (SEM) images for: sulfonated ethylene-propylene-diene terpolymer (sEPDM) (M1) – **(a)**, **(c)** and **(e)**; chitosan (Chi)–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) (M2) – **(b)**, **(d)** and **(f)**.



(**a**)



(**b**)

Figure 5. Energy-dispersive spectroscopy analysis (EDAX) diagram for: sulfonated ethylene-propylene-diene terpolymer (sEPDM) (M1) **(a);** chitosan (Chi)–sulfonated ethylene-propylene–diene terpolymer (Chi–sEPDM) (M2) **(b)**.

Table 3. Energy dispersive spectroscopy analysis (EDAX) for the prepared membranes.

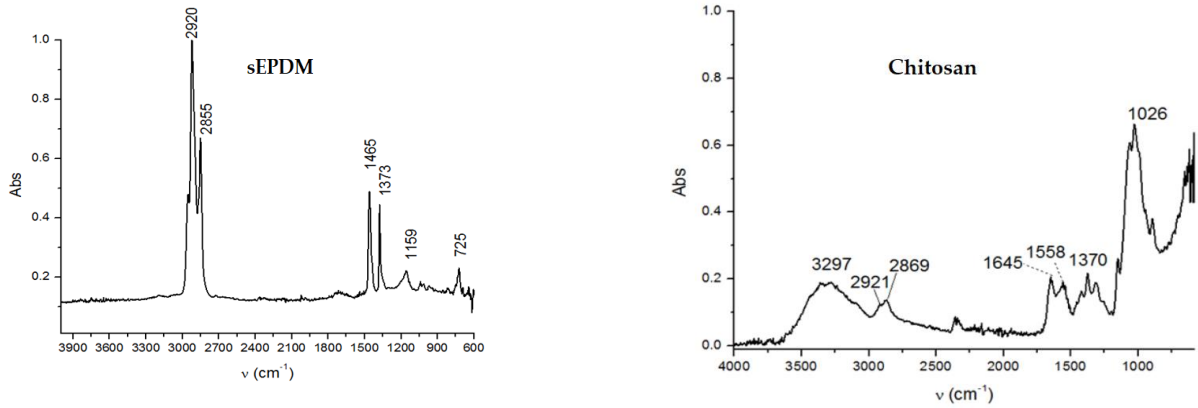
Membranes		**M1**			**M2**	
Surface composition	**Weight (%)**	**Atomic (%)**	**Error (%)**	**Weight (%)**	**Atomic (%)**	**Error (%)**
C K	94.48	95.88	3.07	96.37	97.3	2.29
O K	5.28	4.02	29.5	3.49	2.64	30.79
S K	0.24	0.09	62.31	0.15	0.06	61.64

Although the difference in elemental surface composition is relatively small, the hydrophilicity of the membrane surface changes dramatically (Table 2), the composite membrane (M2) being much more hydrophilic (θ=75°) than the sEPDM membrane (M1, θ=45°).

3.1.2. Fourier Transform InfraRed spectroscopy (FTIR) membrane characteristics

The data obtained from the elemental analysis (EDAX) required a study in the infrared domain both spectrally (FTIR) and by interference reflection microscopy (IRM), which would provide more structural information and surface composition.

Figure 6 shows the spectra of the base materials: sulfonated ethylene-propylene-diene terpolymer (sEPDM) (Figure 6a) and chitosan (Chi) (Figure 6b).



(**a**) (**b**)

Figure 6. Fourier Transform InfraRed spectra for: sulfonated ethylene-propylene-diene terpolymer (sEPDM) **(a)**; and chitosan (Chi) **(b)**.

The spectra obtained were used to select the wave numbers for which the infrared microscopy map (FTIR, 2D) was made, for the two membranes obtained.

Most of the specific wave numbers of the two materials are located in very close areas and therefore cannot be used as safe specific values for the FTIR microscopy study. It should also be emphasized that the sEPDM film subjected to FTIR analysis was obtained from toluene solution, which did not favour the highlighting of hydrogen bonds of the sulfonic group (Figure 6a). The examined chitosan was presented as a powder, and the obtained spectrum is compatible with the literature data.

In another train of thoughts, the two materials used to obtain the composite membrane interact. Thus, the sulfonic groups in sEPDM give a neutralization reaction with amino groups in chitosan, but there are also other possible interactions such as hydrogen bonds, ionic bonds and hydrophobic bonds (Table 1). Figure 7 shows the images of the selected areas (M1 in Figure 7a, M2 in Figure 7b) and Table 4 shows FTIR 2D maps, at randomly selected wave numbers, but targeting each representative range of the spectra: 3345 cm-1, 1385 cm^{-1}, 1050 cm^{-1}, and 728 cm^{-1}.

The associated spectra and the color scale used are shown in figure 8, showing significant differences that can largely justify the differences in hydrophilicity presented by the prepared membranes (Tables 1 and 4).

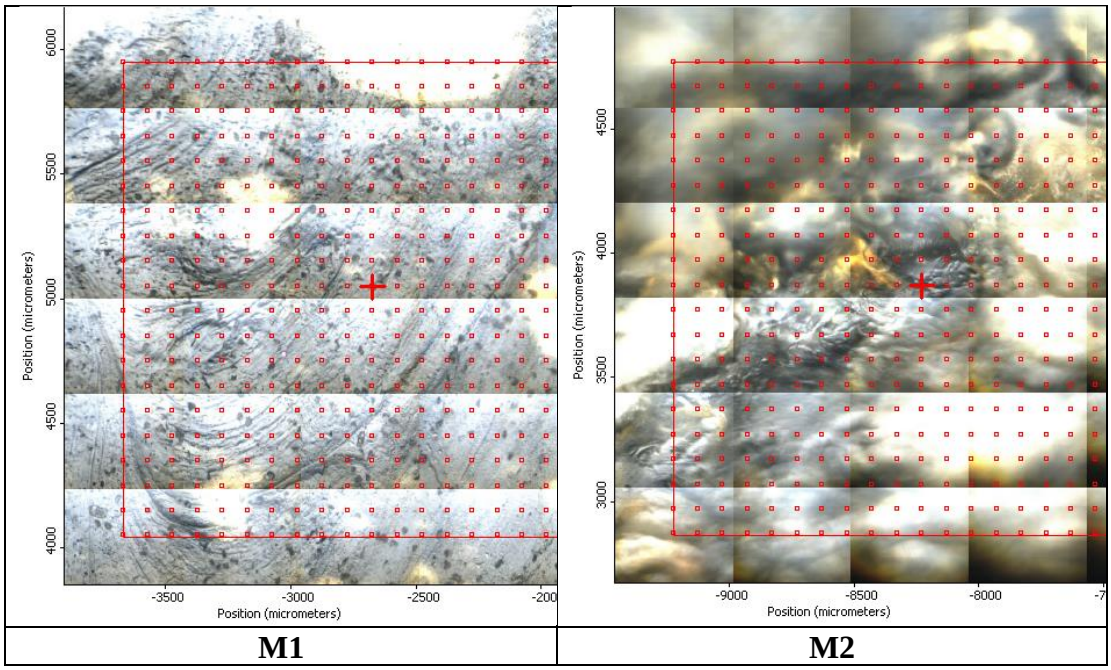
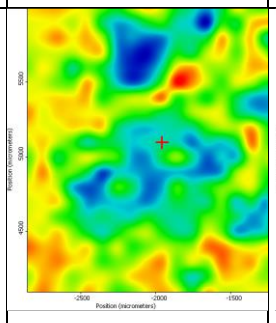
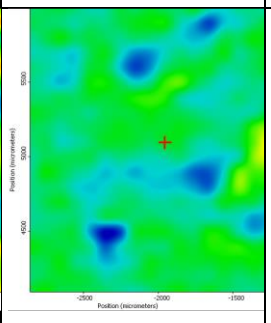
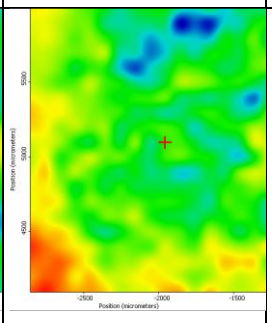
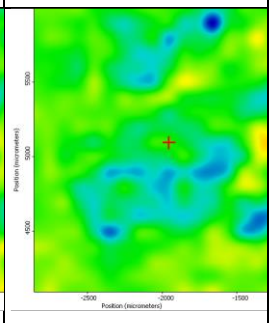


Figure 7. Video-images for sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane **(M1)**; and chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane **(M2)**.

Table 4. The FTIR 2D maps for sEPDM membrane (M1) and composite membrane (M2).

	3345 cm^{-1}	1385 cm^{-1}	1050 cm^{-1}	728 cm^{-1}
M 1				

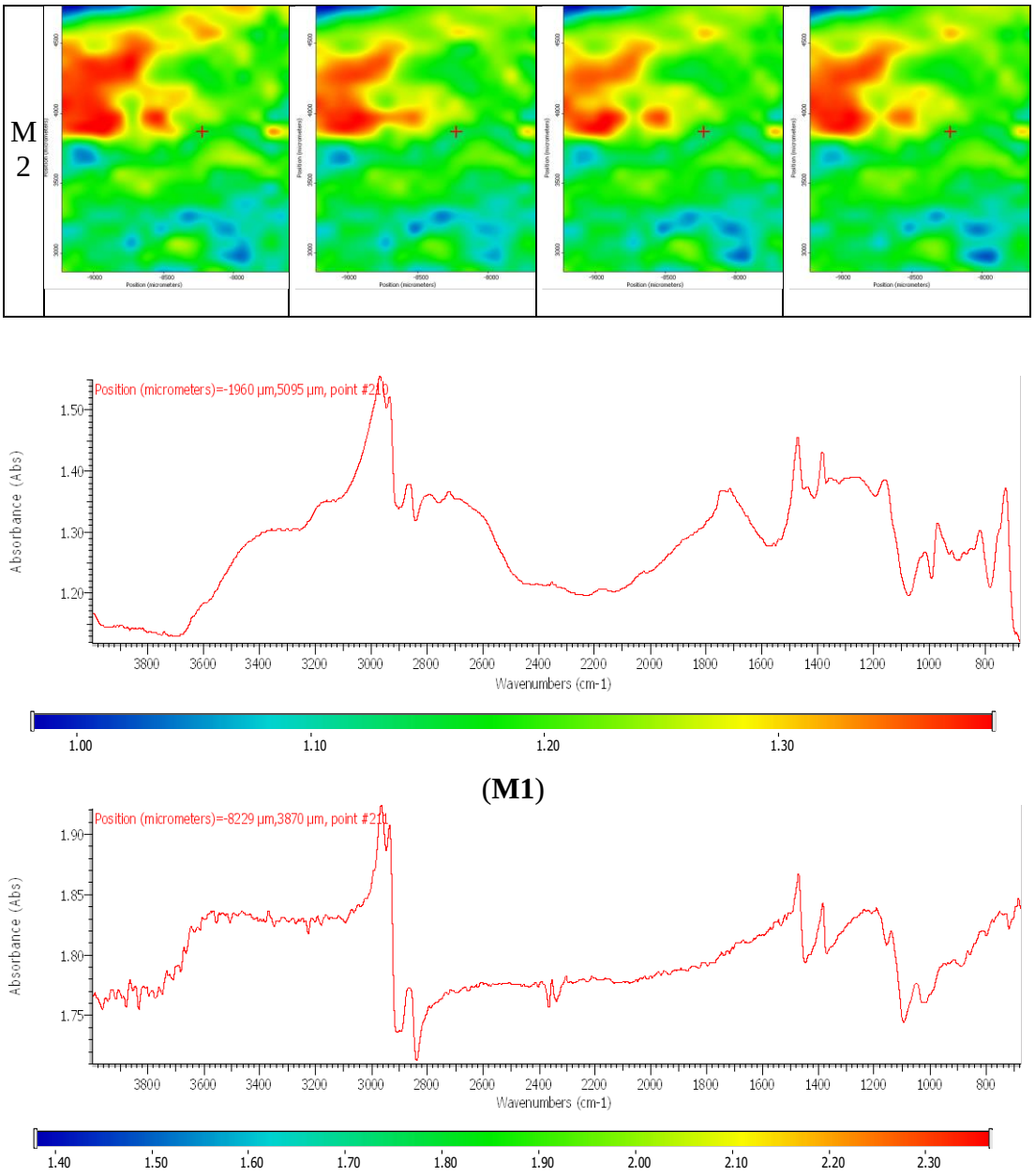


Figure 8. Infrared associated spectrum and colour scales for sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane **(M1)**; and chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane **(M2)**.

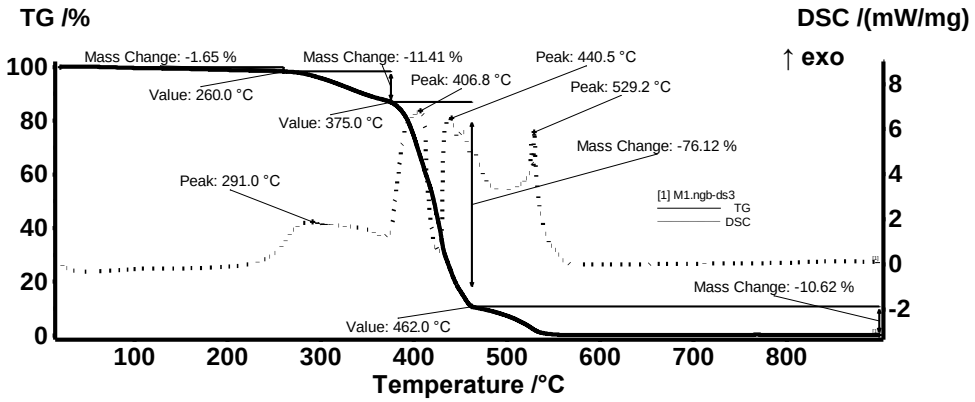
The HD-IR obtained maps show a relatively uniform, regular and repeatable distribution of the surface of the obtained membranes, especially for the sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1). The composite chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2) shows an area which, with the greatest probability, is due to the agglomeration of

chitosan (upper left corner of the images), being more obvious for a wave number of 3345 cm^{-1}, but also present for all other wave numbers (Table 4). This agglomeration was also highlighted in the electron microscopy detail (Figure 4f).

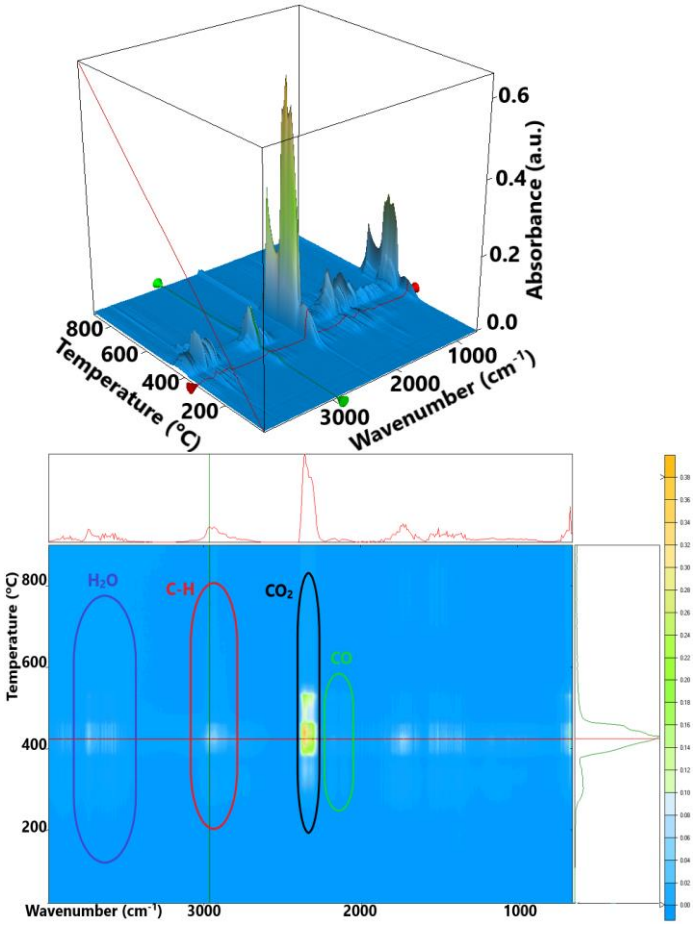
3.1.3. Thermal characteristics of the prepared membranes

The complex thermal analysis had both the role of highlighting the thermal behavior of the membranes at relatively low temperatures (up to 300 °C) and their composition through gas chromatographic analysis coupled with infrared spectrometry of combustion gases (up to 800 °C).

The sample M1 (figure 9) can be considered stable up to 260 °C, losing only 1.65% of its mass, mainly residual solvent but also some sulphur is removed as SO_2 as indicated by the FTIR analysis of the evolved gases. Between 260–375 °C the sample is losing 11.41% of its mass, the process being accompanied by a broad exothermic effect with peak at 291 °C. The main degradation process takes place between 375–462 °C when the sample is losing 76.12% of its mass (Figure 9a). The DSC curve indicates two strong exothermic effects, but the FTIR of the evolved gases indicates a quasi-continuous production of CO_2, H_2O or hydrocarbon fragments, which means that any backbone breaking in smaller fragments is also accompanied by the combustion of those fragments (Figure 9a, b and c). The FTIR spectrum at 429 °C, in the middle of the strongest degradation process, indicates the evolving of H_2O, CO_2 and CO as combustion products, but also of saturated hydrocarbon fragments from pyrolysis of the polymer backbone and SO_2. The residual carbonaceous mass is burned after 460 °C, the process being accompanied by a strong exothermic peak at 529.2 °C. The FTIR analysis of evolved gases at 529 °C indicates that the product is mainly CO_2. It can be seen that some desulfurization processes take also place under 200 °C (Figure 10).



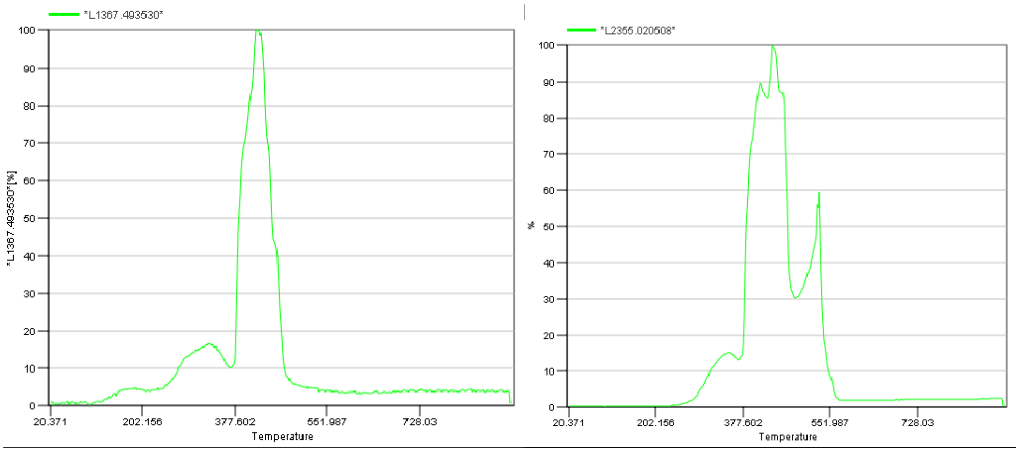
(**a**)



(**b**)

(**c**)

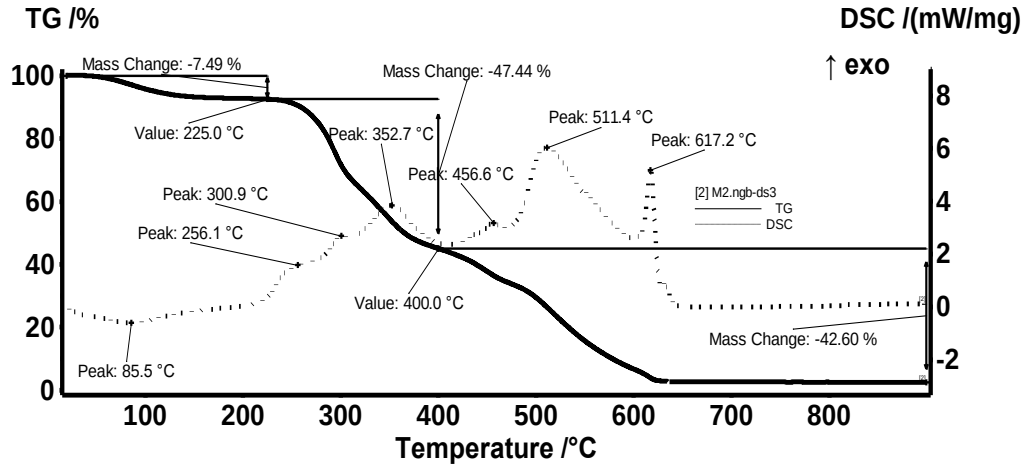
Figure 9. Thermal characteristics of the sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1): **(a)** thermal diagram; **(b)** 3D complex analysis; **(c)** 2D complex analysis.



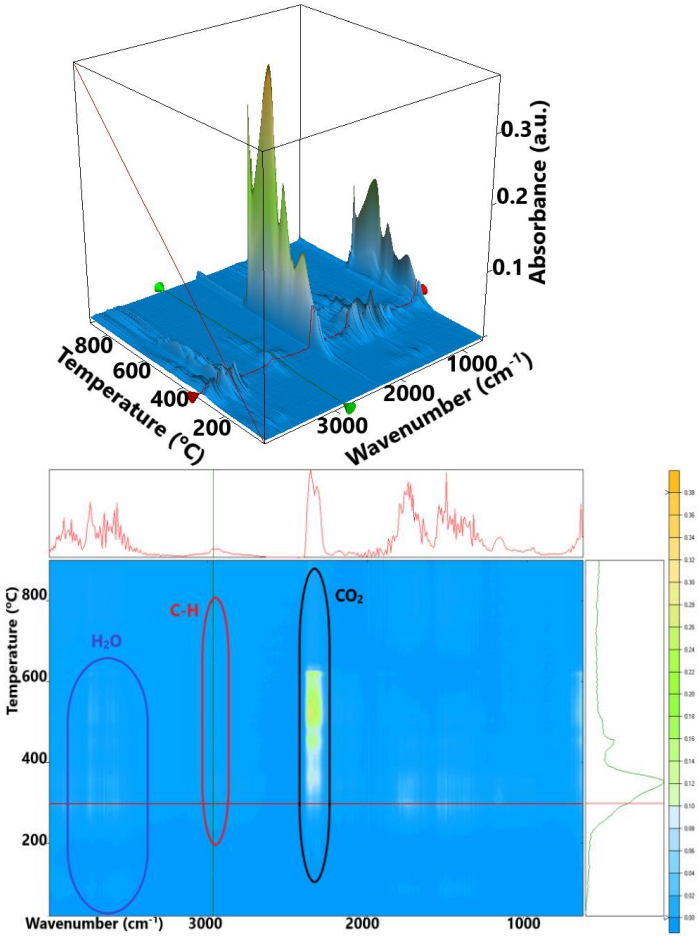
(**a**) (**b**)

Figure 10. Trace for evolving SO_2 (1367 cm^{-1}) vs temperature **(a)**; and trace for evolving CO_2 (2355 cm^{-1}) vs temperature **(b)**.

The sample M2 (Figure 11) is losing 7.49% in the temperature interval RT–225 °C, the associated effect being weak and endothermic with minimum at 85.5 °C. The sample is losing some residual water molecules in this interval, but also the desulfurization processes start (Figure 11a), as indicated by the FTIR of the evolved gases and the traces for individual wavenumbers vs temperature (Figure 12). In the interval 225–400 °C the sample begins to suffer an oxidative degradation, on the DSC curve being visible multiple exothermic peaks, partially overlapped. The FTIR of evolved gases allows identification of combustion products like CO_2, CO and H_2O, but also saturated hydrocarbons from polymer backbone fragmenting and SO_2, indicating the complexity of the thermal degradation (Figure 11 b, c). The majority of SO_2 is evolving in this interval, after 400 °C only minor peaks being identified on the compound trace (Figure 11a). The same can be stated for the saturated hydrocarbons fragments: after 400 °C only a small peak being observable on the trace line (Figure 11c). After 400 °C the sample suffers mostly oxidation processes, as indicated by the evolving of CO_2 and H_2O in larger quantities, culminating with the burning of the residual carbonaceous mass which is accompanied by the strong and sharp exothermic effect from 617.2 °C. The recorded mass loss after 400 °C is 42.60%.



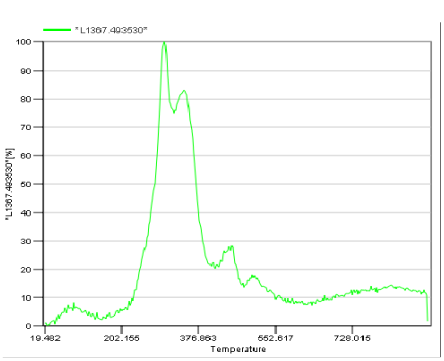
(**a**)

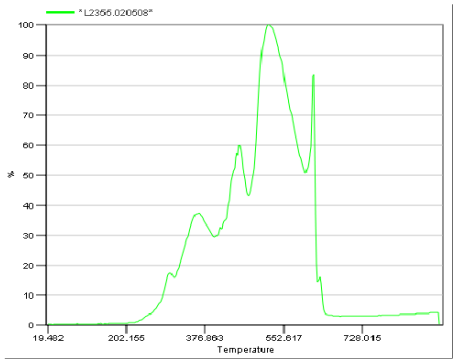


(**b**)

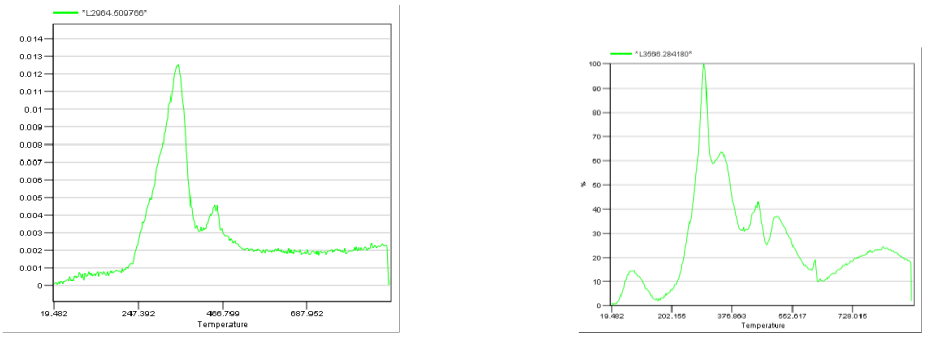
(**c**)

Figure 11. Thermal characteristics of the chitosan–sulfonated ethylene-propylene-diene terpolymer membranes (Chi–sEPDM) (M2): **(a)** thermal diagram, **(b)** 3D complex analysis; **(c)** 2D complex analysis.





(**a**) (**b**)



(**c**) (**d**)

Figure 12. Trace for evolving **(a)** SO_2 (1367 cm^{-1}); **(b)** CO_2 (2355 cm^{-1}); **(c)** hydrocarbons (2964 cm^{-1}); and **(d)** H_2O (3566 cm^{-1}) vs temperature.

3.2. Transport and release of the melatonin through prepared membranes

A natural hormone, synthesized in the body, melatonin can be most of the time administered orally, and the main concern of the researchers was to find the most suitable methods of controlled release [4,12].

However, there are some specific aspects that make melatonin remain constantly in the attention of researchers in order to design new methods of delivery in the body:

- A universal dose of melatonin cannot be prescribed, because each body has its own production [47];
- Age and health greatly affect the production of the pineal gland [48];
- The time of the day is very important because the production of melatonin in the body is cyclical [49];
- In case of accidents, especially those from various sports competitions, local administration is necessary (oral cavity, skin, bones, joints) [50–55].

All these considerations have encouraged the experimental research on the transport and/or release of melatonin through composite membranes of chitosan–sulfonated ethylene-propylene-diene terpolymer membranes (Chi–sEPDM), even if recently a mathematical model of the release of various active substances has been proposed [56].

In this study, the transport through the composite membrane obtained in a two-compartment membrane system and the release of melatonin in an open system (the receiving solution is renewed) were followed.

3.2.1. Transport of melatonin transport through the obtained membranes

The melatonin transport experiments through sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) and chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2) were carried out from a 100 mL

source phase, with a concentration of 2 g/L, and imposed pH (6, 7.0 and 8) or salinity (1%, 3% and 5% NaCl) receptor phases. The compartments of the membrane system were constantly stirred. The results obtained (Figure 13) show that pH influences the transport, especially in the second part of the studied interval (Figure 13a), while sodium chloride has effect on the transport from the beginning of the range, especially at lower concentrations (Figure 13b). The pronounced increase in salinity disfavours the transport, most probably by reducing the solubility of melatonin in the receiving phase.

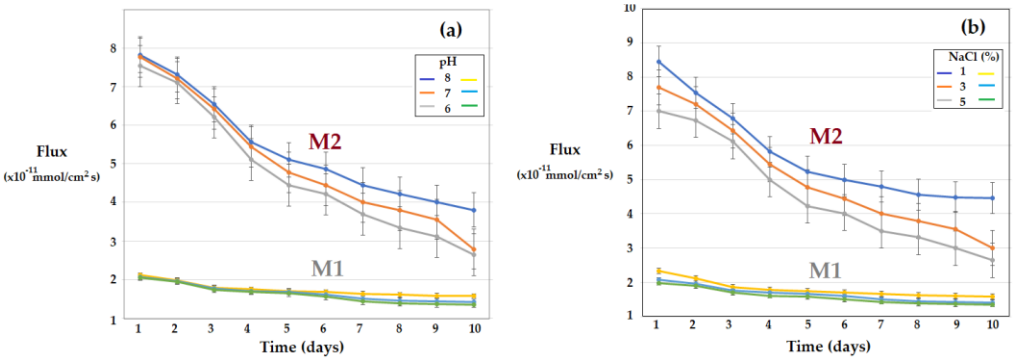
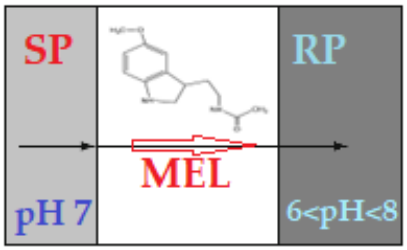
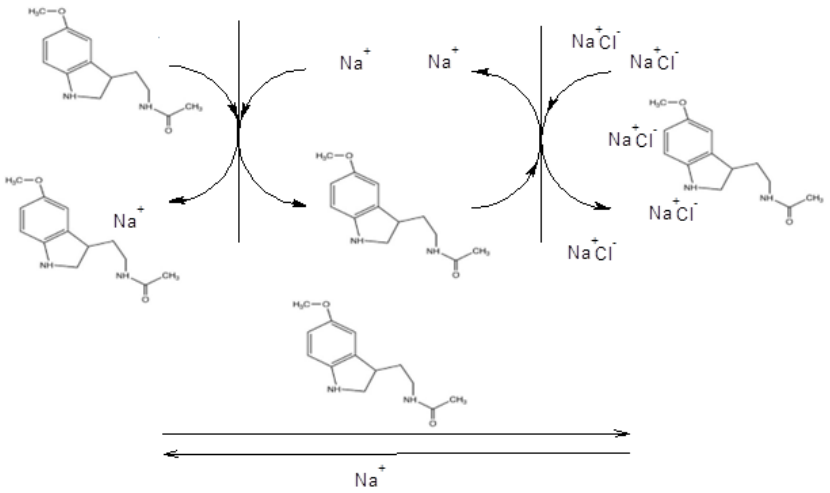


Figure 13. Time variation of melatonin flow through sulfonated ethylene-propylene-diene terpolymer (sEPDM) membranes (M1) and chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membranes (M2), depending on pH **(a)**; and salinity **(b)**.

The transport of melatonin in the system with the receiving phase of variable pH is mainly determined by the difference in concentration between the aqueous phases, so by the solubility of melatonin in the aqueous phases of relatively close composition (Figure 14a), while the transport of melatonin to the receiving phase of controlled salinity corresponds to a coupled transfer mechanism (Figure 14b), in which the melatonin transport from source phase to the receiving phase is coupled with the transport of sodium ions in the opposite direction.



(a)



(b)

Figure 14. Transport schemes in the case of the receiving phase of controlled pH **(a)**; or imposed salinity **(b)**.

3.2.2. Release of melatonin through the obtained membranes

The study of the controlled release of melatonin was carried out for a source phase of 5 mL, with a concentration of 2 g/L and receiving phases of a much larger volume of 5L with imposed pH (6, 7.0 and 8) or salinity (1%, 3% and 5% NaCl). Basically, a set of 100 vials containing the source phase is immersed in a vessel with 5L of recirculated receiving solution, with a flow rate of 100 mL/min. Thus, it can be appreciated that the receiving phase will remain at the imposed pH and salinity. Ten of the vials from the set are taken out daily for analysis, during 10 days, seven of them for averaging the results and three to be sent for the validation of the analyses.

The delivery results of melatonin for ten consecutive days through sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) and chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2) are presented in Figure 15.

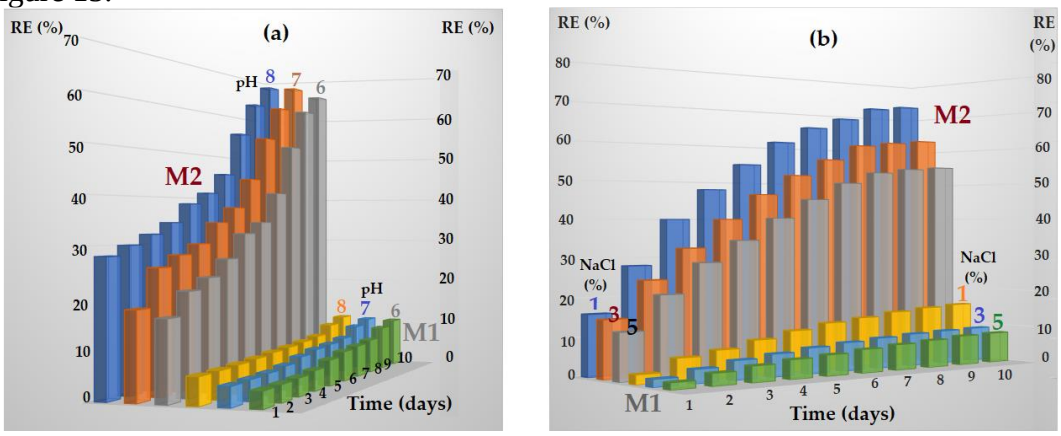
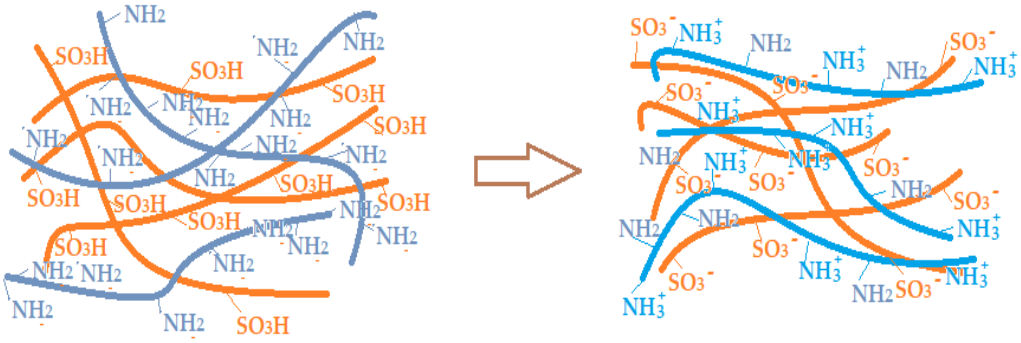


Figure 15. Time variation of melatonin release through sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) and chitosan–

sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2), depending on pH **(a)**; and salinity **(b)**.

The results obtained for the release of melatonin show that chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2) allows a faster transfer and in an amount that approaches the data from the literature, while sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) has a low but relatively constant release over time.

For the sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) that contains sulfonic reactive functional groups (SO3H), the interactions with melatonin during its transport and release are predictable, since at the working pH they are in sulfonate form (SO_3^-). In case of chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) composite membrane (M2) the interactions with melatonin in transport and release are complex because at the working pH the amino groups can be free or ionized (ammonium) (Figure 16).



(**a**) (**b**)

Figure 16. Schematic representation of the polymer mixture: before **(a)**; and after the after the formation of the chitosan–sulfonated ethylene-propylene-diene terpolymer membrane (Chi–sEPDM) (M2).

The ionic situation presented in Figure 16b is close to reality in the case of acidic pH, but at pH=7 or higher, the ammonium groups will change to the amino form and the membrane charge will be slightly negative (due to the sulfonate groups). All these considerations explain to a good extent both the large difference between the hydrophilicity of the prepared membranes, but also the influence of pH and salinity on the transport and release of melatonin.

The study of the sensitivity to pH variation for the case of chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) composite membrane (M2) requires a greater depth compared to the experiments carried out so far, by widening the range both towards strongly acidic and towards strongly basic environments.

4. Conclusions

This chapter presents the preparation and characterization of a composite membrane based on chitosan (Chi) and sulfonated ethylene-propylene-diene

terpolymer (sEPDM) and its controlled release performance in synthetic aqueous solutions.

The membranes were obtained from an 8% sEPDM solution in toluene (w/w) in which chitosan was dispersed in an ultrasonic field (sEPDM:Chi=1:1, w/w), through controlled vacuum evaporation. They were morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with infrared chromatography and analysis, and contact angle measurements, but also from the perspective of performance in the processes of transport and release of melatonin in dedicated environments (aqueous solution with controlled pH and salinity).

The transport of melatonin in the system with the receiving phase of variable pH is mainly determined by the difference in concentration between the aqueous phases, so by the solubility of melatonin in aqueous phases of relatively close composition, while the transport of melatonin to the receiving phase of controlled salinity corresponds to a coupled transfer mechanism in which the transport of melatonin from the source phase to the receptor phase is coupled with the transport of sodium ions in the opposite direction.

The results obtained for the release of melatonin show that chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2) allows a faster transfer and in a quantity that approaches the data from the literature, while sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) has a low but relatively constant release over time.

The prepared membranes can release melatonin in amounts between 0.4 mg/day (M1) and 1.6 mg/day (M2).

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Partea C. ***Concluzii generale și perspectivele cercetării***

C.1.Concluzii generale

The development of the doctoral thesis "Membranes and membrane processes in the transport, separation, and synthesis of products with implications in sports medicine" represents an excellent applied research activity. The research carried out refers to the transport and separation of products of biological interest (chemical species with therapeutic potential) with implications in sports medicine.

The synthesis of specialized literature (Chapter 1) highlighted several significant research directions of membranes and membrane processes:

1. The currently known membranes are classified both according to the nature, structure and type of material from which they are made, as well as according to the field of application

2. According to the nature of the material, the membranes are natural and synthetic

3. Depending on the structure, membranes are porous and non-porous (dense)

4. By material type: polymeric and inorganic

5. From the point of view of pore distribution, porous or non-porous membranes can be isotropic (symmetric), anisotropic (asymmetric) or composite

6. Membrane production methods refer to homogeneous neutral membranes, ion exchange membranes, liquid membranes

7. The membrane processes described are microfiltration, ultrafiltration, electrodialysis and reverse osmosis.

8. Liquid membranes are classified into three categories: bulk, emulsion and supported (on support)

9. Other membrane processes have recently been developed: piezodialysis, diafiltration, membrane distillation and pervaporation.

10. Interest in thermally driven processes has been revived by the development of a new process called membrane distillation.

11. The separation of compounds of biological interest (amino acids, proteins, chemical species with toxicological impact) with the help of membranes has been widely studied due to numerous applications: in environmental protection, purification of proteins from various biological environments, reduction of the organic load of waters, recovery of valuable products from the food industry.

Conclusion of the Chapter 2.1. Transport and separation of the silver ion with *n*–decanol liquid membranes based on 10–undecylenic acid, 10–undecen–1–ol and magnetic nanoparticles

The permeation module with *n*-decanol membrane, undecenoic acid carriers, undecylenyl alcohol and convection promoters of iron oxides / silver and iron oxides magnetic nanoparticles allows the verification of the characteristics of silver and lead ion transport by: varying the flow of source and receiving phases, pH adjustment of the receiving phase and stirring regime with magnetic nanoparticles.

Under the conditions of the optimized experimental results (pH=7 of the source phase, pH=1 of the receiving phase, flow rate of 30 mL/min for the source phase and 9 mL/min for the receiving phase, 150 rot/min agitation of magnetic nanoparticles) separation efficiencies of silver ions of over 90% were obtained for the transport of undecenoic acid and about 80% for undecylenyl alcohol.

In the case of the considered carriers, undecylenic acid and 10–undecylenyl alcohol, the use of iron oxide nanoparticles is more effective than the use of silver and iron oxide nanoparticles, most likely due to the effect of the alkylene group.

The separation of silver and lead ions in the studied system leads to separation factors between 6 and 9, under the specified hydrodynamic conditions the most efficient system being *n*–decanol–10–undecylenic acid–iron oxide nanoparticles.

Conclusion of the Chapter 2.2. Reactional Processes on Osmium-Polymeric Membranes for 5–Nitro benz imidazole Reduction to 5-Aminobenzimidazole

The paper presents the results obtained at the reduction of 5–nitrobenzimidazole by transformation into 5–aminobenzimidazole, in the reaction system with osmium–polymer membrane (Os–P) with molecular hydrogen, in an aqueous membrane system, with pH=6 in the source phase and pH=1 for the receiving phase.

This study opens the research direction of metallic osmium nanoparticles–polymer membranes to redox processes (reduction or oxidation) of organic compounds of biological interest that should not be contaminated with metal ions.

The osmium-polymer membranes (OS–P) were obtained using cellulose acetate membranes and polysulfone (PSf) membranes as support, obtained by phase inversion and commercial polypropylene hollow fiber (PP). The osmium in the form of

nanoparticles was generated by the reduction reaction of osmium tetroxide in tert–butyl alcohol with molecular hydrogen.

The membranes obtained, based on osmium–cellulose acetate (OS–CA), osmium–polysulfone (Os–PSf) and osmium–polypropylene hollow fiber (Os–PP) membranes were characterized from a morphological and structural point of view, using scanning electron microscopy (SEM), high resolution SEM (HR–SEM), energy dispersive spectroscopy analysis (EDAX) and thermogravimetric analysis (TGA, DSC).

The process performance was tested at reduction of 5-nitrobenzimidazol solution 0.5g/L to 5-aminobenzimidazol with molecular hydrogen, by varying the nature and surface of the membrane, the molecular hydrogen flow and the operating time.

The results obtained show that:

- The conversion of 5–nitrobenzimidazol to 5–aminobenzimidazol in the reaction system with osmium–polymer (Os–P) membrane depends on the nature of the polymer,

- The conversion of 5-nitrobenzimidazol to 5-aminobenzimidazol in the reaction system with osmium–polymer (Os–P) membrane is slightly independent of the hydrogen flow in the system,

- The efficiency of 5–aminobenzimidazol separation depends on the operating time, being correlated with the conversion of 5–nitrobenzimidazol to 5–aminobenzimidazol, in the reaction system with osmium-polymer membrane (Os–P).

Both the 5–aminobenzimidazol separation efficiency (EE) and the 5–nitrobenzimidazol to 5–aminobenzimidazol conversion efficiency (η) vary in the same order:

$EE_{Os–PSf} \leq EE_{Os–CA} \leq EE_{Os–PP}$ and, respectively, $\eta_{Os–PSf} \leq \eta_{Os–CA} \leq \eta_{Os–PP}$.

Aspects of the possible mechanism of conversion of 5–nitrobenzimidazole to 5–aminobenzimidazole with hydrogen gas in the reaction system with osmium–polymer membrane (Os–P) are presented and a proposal is made to solve it by using deuterium (^2H or D) instead of hydrogen or heavy water (D_2O) as the reaction medium.

Conclusion of the 2.3.1. Chitosan-polypropylene hollow fibers composite membrane for ions transport

Separation and/or recovery of copper and zinc from waste electronics and electrotechnical industries can be achieved by pertraction using both membranes and composite membranes.

In the present study, the separation of copper and zinc from 3 mol/L hydrochloric acid solutions was addressed using both polypropylene hollow fiber membrane (PPHFM) and chitosan–polypropylene hollow fiber composite membrane (Chi–PPHFM). The chitosan–polypropylene hollow fiber (Chi–PPHFM) composite membrane was made by ultrafiltration of a chitosan solution through the polypropylene hollow fiber support membrane (PPHFM) and was characterized by electron microscopy, FTIR spectroscopy and process performance.

The results for the composite membrane are better both in terms of extraction efficiency and achieving a higher separation factor. Thus, for dilute solutions (10^{-6} mol/L) it is possible to achieve a pertraction efficiency almost 15 times higher for zinc and a concentration factor of approximately 10.

It can be appreciated that the contribution of chitosan to the improvement of the performance of the composite membrane compared to the support membrane is about 90%.

Conclusion of the 2.3.2. Chitosan/sEPDM composite membranes for melatonin transport and release

This chapter presents the preparation and characterization of a composite membrane based on chitosan (Chi) and sulfonated ethylene-propylene-diene terpolymer (sEPDM) and its controlled release performance in synthetic aqueous solutions.
The membranes were obtained from an 8% sEPDM solution in toluene (w/w) in which chitosan was dispersed in an ultrasonic field (sEPDM:Chi=1:1, w/w), through controlled vacuum evaporation. They were morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with infrared chromatography and analysis, and contact angle measurements, but also from the perspective of performance in the processes of transport and release of melatonin in dedicated environments (aqueous solution with controlled pH and salinity).
The transport of melatonin in the system with the receiving phase of variable pH is mainly determined by the difference in concentration between the aqueous phases, so by the solubility of melatonin in aqueous phases of relatively close composition, while the transport of melatonin to the receiving phase of controlled salinity corresponds to a coupled transfer mechanism in which the transport of melatonin from the source phase to the receptor phase is coupled with the transport of sodium ions in the opposite direction.

The results obtained for the release of melatonin show that chitosan–sulfonated ethylene-propylene-diene terpolymer (Chi–sEPDM) membrane (M2) allows a faster transfer and in a quantity that approaches the data from the literature, while sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1) has a low but relatively constant release over time.

The prepared membranes can release melatonin in amounts between 0.4 mg/day (M1) and 1.6 mg/day (M2).

C2. Originality of research

In the research of the doctoral internship of the thesis "Membranes and membrane processes in the transport, separation and synthesis of products with implications in sports medicine" the following were obtained or addressed:

1. Three new types of membranes:

- Composite membranes for the transport of silver ions.
- Composite membranes based on osmium.
- sEPDM composite membranes

2. The transport or synthesis of compounds of interest for sports medicine - silver, copper or zinc ions with bactericidal or bacteriostatic potential
- 5-aminobenzimidazole
- melatonin

3. Innovative methods of characterization of the obtained composite membranes were approached, which allowed the publication of 8 papers, 7 of which in Q1 magazines (only four were included in the current thesis).

4. Part of the research not included in this thesis could be used in a separate thesis on "Synthetic membrane retardation systems".

C3. Research development perspectives

The research carried out within the doctoral research program "Membranes and membrane processes in the transport, separation, and synthesis of products with implications in sports medicine" led to the development of new applications of the separation processes through composite membranes in the transport and separation of some chemical species of interest for sports medicine.

Lista de lucrari publicate Florentina Mihaela Păncescu

Scopus EXPORT DATE: may 2023

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IF (ISI) = 4.562

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DOI: 10.3390/nano11102526
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Acceptat pentru publicare:
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