

Ministry of Education

University Politehnica from Bucharest

Faculty of Chemical Engineering and Biotechnologies

Doctoral School Chemical Engineering and Biotechnologies

Abstract

PhD Thesis

Decision No. 1058 din 10 July 2023

Retard systems with synthetic membranes /

Sisteme retard cu membrane sintetice

PhD Student:

Andreea FERENCZ (Dinu)

Supervisor:

Prof.dr.eng. Gheorghe NECHIFOR

September 2023

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Andreea FERENCZ (DINU)

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September 2023, Bucharest

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Abreviation list

D - dialysis.

ED - electro dialysis.

EDI - reverse electro dialysis.

MF - microfiltration.

UF - ultrafiltration.

RO - reverse osmosis.

DM - membrane distillation.

SG - gas separation.

PV - pervaporation.

ELM - liquid membrane extraction.

TC - facilitated transport.

BLM (MLV) - Bulk liquid membranes

HLM - hybrid liquid membranes

HFCLM - liquid membranes thin capillary or tubular fibers

HFLM - hollow fiber liquid membranes

HMS - hybrid multi-membrane systems

Introduction

The retard systems addressed in the doctoral thesis "Retard systems with synthetic membranes" is a work in which the main aspects of the systems that transport, separate, or synthesize chemical species of biological interest and/ or biomedical through the intervention of synthetic membranes.

The paper includes Part A. Synthesis of data from the literature, Part B. Experimental Part and Part C. General conclusions, originality and research perspectives.

The part containing the original experiments refers to:

Chapter 2.1. pH and Design on *n*-alkyl Alcohols Bulk Liquid Membranes for Improving Phenol Derivatives Transport and Separation

Chapter 2.2. Operational limits of the bulk hybrid liquid membranes based on dispersion systems

Chapter 2.3. Osmium Recovery as Membrane Nanomaterials through 10-Undecenoic Acid Reduction Method

Chapter 2.4. Simultaneously release of silver ions and 10-undecenoic acid from silver-iron oxide nanoparticles impregnated membranes

B. EXPERIMENTAL PART

The objectives of the doctoral thesis

The objective of the doctoral thesis "**Retard systems with synthetic membranes**" refers to the transport, separation and the synthesis of products of biological interest (chemical species with therapeutic potential) with biomedical implications usable in biomedicine and sports medicine.

Specific objectives

- Obtaining composite membranes based on dispersions
- Physico-chemical and morpho-structural characterization of the new membranes

- pH and Design on *n*-alkyl Alcohols Bulk Liquid Membranes for Improving Phenol Derivatives Transport and Separation
- Operational limits of the bulk hybrid liquid membranes based on dispersion systems
- Osmium Recovery as Membrane Nanomaterials through 10-Undecenoic Acid Reduction Method

- Simultaneously release of silver ions and 10-undecenoic acid from silver-iron oxide nanoparticles impregnated membranes

Chapter 2.1.

pH and Design on *n*-alkyl Alcohols Bulk Liquid Membranes for Improving Phenol Derivatives Transport and Separation

Abstract: Regardless of the type of liquid membrane (LM): Bulk Liquid Membranes (BLM), Supported Liquid Membranes (SLM) or Emulsion Liquid Membranes (ELM), transport and separation of chemical species are conditioned by operational (OP) and constructive, design parameters (DP) of the permeation module. In the present study, the pH of the aqueous source phase (SP) and receiving phase (RP) of the proposed membrane system were selected as operational parameters. The mode of contacting the phases was chosen as convective transport generator. The type of membrane considered in the experiments is BLM with spheres in free rotation, as film contact elements of the aqueous phases with the membrane. The target chemical species were selected in the range of phenol derivatives (PD), 4-nitrophenol (NP), 2,4-dichlorophenol (DCP) and 2,4-dinitrophenol (DNP), all being substances of technical-economic and environmental interest. Due to their acid character, they allow the evaluation of the influence of pH as a determining operational parameter of transport and separation through a membrane consisting of *n*-octanol or *n*-decanol (*n*-AlcM). The comparative study performed for the transport of 4-nitrophenol (NP) shows that the module based on spheres (Ms) is more performant than the one with phase dispersion under the form of droplets (Md). The sphere making material influences the transport of 4-nitrophenol (NP). The transport module with glass spheres (Gl) is superior to the one using copper spheres (Cu), but especially with the one with steel spheres (St). In all the studied cases the sphere based module (Ms) has superior transport results compared to the module with droplets (Md). The extraction efficiency (EE) and the transport of 2,4-dichlorophenol (DCP) and 2,4-dinitrophenol (DNP), studied in the module with glass spheres, show that the two phenolic derivatives can be separated by adjusting the pH of the source phase. At acid pH of the source phase (pH = 2) the two derivatives are extracted with good results (EE>90%), while for pH ranging from 4 to 6 they can be separated, DCP having doubled separation efficiency compared to DNP. At a pH = 8 of the source phase, the extraction efficiency halves for both phenolic compounds.

Keywords: liquid membranes design; permeation module design; pH operational parameter; bulk liquid membranes; *n*-octanol membranes; *n*-decanol membranes, phenol derivatives transports; phenol derivatives separation.

Chapter 2.2. Operational limits of the bulk hybrid liquid membranes based on dispersion systems

Abstract: Liquid membranes usually have three main constructive variants: bulk liquid membranes (BLM), supported liquid membranes (SLM) and emulsion liquid membranes (ELM). Designing hybrid variants is very topical, with the main purpose of increasing the flow of substance through the membrane, but also improving the selectivity. This chapter presents the operational limits of some kind of hybrid membrane constituted as a bulk liquid membrane (BLM), but which works by dispersing the aqueous source (SP) and receiving (RP) phases, the membrane itself being a dispersion of nanoparticles in an organic solvent (NP-OSM). The approached operational parameters are: the volume of phases of the hybrid membrane system, the thickness of the liquid membrane, the working temperature, the flow of aqueous phases, the droplet size of the aqueous phases dispersed across the membrane, the nature and concentration of nanoparticles in the membrane, the pH difference between the aqueous phases, the nature of the organic solvent, the salt concentration in aqueous phases and the nature of transported chemical species. For this study, silver ion (SI) and *p*-nitrophenol (PNP) were chosen as transportable chemical species, the *n*-aliphatic alcohols (C₆...C₁₂) as membrane organic solvent, 10-undecenoic acid (UDAc) and 10-undecylenic alcohol (UDAl) as carriers and magnetic iron oxides as nanoparticles dispersed in the membrane phase. Under the experimentally established operating conditions, separation efficiencies of over 90% are obtained for both ionic and molecular chemical species (silver ions and *p*-nitrophenol). The results show the possibility of increasing the flow of transported chemical species, of almost 10 times for the silver ion and approx. 100 times for *p*-nitrophenol, by the appropriate choice of operational parameters, but also expose their limits in relation to the stability of the membrane system.

Keywords: liquid membranes; hybrid design liquid membranes; operational parameters; silver ion transport; *p*-nitrophenol transports; membrane flux; membrane selectivity; membrane system stability.

Chapter 2.3. Osmium Recovery as Membrane Nanomaterials through 10-Undecenoic Acid Reduction Method

Abstract: Significant amounts of osmium can be found as waste in the laboratories of electron microscopy, microbiology, organic chemistry or biochemistry, in the form of solutions of osmium tetroxide solutions (OsO_4). The recovery of osmium from residual osmium-tetroxide is a necessity imposed by its high toxicity, but also by the technical-economic value of metallic osmium. An elegant and extremely useful method is the recovery of osmium as a membrane catalytic material, in the form of nanoparticles obtained on a polymeric support. This paper presents the preparation and characterization of a composite membrane of active metallic nanoparticle – polymer support type, based on osmium nanoparticles obtained in situ on a polypropylene hollow fiber membrane. The method of reducing osmium tetroxide on the polymeric support is based on the use of 10-undecenoic acid (10-undecenoic acid) (UDA) as a reducing agent. The influence of the osmium tetroxide solvent on the characteristics of the osmium nanoparticles obtained in/on polypropylene hollow fiber membrane by reduction with UDA, took into account n-aliphatic alcohols. The membranes containing osmium nanoparticles (Os-NP) generated from the solution of osmium tetroxide in n-alkyl alcohols by reduction with 10-undecenoic acid on the polypropylene hollow fiber (Os-PPM) support were characterized in terms of 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 and thermal gravimetric analysis, differential scanning calorimetry (TGA, DSC). The preliminary process performance was tested in a redox process of an organic marker, p-nitrophenol. The obtained results show that the osmium-polypropylene composite membrane constitutes a membrane catalytic material of very wide applicative interest.

Keywords: osmium nanoparticle, osmium nanoparticle-polymer membranes, 10-undecenoic acid, composite polypropylene hollow fiber membranes, osmium nanoparticle-polypropylene hollow fiber membranes, redox processes, membrane reactor, 10-undecylenic acid.

Chapter 2.4. Simultaneously release of silver ions and 10–undecenoic acid from silver-iron oxide nanoparticles impregnated membranes

Abstract: The bio-medical benefits of silver ions and 10-undecenoic acid in various chemical-pharmaceutical preparations are indisputable, thus justifying the numerous researches of delayed and / or controlled release. This chapter presents the effect of the polymer matrix in the simultaneous release of silver ions and 10-undecenoic acid in an aqueous medium of controlled pH and ionic strength. The study took into consideration polymeric matrices consisting of cellulose acetate (CA) and polysulfone (PSf), which were impregnated with oxide nanoparticles containing silver and 10-undecenoic acid. The studied oxide nanoparticles are nanoparticles of iron and silver oxides obtained by an accessible electrochemical method. The obtained results show that silver can be released, simultaneously with 10-undecenoic acid, from an impregnated polymeric membrane, at concentrations that ensure the biocidal and, respectively, the fungicidal capacity. Concentrations of active substances can be controlled by choosing the polymer matrix or, in some cases, by changing the pH of the target medium. In the studied case, higher concentrations of silver ions are released from the polysulfone matrix, while higher concentrations of 10-undecenoic acid are released from the cellulose acetate matrix. The results of the study show that a correlation can be established between the two released target substances, which is dependent on the solubility of the organic compound in the aqueous medium and the interaction of this compound with the silver ions. The ability of 10–undecenoic acid to interact with the silver ion, both through the carboxyl and alkene groups contributes to the increase in the content of the silver ions transported in the aqueous medium.

Keywords: control release; composite membranes; impregnated membranes; silver-iron oxide nanoparticles; silver ions; 10-undecenoic acid; cellulose derivatives; cellulose acetate, 2-hydroxyethylcellulose.

1. Introduction

Controlled, delayed or directed release of various chemical species with chemical, bio-chemical or biological activity is one of the most important applications of membranes [1,2]. They are released under control, through or from membranes, in specific environments: drugs, pharmaceuticals and phyto-pharmaceuticals, detergents and dyes, fertilizers, nutrients, pesticides, fungicides, or herbicides with technical, economic and environmental benefits [3-5].

In all these cases, the membrane (M) is the one that releases, in a controlled, delayed or directed way, the active chemical species (A), which it incorporates in a dedicated target environment (Figure 1).

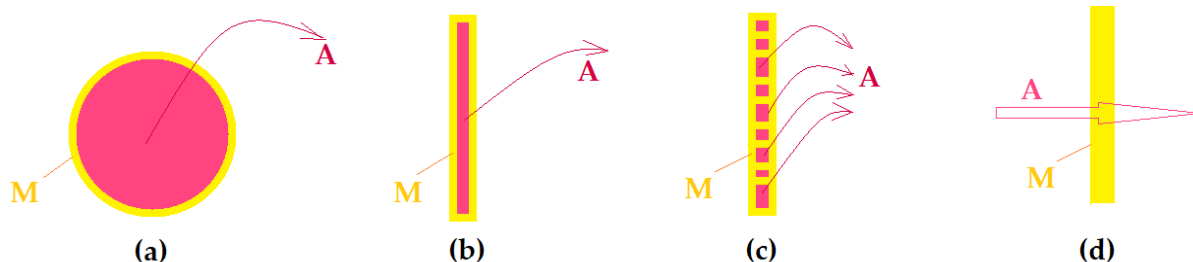


Figure 1. Schematic representation of releasing of an active species (A): from ((a), (b) and (c)); or through ((d)); a membrane (M).

This technique of administration of an active chemical species leads to the reduction of the consumption of valuable active substances, to the dosage at a constant and controllable level, to the prolongation of the duration of action, to the avoidance of overdose and to the decrease of the impact on the environment [6-8].

Among the chemical species of interest for controlled release, silver ions [9] and 10–undecenoic acid [10] have attracted the attention of researchers.

In particular, silver nanoparticles have been extensively studied [11-15] for their biocidal (bactericidal) action, being known and accepted three mechanisms of action on cells (bacteria):

- attachment to the surface cell membrane of the silver nanoparticle with dimensions below 10 nm, leading to disturbance of respiration and / or cell permeability [16];
- penetration of the cell membrane, having the effect of blocking the functions containing sulphur or phosphorus [17];
- the release of silver ions by the nanoparticle, amplifying its local effect [18].

On the other hand, the fungicidal action of 10-undecenoic acid has been the subject of research [19-21] because it is a very accessible compound [22-24], but also because it can be administered in various ways (creams, ointments, sprays, oxide dispersions) [25-27].

The research in this study was initiated after the loss of membrane material, in the aqueous contact phases, of a liquid membrane system based on *n*-alkyl alcohols - oxide nanoparticles containing silver and 10-undecenoic acid [28-30]. If in the considered membrane system, the loss of membrane material (silver ions and 10-undecenoic acid) was a disadvantage of using that device, the present research aims at the simultaneous release, either from a polymeric membrane or through an impregnated polymeric membrane, of the two chemical species.

Thus, this paper studies the simultaneous release of silver and 10-undecenoic acid ions from a membrane system with a matrix of cellulose derivatives (cellulose acetate (CA) and polysulfone (PSf)) with inclusions of oxide nanoparticles containing silver and 10- undecenoic acid as a dispersion medium.

2. Materials and Methods

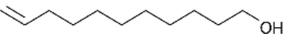
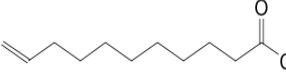
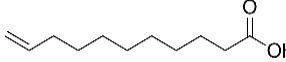
2.1. Reagents and materials

2.1.1. Reagents

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, silver nitrate, iron wires, sodium chloride, sodium hydroxide, dimethylformamide (DMF), ethylic alcohol, 10–undecen–1–ol (UDAl), 10–undecenoyl chloride (UDCl), and 10–undecylenic acid (UDAc).

The characteristics of the organic compounds used in the silver ion release study are presented in Table 1.

Table 1. The characteristics of the used organic compounds

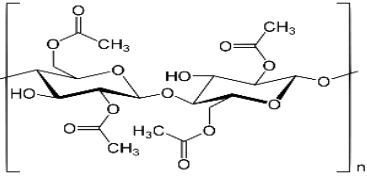
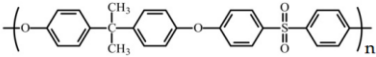
Organic compounds	Name and Symbol	Molar mass (g/mol)	Density (g/mL)	Solubility in water (g/L)	pKa
	10–undecen–1–ol (UDAl)	170.29	0.848	0.014 <i>estimated</i> 0.044 <i>exp.</i>	16.84
	10-undecenoyl chloride (UDCl)	202.72	0.944	-	none
	10–undecylenic acid (UDAc)	184.28	0.912	0.019 <i>estimated</i> 0.0737 <i>exp.</i>	5.02

The purified water characterized by 18.2 $\mu\text{S}/\text{cm}$ conductivity was obtained with a RO Millipore system (MilliQ® Direct 8 RO Water Purification System, Merck, Darmstadt, Germany).

2.1.2. Materials

Polymeric materials: polysulfone (PSf), transparent pellets, $M_w = 35.000$ g/mol, $\rho = 1.24$ g/cm³ (Aldrich, USA); Cellulose acetate (CA), powder, $M_w = 50.000$ g/mol, $\rho = 1.3$ g/cm³, (Sigma-Aldrich, USA).

Table 2. The characteristics of polymers for the obtained membranes.

Polymer	Chemical formula	Molar weight	Membrane Symbols
Cellulose acetate (CA)		50,000	CA-UDAc-NP CA-UDAl-NP CA-UDCl-NP
Polysulfone (PSf)		35,000	PSf-UDAc-NP PSf-UDAl-NP PSf-UDCl-NP

2.2. Methods

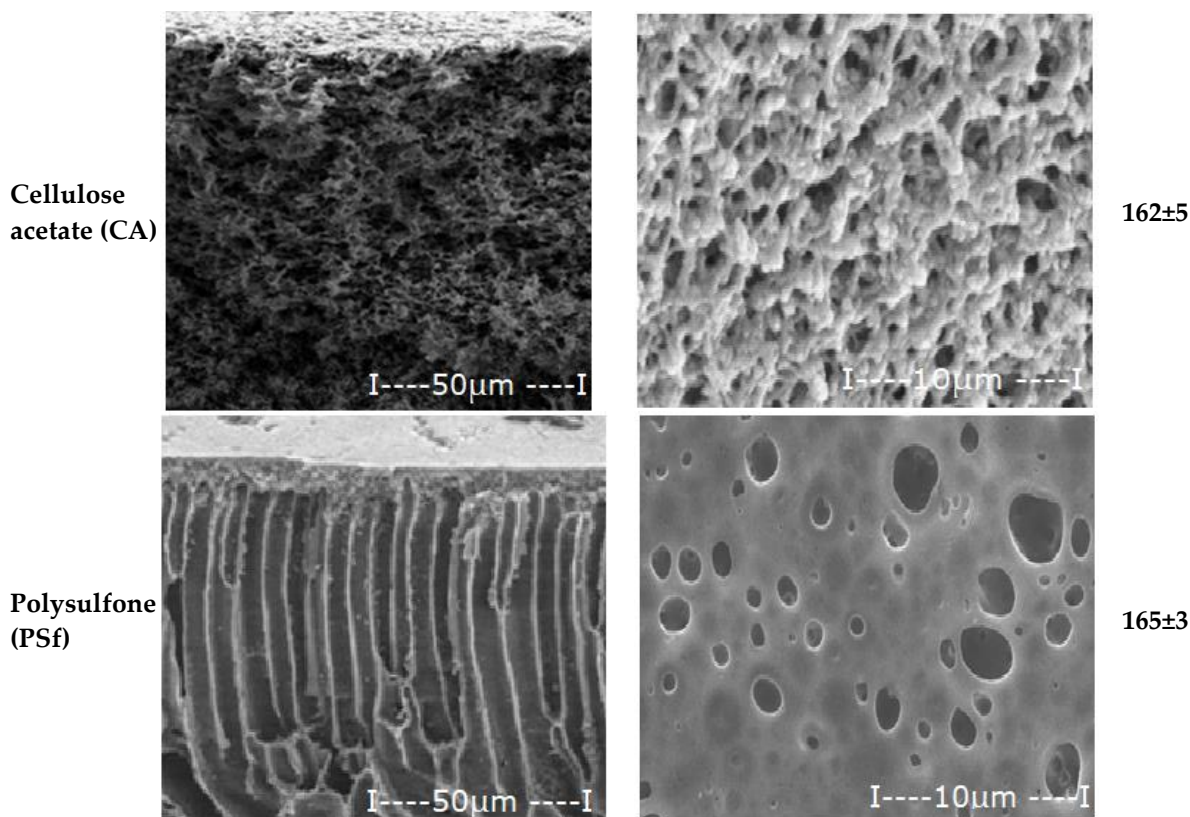
2.2.1. Obtaining and characterizing support membranes

The matrix polymeric membranes were prepared by inversion technique, from polymer solution films (10% weight) in dimethylformamide, coagulated in ethanol coagulation bath: water (1v / 1v), the phase inversion being previously presented in detail [31,32]. After abundant washing with deionized water and storage for 48 hours in pure water, the obtained membranes were dried in a vacuum of 100 mmHg for 72 hours. The dry membranes were cut to a size of 100 mm x 100 mm for impregnation with a dispersion of silver-containing oxide nanoparticles.

The general characteristics are presented in Table 3, being determined by scanning electron microscopy (SEM), in section and on the surface intended for contact with the expected working environment [33], by measuring the thickness with micrometer [34] and determining the porosity by gravimetric method [34,35].

Table 3. The characteristics of the membrane support.

Membrane	Scanning Electron Microscopy (SEM)		Thickness (µm)
	Cross-section	Bottom	



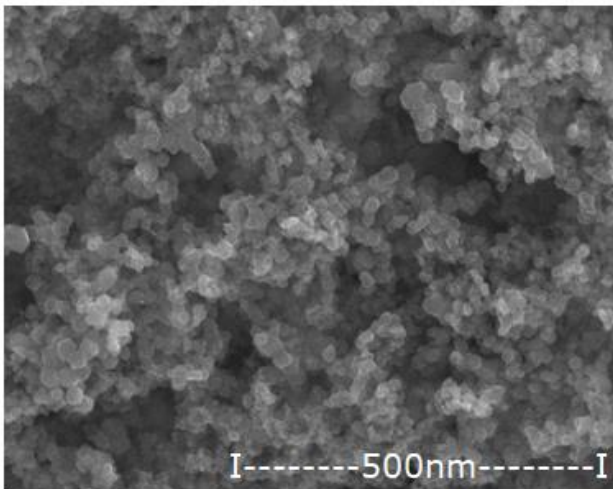
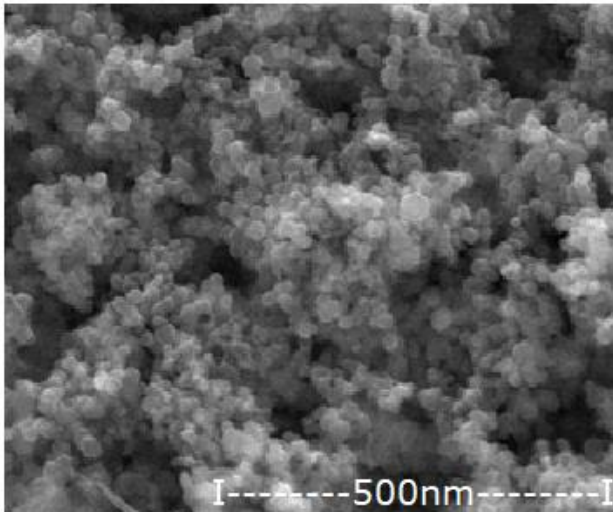
2.2.2. Obtaining and characterizing oxide nanoparticles containing silver

The iron-based magnetic nanoparticles were obtained by the electrochemical method, previously presented in detail [36,37]. In this case, the electrolysis with iron electrodes was performed in pure water (to obtain magnetic nanoparticles of iron oxides) and in a silver nitrate electrolyte of 10^{-3} – 10^{-1} mol/L. In the particular case of the present paper, the aim was to obtain oxide nanoparticles with a variable silver content.

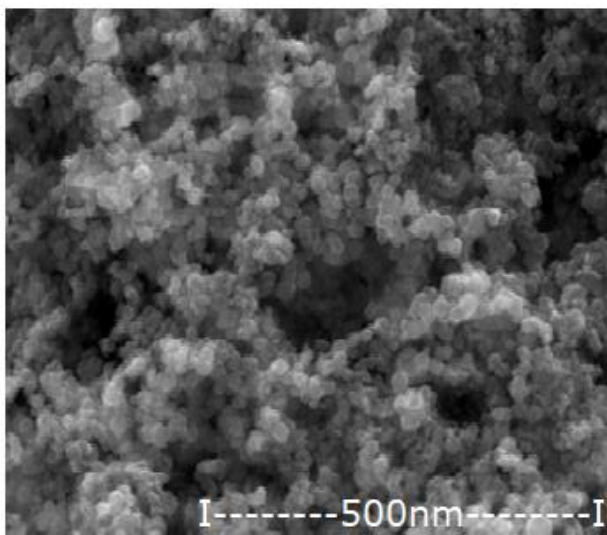
The nanoparticles obtained by the electrochemical method are dialyzed in a cylindrical Visking membrane (Medicell Membranes Ltd., London, UK) to neutral pH. After magnetic recovery and washing with ethanol, the nanoparticles were dried at

room temperature by standing in an oven with laminar air flow. The essential characteristics (morphology, average size and silver content) necessary for use in impregnating the considered membranes are presented in table 4.

Table 4. The characteristics of the silver-iron oxide nanoparticles.

Oxide nanoparticle (Ag-NP)	Scanning Electron Microscopy (SEM)	Medium diameter (nm)	Medium content (%)	Silver
NP0.55		42.8	0.55	
NP1.12		45.4	1.12	

NP1.63



47.1

1.63

2.2.3. Obtaining the impregnated membrane and the procedure for evaluating the release effect

The dry polymer membranes, having the size of 100 mm x 100 mm, were placed on a glass for chromatographic use, and under this was placed a ferrite with high magnetization (150 mm x 100 mm x 30 mm, power of 20 Kg) and were impregnated with a dispersion of iron oxide nanoparticles containing about 0.5–1.5% silver (NP) [36,37], in the desired organic solvent by dosing with a 3D printer programmed for a constant deposition rate (Figure 2).

Dispersions of oxide nanoparticles 5gNP/5g organic compound from Table 1, impregnated on cellulose acetate and polysulfone membranes lead to symbolized as in Table 2.

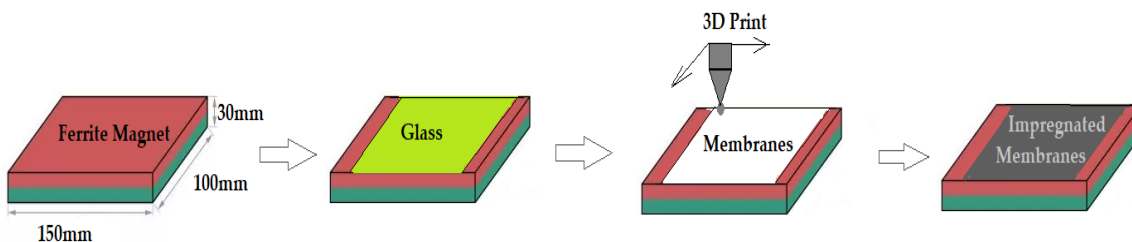


Figure 2. Schematic representation of the procedure for obtaining impregnated membranes.

The membranes were cut into 1 cm² disks, containing an average of 0.05 g nanoparticles and 0.05 g organic dispersion compound.

The impregnated membrane discs are placed in the lids of 2 cm³ glass bottles. 1.0 mL of controlled pH and ionic strength aqueous solution is introduced into the glass vials, the cap is sealed with an impregnated membrane and placed with the cap down in a cup in which 100 vials can be inserted simultaneously (Figure 3).

The cup of vials is positioned centrally on the ferrite also used to impregnate the membranes, to ensure that the nanoparticles are maintained in the support membrane throughout the study, regardless of the amount of dispersion solvent that would be extracted in the test solutions.

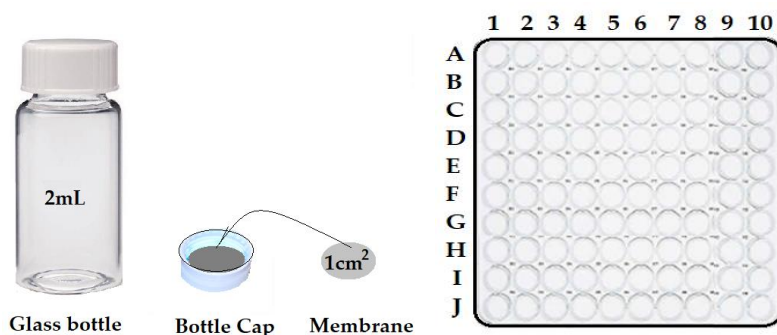


Figure 3. Schematic representation of the membrane arrangement the lid and the positioning of the sample vials for the controlled release of silver ions / 10-undecenoic acid.

Seven vials are retrieved daily for analysis so that the results of the silver analysis can be mediated, and three vials are stored as control samples. Analyses on an atomic absorption spectrometer, to determine silver, are performed independently by two researchers, and the devices used are calibrated daily with standard solution. The validation of the results is performed periodically by electrochemical and / or UV-Vis methods, at an independent laboratory.

UV-Vis spectrometric analysis to determine 10-undecenoic acid is performed daily and independently by two researchers, and periodic validation of the results is performed by gas chromatography at an independent laboratory.

2.3. Equipment

The surface characteristics of the membranes were determined with a scanning electron microscopy (SEM) equipped with a probe for energy dispersive spectroscopy analysis (EDX). Hitachi S4500 system (Hitachi High-Technologies Europe GmbH, Krefeld, Germany) was used [38,39].

The electrochemical processes for silver-iron nanoparticle obtaining were followed up with a PARSTAT 2273 Potentiostat (Princeton Applied Research, AMETEK Inc., Berwyn, PA, USA). A setup based on a glass cell with three electrodes has been used [36,37].

Determination and monitoring of pH 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].

To assess and validate the content in metal ions, an atomic absorption spectrometer AAnalyst 400 AA Spectrometer (Perkin Elmer Inc., Waltham, MA, USA) with WinLab32-AA software (Perkin Elmer Inc., Waltham, MA, USA), with a single-element hollow-cathode lamp was used. The operating current was set up at 2 mA, wavelength 248.3 nm, and 0.2 nm spectral bandwidth for determining the iron content. For silver, the experimental parameters were 328.1 nm wavelength and 0.7 nm spectral bandwidth at an operating current of 5 mA [37,40-42].

The UV-Vis spectra of the 10-undecenoic acid 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) [43].

Also, the UV–Vis validation analysis of the 10-undecenoic acid 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 [36,37].

All determinations were performed on the same day, for each scheduled experiment, by two experienced analysts from different laboratories, based on 7 specimens taken for each sample, and to ensure the quality of chemical measurements the specific EURACHEM guide was followed [44, 45].

3. Results and discussions

Delayed and / or controlled release of chemical species of pharmaceutical interest is a particular aspect of membrane use. If the system from which a compound is released through the membrane has a single target component, both the membrane transport experiments, and their modelling have been extensively and thoroughly studied [46-50]. For systems that simultaneously release two or more target chemical species, both experiments, but especially process modelling, become much more complex [51-53].

In the case studied in this paper, the aim was to release silver ions and 10-undecylenic acid from a membrane matrix based on cellulose acetate or polysulfone. The materials were chosen for the watering difference: the polysulfone being hydrophobic and the cellulose acetate being hydrophilic. Silver ions and 10-undecylenic acid are introduced into the membrane polymer matrix as a dispersion of iron and silver oxide nanoparticles in 10-undecenoic acid. The receiving solution of the two chemical species is aqueous in nature, with a predetermined pH and sodium chloride concentration (Figure 4).

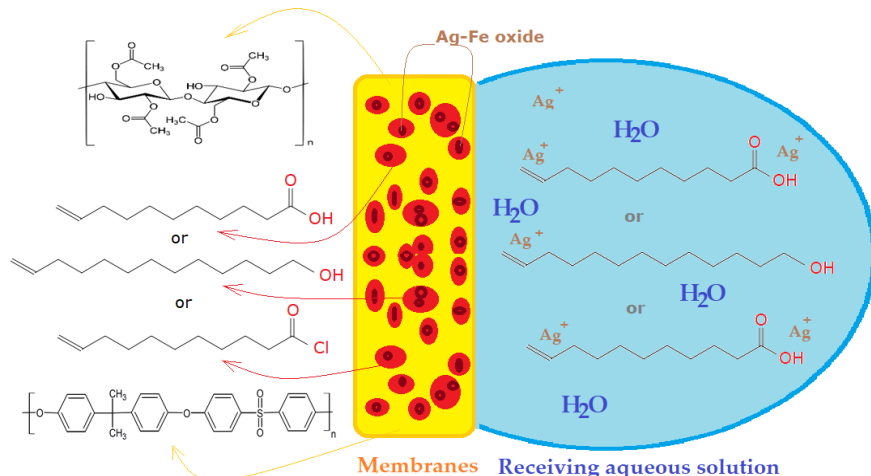


Figure 4. Schematic representation of the system of releasing silver ions and 10-undecenoic acid from the impregnated polymer membrane in an aqueous solution.

The experiments followed the effect of the nature of the organic compound and the membrane polymer matrix, the influence of pH and ionic strength of the receiving solution and the contribution of silver concentration in oxide nanoparticles to the concentration of target substances released in a considered aqueous system.

3.1. The influence of the organic compound and the polymeric matrix on the release of silver ions

The organic compounds: 10-undecen-1-ol (UDAl), 10-undecenoyl chloride (UDCl), and 10-undecylenic acid (UDAc) in which the dispersion of oxide nanoparticles containing 1.63 % silver is performed were chosen so as to highlight the effect of the functional groups of 10-undecenoic acid (alkene and carboxylic) on the release of silver ions in aqueous solutions can be highlighted.

The aqueous receiving solutions have the required pH values: 5.0; 6.8; 7.0; and 7.2, specific to determinations for systems in contact with biological environments [54,55].

The results obtained for the two types of membrane polymeric matrices (cellulose acetate and polysulfone) and the three organic compounds (Figures 5, 6 and 7) show the evolution of the release of silver ions in the considered aqueous systems. In all dispersant cases, the cellulose acetate membrane (Figures 5, 6 and 7) releases silver ions harder than the polysulfone membrane (Figures 5, 6 and 7).

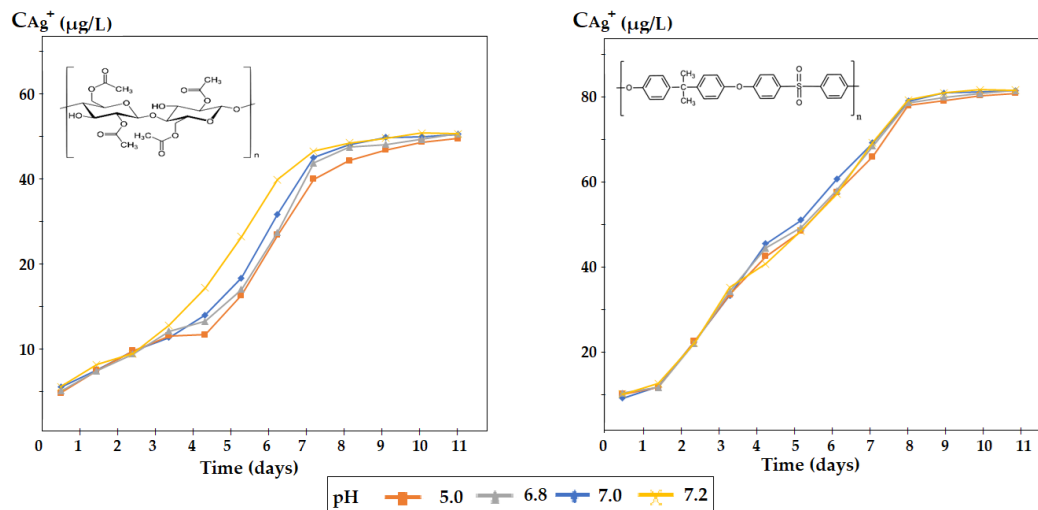


Figure 5. Concentration of silver ions released in the receiving aqueous phase of pH: 5.0; 6.8; 7.0; and 7.2 for cellulose acetate and polysulfone membrane in the case of 10-undecilenic acid as dispersant and oxide nanoparticles with 1.63% sil-ver.

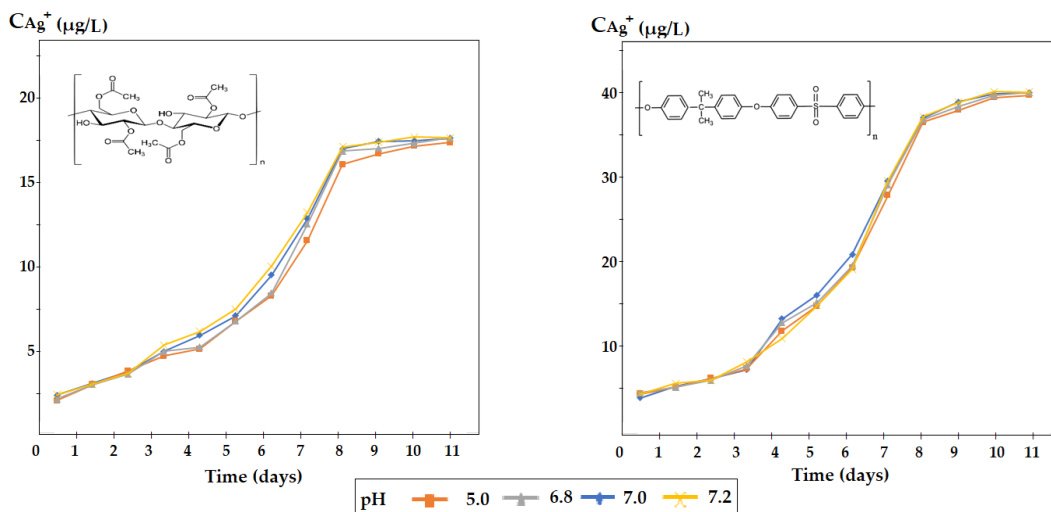


Figure 6. Concentration of silver ions released in the receiving aqueous phase of pH: 5.0; 6.8; 7.0; and 7.2 for cellulose acetate and polysulfone membrane in the case of 10-undecen-1-ol as dispersant and oxide nanoparticles with 1.63% sil-ver.

The lower release of silver ions in the case of cellulose acetate can be correlated with the more pronounced interaction of silver ions on the hydrophilic support matrix, which retains them both by ion-dipole interactions (silver-carbonyl or hydroxyl groups) and by hydrogen bonds between the hydroxyl and / or carbonyl groups and the hydration coating of the aqua-complex silver ion. For both matrices, the concentration of silver ions after the third day of exposure is sufficient to ensure both the biocidal (bactericidal) and the cytotoxic effect. For both matrices, the concentration of silver ions after the third day of exposure is sufficient to ensure both the biocidal (bactericidal) and the cytotoxic effect. Depending on the application pursued and the environment in which both polymer matrices will be used they may be useful, but in the present study the experiments will be continued only with the polysulfone matrix.

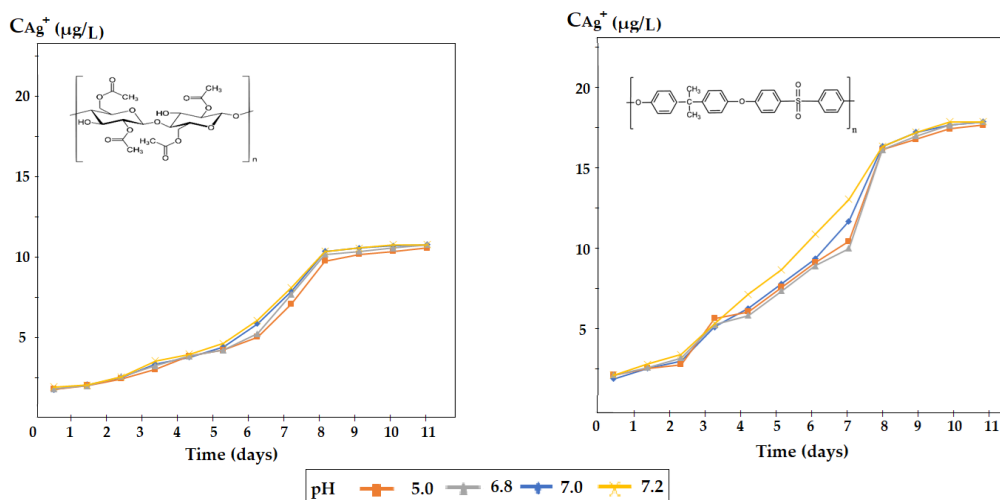


Figure 7. Concentration of silver ions released in the receiving aqueous phase of pH: 5.0; 6.8; 7.0; and 7.2 for cellulose acetate and polysulfone membrane in the case of 10-undecenoic chloride as dispersant and oxide nanoparticles with 1.63% silver.

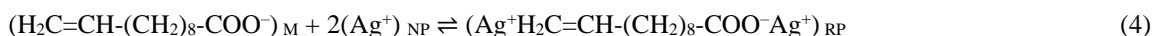
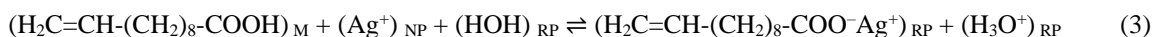
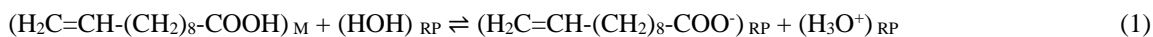
From the point of view of the 10-undecenoic acid dispersant, it allows the release of silver ions in the aqueous phase much more easily (Figures 5), compared to 10-undecen-1-ol (Figure 6) and of almost an order of magnitude more than 10-undecenoyl chloride (Figure 7), when comparing polysulfone (Figure 5) with cellulose acetate (Figure 7).

The results of the release of silver ions depending on the nature of the dispersant correlate with the solubility of the dispersants in water (Table 1), but also with the possibility of interaction of silver ions with these organic compounds. Their choice was made because they can interact with the silver ion through both the alkenic group and the carboxyl or hydroxyl groups. Basically, the sequence observed for the release of silver ions (see Figures 5, 6 and 7): 10-undecylenic acid (UDAc) > 10-undecen-1-ol (UDAl) >>> 10-undecenoyl chloride (UDCl), shows us that the first compound has a strong interaction center (carboxyl group) as well as a medium interaction center (alkenic group), the second has two medium interaction groups (hydroxyl and alkylene

groups), and the third a group of medium interaction (alkylene) and one low interaction (carbonyl). It is interesting that 10-undecenol chloride, being insoluble in water, does not favor the transfer of silver ions in the aqueous receiving solution.

Figures 5, 6 and 7 do not clearly show the effect of the pH of the receiving aqueous phase on the release of silver ions, most likely due to the rather narrow range of the chosen value. However, it can be seen that at pH = 5.0, the release of silver ions is slightly faster. The capping of the concentration in the receiving aqueous phase after the seventh working day indicates the achievement of a trans-membrane equilibrium that depends on both the type of polymeric matrix and the organic dispersing compound.

The simultaneous release of silver ions and 10-undecenoic acid from the impregnated membrane is a complex process characterized by several equilibria in which pH plays an important role (1–5):



M denoting the membranes, NP the oxide nanoparticles and RP the receiving phase.

Other interphase equilibria can certainly be considered, but those presented justify the obtained results and are illustrated in Figures 5, 6, 7 and 9. The defining factors are two centres of interaction of 10-undecenoic acid (4), but also the possibility of silver ions to be complexed in excess by chloride ions (6).

3.2. Influence of membrane support morphology and silver content of oxide nanoparticles on the release of silver ions in aqueous solution

For the polysulfone support membrane matrix, which provided the highest concentrations of released silver ions, the effect of macro-porous surface morphology (Figure 8) on the release process using the three types of oxide nanoparticles was studied, containing: 0.55%; 1.12%; and 1.63% silver, respectively (Figure 9).

The morphology of support membranes, which is obtained by controlling by adjusting the standing time of the film in the medium before coagulation [56,57] moderately influences the release in the aqueous test solution, during 2–5 days of monitoring. The concentration palier of silver ions is determined by their concentration in oxide nanoparticles in the 10–undecenoic acid dispersion. Thus, the higher the concentration of silver in the oxide nanoparticles, the higher the limit of the concentration of silver ions in the aqueous solution of $\text{pH} = 7$ (Figures 9a, 9b and 9c).

These observations are in agreement with the results obtained previously [28–30] and are correlated with the size and distribution of macroporous pores of the membrane surface on which the dispersion of silver-containing oxide nanoparticles is impregnated in the first days of contact (Figure 8). At a longer operating time a balance is achieved, between the concentration of ions in the impregnated membrane and that of the ions in the receiving aqueous system.

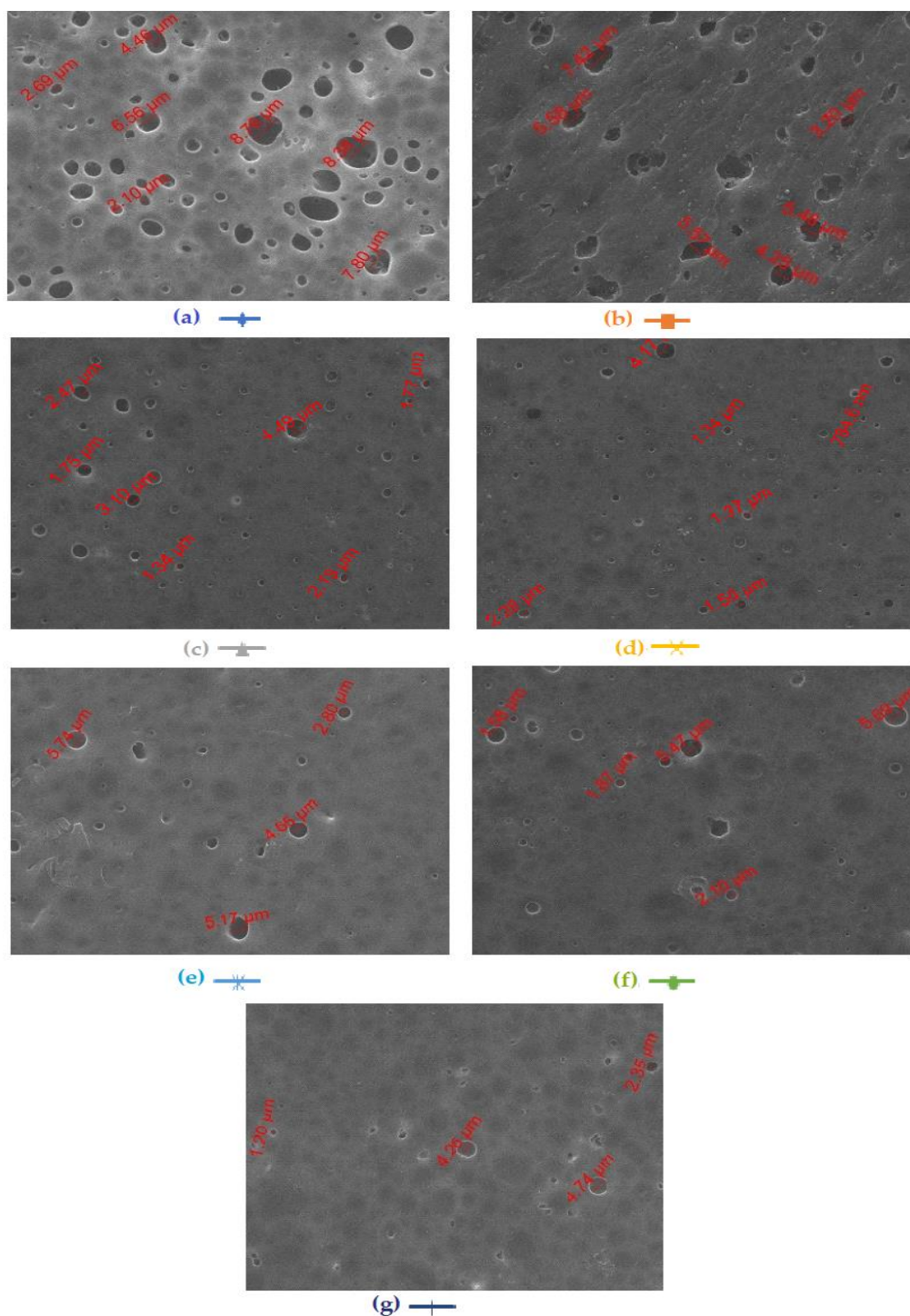


Figure 8. Morphology of polysulfone support membranes obtained by different exposure to the polymeric film before coagulation.

It is interesting that for the case study the ratio of the concentration of silver ions in the receiving solution and, respectively, in the concentration of silver in the oxide nanoparticles is relatively constant, suggesting a Donnan-type transmembrane equilibrium [58-60].

The data provided by these experiments allow the control of the limiting concentration of silver ions in a given aqueous solution, by adjusting the concentration of silver in the oxide nanoparticles.

For the practical use of these experimental observations, the following must be taken into account: the nature of the polymer from which the support membrane is made, the type of the organic compound in which the oxide nanoparticles are dispersed and the concentration of silver in these nanoparticles.

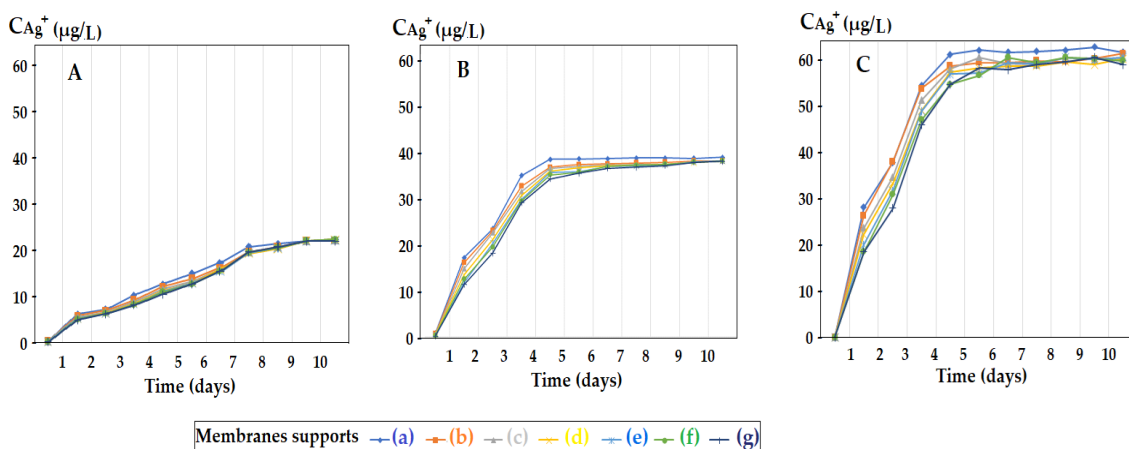


Figure 9. Concentration of silver ions released in the receiving aqueous phase of $\text{pH} = 7$, as a function of time, for seven morphologies of the polysulfone support and for oxide nanoparticles containing silver: (A) 0.55%; (B) 1.12%; and, (C) 1.63%, respectively.

3.3. The influence of the receiving phase pH of the silver ions and 10-undecenoic acid simultaneous release

For the polysulfone - 10–undecenoic acid - aqueous solution matrix system, the influence of extreme pH on the release of silver ions and of 10–undecenoic acid from a membrane impregnated with oxide nanoparticles containing 1.63 % silver and 10–undecenoic acid as dispersing agent, was followed (Figure 10).

These pH values: 1; 3; 11 and 13 are allowed by the resistant polysulfone membrane support, over the entire pH range [61,62].

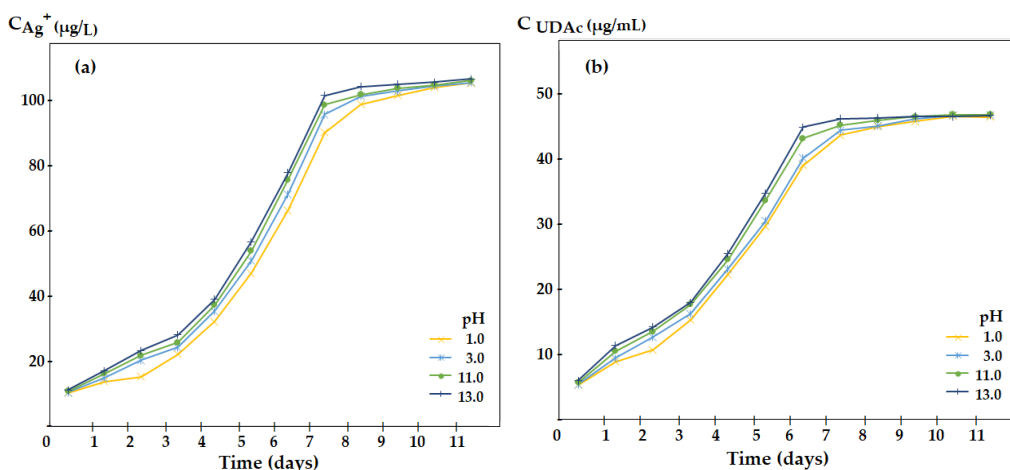
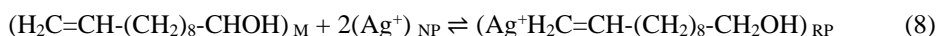
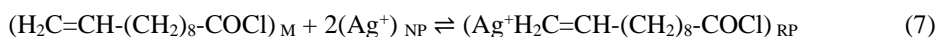


Figure 10. Concentration of silver ions (a); and of 10–undecenoic acid (b); released in the receiving aqueous phase of variable pH, depending on the type of contact.

The test of the polysulfone – 10–undecenoic acid – oxide nanoparticles system containing 1.63 % silver for the simultaneous controlled release of silver ions and 10–undecenoic acid, shows that at extreme pH values, the concentration of silver ions covering the bactericidal and cytotoxic requirements is obtained quickly, and the concentration level after 7 days of contact is slightly higher than at a pH close to neutral pH (Figures 5 and 10a). At the studied pH values, the release of 10–undecenoic acid follows the shape of the curves for silver ions, but its concentration is lower (Figure 10b). However, the 10–undecenoic concentration slowly exceeds the limit of its solubility in pure water, thus contributing to the fungicidal effect of the studied system [63].

Thus, it can be understood why the compounds derived from 10-undecenoic acid allow the release in smaller quantities of silver ions, equilibria (7) and (8). They have a single center of interaction composed of organic-silver ions compared to 10-undecenoic acid, which may have two centers of equilibrium (3) and (4).



3.3. The influence of the ionic strength of the silver ions and 10-undecenoic acid simultaneous release

Equilibria (5), but especially (6) have required the study of the influence of sodium chloride concentration of the receiving aqueous phase. The use of sodium chloride is justified both by the fact that no additional anions are introduced compared to the study in the previous section, and by the similarity with the biological environment in which this impregnated membrane could come into contact. For a matrix system of polysulfone – 10-undecenoic – aqueous solution the influence of electrolyte concentration (NaCl) on the release of silver ions and 10-undecenoic acid from the membrane impregnated with oxide nanoparticles containing 1.63 % silver in the dispersing agent was followed (Figure 11). In order not to alter the results of the study, the chloride ion that could come from the receiving solution acidified with hydrochloric acid, the experiments are performed with a receiving phase of concentrations 0.5; 1.0 and 1.5 % (gravimetric) sodium chloride in pure water. The concentration of both 10-undecenoic acid (Figure 11a) and the silver ions released were monitored (Figure 11b).

The presence of sodium chloride in the receiving aqueous phase negatively influences the release of 10-undecenoic acid (Figure 11a), the limiting concentration at 10 days (approx. 20 $\mu\text{g}/\text{mL}$) being much lower than that obtained in non-saline solution for the same tracking period (approx. 45 $\mu\text{g}/\text{mL}$). This observation is in agreement with previous data, which showed that the loss of 10-undecylenic acid in a membrane can be reduced by using electrolyte additives (NaCl or NaNO_3) [28-30].

On the other hand, the effect of sodium chloride is favorable for the release of silver ions in the receiving aqueous phase (Figure 11b), the concentration limit at more than 10 days of contact between the impregnated membrane and the aqueous saline solution exceeding $120 \mu\text{g/L}$. What is noteworthy in this case is the much faster release of silver ions in solution (Figure 11b) compared to Figures 5, 6, 7 and 10a. Consequently, the equilibrium (6), forming the complex $[\text{AgCl}_2]^-$, is completely shifted to the left due to excess of chloride ions.

The two opposite aspects of the release of silver ions and 10-undecenoic acid from the membrane impregnated with oxide nanoparticles containing silver in the dispersing agent must be considered for use in saline biological media, as the bactericidal effect improves, and the fungicidal effect decreases. For example, when using the system for high-performance athletes, who exert salts in perspiration, the fungicidal effect of 10-undecenoic acid is diminished.

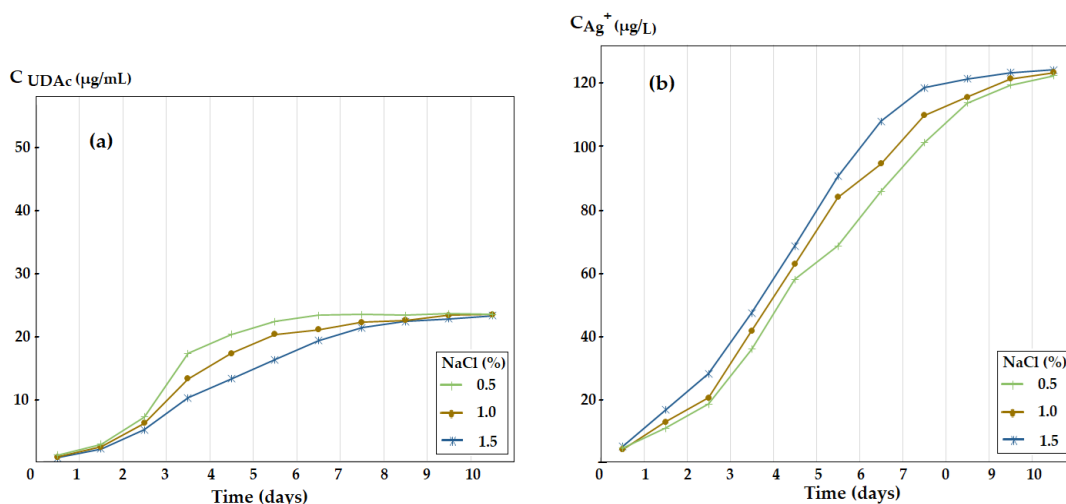


Figure 11. Concentration of 10-undecenoic acid (a); and of silver ions (b); released in the receiving aqueous phase, of variable ionic strength (NaCl), depending on the type of contact.

The application of the system based on controlled release of silver ions and 10-undecenoic acid from membranes impregnated with oxide nanoparticles containing silver in the dispersing agent requires extensive studies on release in real biological mediums: blood, saliva, perspiration or urine.

For instance, in order to answer to the necessities of sport medicine, the tests with various biological fluids must include other polymeric matrices or dispersion media than those addressed in the present paper.

4. Conclusions

This chapter presents the studies the effect of the polymer matrix on the simultaneous release of silver ions and 10-undecenoic acid in an aqueous medium of controlled pH and ionic strength.

Polymeric matrices consisting of: cellulose acetate (CA) and polysulfone (PSf), which have been impregnated with oxide magnetic nanoparticles containing silver ions and 10-undecenoic acid. The polymeric matrices are prepared as microporous membranes by the phase inversion method, and the oxide nanoparticles are obtained by electrolysis of silver nitrate solutions with iron electrodes.

Impregnated membranes are made by printing the dispersion of oxide magnetic nanoparticles containing 0.63; 1.12 and 1.63% (mass) silver, in organic compounds: 10-undecen-1-ol (UDAl), 10-undecenoyl chloride (UDCl), and 10-undecenoic acid (UDAc).

The study of the release of silver ions in aqueous solutions of imposed pH and sodium chloride concentration, carried out over a maximum 11 days, shows that after the first day the silver ions reach the concentration that ensures the bactericidal and/or cytotoxic effect, and after 5–7 days the concentration is capped at values that are determined by the matrix type and morphology, the silver concentration of the nanoparticles and the nature of the organic compound. Higher silver concentration limit values are obtained for the polysulfone matrix, 10-undecenoic acid dispersant, neutral or basic pH or higher sodium chloride concentration.

For the polysulfone – 10–undecenoic acid – aqueous solution matrix, were monitored the influence of the electrolyte concentration (NaCl) on the simultaneous release of silver ions and 10-undecenoic acid from the membrane impregnated with oxide nanoparticles containing 1.63 % silver in the dispersing agent.

The presence of sodium chloride in the aqueous receiving phase negatively influences the release of 10–undecenoic acid, but on the other hand, the effect of sodium chloride is favorable for the release of silver ions in the receiving aqueous phase. The two antagonistic aspects of the release of silver ions and 10–undecenoic acid from the membrane impregnated with oxide nanoparticles containing silver in the dispersing agent must be considered for use in saline biological media, as the bactericidal effect improves, and the fungicidal effect decrease.

The application of the controlled release system of silver ions and 10-undecenoic acid from polymeric membranes impregnated with silver-containing oxide nanoparticles in the dispersing agent requires extensive studies on the release in real biological environments: blood, saliva, perspiration, or urine.

Part C

General Conclusions and Perspective Research

C.1. General Conclusions

The development of the doctoral thesis "**Retard systems with synthetic membranes**" 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. pH and Design on *n*-alkyl Alcohols Bulk Liquid Membranes for Improving Phenol Derivatives Transport and Separation

Starting from the obtained results for the separation and transport of the chemical species in a permeation module with dispersion of aqueous phases, in the form of droplets, in this paper we studied the effect of interposing spheres in free rotation between the droplets and the membrane phase. These spheres determine the contact of aqueous phases in the form of a film with the membrane phase of the organic solvent. The study was performed in a membrane system in which the variable pH source phase consists of phenolic derivatives of technical-economic and environmental interest ((PD), 4-nitrophenol (NP), 2,4-dichlorophenol (DCP) and 2,4-dinitrophenol (DNP)), membrane of *n*-alkyl alcohols (*n*-octanol and *n*-decanol) and the receiving phase of high pH aqueous solution.

The transport of 4-nitrophenol is determined both by the difference in pH between the aqueous phases, the nature of the membrane solvent and the nature of the spherical material. Thus, the transport in which the module has glass spheres (GI) is superior to

that using copper spheres (Cu), but especially those made of steel (St). In all the studied cases the module with spheres (Ms) has superior transport results to the module with drops (Md).

The extraction efficiency (EE) and the transport of 2,4-dichlorophenol (DCP) and 2,4-dinitrophenol (DNP), studied in the module with glass spheres, show that the two phenolic derivatives can be separated by adjusting the pH of the source phase. At a source phase with strong acid character (pH = 2) the two derivatives are extracted with good results (EE > 90%), while at pH in the range [4, 6] they can be separated, DCP having doubled separation efficiency compared to DNP. At a pH = 8 of the source phase, the extraction efficiency halves for both phenolic compounds.

The influence of the material of the spheres in the extraction module suggests possibilities to control the performance of the membrane process by chemically modifying the surface of the spheres, especially those made of glass.

Conclusion of the **Chapter 2.2. Operational limits of the bulk hybrid liquid membranes based on dispersion systems**

This chapter presents the operational limits of a type of hybrid membrane constituted as a bulk liquid membrane (BLM), but which works by dispersing the aqueous source phase (SP) and receiving phase (RP), the membrane itself being a dispersion of nanoparticles in an organic solvent (NP-OSM).

The main features and recommendations in operating the proposed experimental hybrid membrane system are: source phase volume of 5000–15000 mL, receiving phase volume of 500 mL, membrane solvent volume of 300–500 mL, volume ratio between the source and receiving phase of 10–20:1, volume ratio between receiving phase and membrane of 1–5:1, membrane thickness of 30–40 mm, aqueous phase flow through a single droplet mouth of 20 mL/min, aqueous droplets diameter of 4–5 mm, *n*-octanol or *n*-decanol as membrane solvent, magnetic nanoparticles (diameter of 40

nm \pm 10 nm), ionic or molecular chemical species (silver ions and *p*-nitrophenol), stirring speed of the magnetic rods of 100 rot/min and the operating temperature in the range 15–35 °C.

Under the exposed conditions, separation efficiencies of over 90% are obtained, for both ionic and molecular chemical species (silver ions and *p*-nitrophenol).

The liquid membrane system with dispersed phases, presented in this paper, has superior results compared to the classical mechanically agitated liquid membrane systems (both the mass transfer surface and the convective transport increase). However, the proposed system does not cover the enormous mass transfer surfaces provided by emulsion membranes, but neither does it require specific methods of breaking the emulsions.

Conclusion of the **Chapter 2.3. Osmium Recovery as Membrane Nanomaterials through 10-Undecenoic Acid Reduction Method**

The chapter 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 on osmium recovery as membrane manomaterials 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 **2.4. Simultaneously release of silver ions and 10–undecenoic acid from silver-iron oxide nanoparticles impregnated membranes**

This paper studies the effect of the polymer matrix on the simultaneous release of silver ions and 10-undecenoic acid in an aqueous medium of controlled pH and ionic strength.

Polymeric matrices consisting of: cellulose acetate (CA) and polysulfone (PSf), which have been impregnated with oxide magnetic nanoparticles containing silver ions and 10-undecenoic acid. The polymeric matrices are prepared as microporous membranes by the phase inversion method, and the oxide nanoparticles are obtained by electrolysis of silver nitrate solutions with iron electrodes.

Impregnated membranes are made by printing the dispersion of oxide magnetic nanoparticles containing 0.63; 1.12 and 1.63% (mass) silver, in organic compounds: 10-undecen-1-ol (UDAl), 10-undecenoyl chloride (UDCl), and 10-undecenoic acid (UDAc).

The study of the release of silver ions in aqueous solutions of imposed pH and sodium chloride concentration, carried out over a maximum 11 days, shows that after the first day the silver ions reach the concentration that ensures the bactericidal and/or cytotoxic effect, and after 5–7 days the concentration is capped at values that are determined by the matrix type and morphology, the silver concentration of the nanoparticles and the nature of the organic compound. Higher silver concentration limit values are obtained for the polysulfone matrix, 10-undecenoic acid dispersant, neutral or basic pH or higher sodium chloride concentration.

For the polysulfone – 10-undecenoic acid – aqueous solution matrix, were monitored the influence of the electrolyte concentration (NaCl) on the simultaneous release of silver ions and 10-undecenoic acid from the membrane impregnated with oxide nanoparticles containing 1.63 % silver in the dispersing agent.

The presence of sodium chloride in the aqueous receiving phase negatively influences the release of 10-undecenoic acid, but on the other hand, the effect of sodium chloride is favorable for the release of silver ions in the receiving aqueous phase. The two antagonistic aspects of the release of silver ions and 10-undecenoic acid from the

membrane impregnated with oxide nanoparticles containing silver in the dispersing agent must be considered for use in saline biological media, as the bactericidal effect improves, and the fungicidal effect decrease.

The application of the controlled release system of silver ions and 10-undecenoic acid from polymeric membranes impregnated with silver-containing oxide nanoparticles in the dispersing agent requires extensive studies on the release in real biological environments: blood, saliva, perspiration, or urine.

C2. Originality of research

Recommended advantages, limits, and parameters for the proposed hybrid membrane system

The hybrid membrane system, proposed at this stage for laboratory experiments, combines the advantages of bulk liquid membranes (BLM) with those of emulsion membranes (ELM):

- ✓ Wide possibilities for varying the physical-chemical parameters of both the membrane and the aqueous phases.
- ✓ Large interphase transfer surface, ensuring convection both by means of source/receiving phase droplets passing through the membrane and of magnetic nanoparticles engaged by a rotating magnetic field (which can be achieved by electromagnetic means without moving elements).
- ✓ Easily adjustable recirculation rates of the aqueous phases.
- ✓ Easily adjusted thickness of the membrane.
- ✓ The volume of the source and receiving phase can be varied and their ratio can be increased.
- ✓ Does not require surfactants to stabilize the drops.
- ✓ Does not require the breaking of an emulsion (the droplet size, imposed by the flow of the aqueous phases, is relatively large).
- ✓ Membrane solvents are biodegradable.

- ✓ The magnetic nanoparticles in the membrane phase can promote turbulence, but also act as carriers.
- ✓ The proposed hybrid system can be physically made with accessible means: the body of the permeation module made of glass or polyethylene (a cylindrical vessel and a frustum funnel), four-way peristaltic pump with adjustable flow, flexible silicone rubber tubes (medical type, tourniquet).

On the other hand, some operating limitations or disadvantages must be emphasized:

- ✓ The membrane solvents are lost (at the solubility limit) in aqueous phases,
- ✓ Special attention is needed to adjust the pH of aqueous phases (strong basic pH favors the appearance of emulsification and/or the increase in membrane solvent losses),
- ✓ The working temperature cannot be increased (because both the volatility and solubility of the membrane solvent will also increase),
- ✓ The flow at a single drip hole is limited and must be determined so that the drops are relatively large,
- ✓ The flow rate increases only by multiplying the drip holes,
- ✓ The volume of the membrane phase is still large and the solvent losses in the aqueous phases are significant,
- ✓ The membrane solvents must be biodegradable.

The transport of 4-nitrophenol is determined both by the difference in pH between the aqueous phases, the nature of the membrane solvent and the nature of the

spherical material. Thus, the transport in which the module has glass spheres (Gl) is superior to that using copper spheres (Cu), but especially those made of steel (St). In all the studied cases the module with spheres (Ms) has superior transport results to the module with drops (Md).

Four types of osmium nanoparticles-alcohol-polypropylene hollow fiber membranes (Os-PPM) were prepared: Os-PPMi from OsO₄-*i*-propanol-10-undecenoic acid, Os-PPMt from OsO₄-*t*-butanol-10-undecenoic acid, Os-PPMn from OsO₄-*n*-decanol-10-undecenoic acid and Os-PPMp from OsO₄-pure 10-undecenoic acid, which by testing in the catalytic reduction reaction with sodium tetraborate solution of *p*-nitrophenol to *p*-aminophenol led to constant catalytic rates between 2.04×10^{-4} mmol s⁻¹ and 8.05×10^{-4} mmol s⁻¹.

The application of the controlled release system of silver ions and 10-undecenoic acid from polymeric membranes impregnated with silver-containing oxide nanoparticles in the dispersing agent requires extensive studies on the release in real biological environments: blood, saliva, perspiration, or urine.

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The hybrid membrane system, proposed at this stage for laboratory experiments, combines the advantages of bulk liquid membranes (BLM) with those of emulsion membranes (ELM):

- ✓ Wide possibilities for varying the physical-chemical parameters of both the membrane and the aqueous phases.
- ✓ Large interphase transfer surface, ensuring convection both by means of source/receiving phase droplets passing through the membrane and of magnetic nanoparticles engaged by a rotating magnetic field (which can be achieved by electromagnetic means without moving elements).

- ✓ Easily adjustable recirculation rates of the aqueous phases.
- ✓ Easily adjusted thickness of the membrane.
- ✓ The volume of the source and receiving phase can be varied and their ratio can be increased.
- ✓ Does not require surfactants to stabilize the drops.
- ✓ Does not require the breaking of an emulsion (the droplet size, imposed by the flow of the aqueous phases, is relatively large).
- ✓ Membrane solvents are biodegradable.
- ✓ The magnetic nanoparticles in the membrane phase can promote turbulence, but also carriers.
- ✓ The proposed hybrid system can be physically made with accessible means: the body of the permeation module made of glass or polyethylene (a cylindrical vessel and a frustum funnel), four-way peristaltic pump with adjustable flow, flexible silicone rubber tubes (medical type, tourniquet).

On the other hand, some operating limitations or disadvantages must be emphasized:

- ✓ The membrane solvents are lost (at the solubility limit) in aqueous phases,
- ✓ Special attention is needed to adjust the pH of aqueous phases (strong basic pH favors the appearance of emulsification and/or the increase in membrane solvent losses),
- ✓ The working temperature cannot be increased (because both the volatility and solubility of the membrane solvent will also increase),
- ✓ The flow at a single drip hole is limited and must be determined so that the drops are relatively large,

- ✓ The flow rate increases only by multiplying the drip holes,
- ✓ The volume of the membrane phase is still large and the solvent losses in the aqueous phases are significant,
- ✓ The membrane solvents must be biodegradable.

The transport of 4-nitrophenol is determined both by the difference in pH between the aqueous phases, the nature of the membrane solvent and the nature of the spherical material. Thus, the transport in which the module has glass spheres (Gl) is superior to that using copper spheres (Cu), but especially those made of steel (St). In all the studied cases the module with spheres (Ms) has superior transport results to the module with drops (Md).

Four types of osmium nanoparticles-alcohol-polypropylene hollow fiber membranes (Os-PPM) were prepared: Os-PPMi from OsO₄-*i*-propanol-10-undecenoic acid, Os-PPMt from OsO₄-*t*-butanol-10-undecenoic acid, Os-PPMn from OsO₄-*n*-decanol-10-undecenoic acid and Os-PPMp from OsO₄-pure 10-undecenoic acid, which by testing in the catalytic reduction reaction with sodium tetraborate solution of *p*-nitrophenol to *p*-aminophenol led to constant catalytic rates between 2.04×10^{-4} mmol s⁻¹ and 8.05×10^{-4} mmol s⁻¹.

The application of the controlled release system of silver ions and 10-undecenoic acid from polymeric membranes impregnated with silver-containing oxide nanoparticles in the dispersing agent requires extensive studies on the release in real biological environments: blood, saliva, perspiration, or urine.

C3. Research development perspectives

The research carried out within the doctoral research program " **Retard systems with synthetic membranes**" 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 in retard systems with biological and medical applications.

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