Ministery of National Education

Polytechnic University of Bucharest

FACULTY OF CHEMICAL ENGINEERING AND BIOTECHNOLOGIES

Doctoral School of chemical Engineering and Biotechnologies

Abstract

Doctoral Thesis

Eco-friendly technologies with composite and liquid membranes

PhD student:

Ch. eng. Anca – Maria CIMBRU (ANDREI)

Scientific leader:

Prof. dr. eng. Gheorghe NECHIFOR

București 2022

CONTENT

1 Thanks

The entire doctoral research effort would not have been possible without the support of many collaborators, colleagues, family, and friends. Now I have the opportunity and the time to thank them for their moral and material support all this time.

First of all, I would like to give special thanks to my scientific coordinator, ***Professor Dr. eng. Gheorghe NECHIFOR***, who constantly offered me guidance, support, and encouragement throughout the preparation of the doctoral thesis and especially in the drafting of the thesis. Thanks for the trust, professionalism, quality of scientific information provided and especially for the patience and understanding it has shown during this period.

I would particularly like to thank ***Professor Dr. eng. Aurelia Cristina NECHIFOR***, who was my guide and mentor, a companion in the twelve years spent at the Polytechnic University of Bucharest.

My sincere thanks to the members of the guidance committee within the membrane and membrane processes department, for the valuable time, invaluable scientific advice and for the competent and constant supervision for the development and completion of this doctoral thesis.

At the same time, I would like to thank all the wonderful people who have given me the courage to believe that I will succeed, and all those who directly or indirectly helped, encouraged, and inspired me to carry out this work.

Last but not least, I would like to thank ***Professor Florica Chiar*** for all her love, the patience and understanding he showed in presenting the secrets of chemistry from the high school years spent at the “Alexandru Ioan Cuza” national College in Alexandria and for the unconditional guidance offered in the numerous competitions and chemistry Olympiads we participated in together.

With special gratitude and love, I dedicate this work to my parents who accompanied me with love and patience during this time and supported me in every way.

2 Introduction

The research topic addressed, within the doctoral thesis, “ecological technologies with composite and liquid membranes”, is of particular importance, justified by the priority scientific directions in which they fall:

- √ membrane materials and membrane processes.
- √ ecological and greening technologies.
- √ applications of colloidal chemistry and molecular compounds.
- √ chemical engineering in environmental protection.

The present chapter illustrates the possibility of achieving iono-molecular separations using colloidal ultrafiltration with polysulphone membranes of synthetic solutions of nitrophenolics and cupric ions by means of polysulphone-based composite polymer nanoparticle-assisted ultrafiltration.

Based on the excellent results of solid (polymeric) phase extraction, this chapter combines nitrophenol adsorption (O, m, and p-nitrophenol) on polymer nanoparticles (NP-PSf) and composites (NP-PSf-PANI) with colloidal ultrafiltration. In this chapter, we studied the pre-vaporization of mono-nitrophenols in a laboratory installation of the membrane, materials, and membrane processes Group of the Polytechnic University of Bucharest, from synthetic aqueous solutions to composite membranes with polysulphone matrix (PSF) and nanometre inclusions respectively, polyaniline (PANI), carbon nanotubes (CNT), Magnetic nanoparticles (MNP) and sulphonated polyetherketones (PEEKS).

The importance of removing and/or separating nitro-phenols from aqueous solutions through membranes is supported by the multitude of recent research in the field, which largely justifies both the economic and environmental reasons for such an approach.

The separation and removal of nitrophenolics from aqueous effluents is primarily an environmental protection issue, but at the same time can be an important technological and technical-economic application.

The objectives of the doctoral thesis were subordinated to the need to improve the methods of removal of nitro-phenols by promoting membrane techniques and methods of separation and concentration:

√ Removal and recovery separation of nitrophenolics is a permanent goal of membrane scientists.

√ The separation or removal of nitrophenolics from dilute aqueous solutions has been a permanent objective for the protection of the environment due to toxicity, but also for the concentration and revalorisation of these compounds of high technological interest for medicinal products, dyes, explosives, pesticides, and phenolic resins.

√ The nitrophenolic removal experiments aimed at establishing optimal conditions of the composite membrane separation process (PSf-PANI), taking into account the influence of polymer nanoparticles (NP-PSf-PANI) and the coupling of the process with proton transfer reactions capable of providing induced separation.

√ Development of ecological technologies with composite membranes.

√ Iono-molecular separations with composite membranes. Preparation and characterization of polysulphone and composite nanoparticles.

√ Neutralization with simultaneous separation of aluminum and copper ions from condensed water by polypropylene capillaries and cellulose derivatives. Environmental problems arising from acid waters containing aluminum and copper in condensing boilers can be adequately addressed using membrane processes.

√ Membranes based on polysulphone.

The doctoral thesis consists of two parts: The theoretical part and the experimental part, divided in turn into five chapters:

√ **Chapter 1** – membranes and membrane processes

√ **Chapter 2** - technological processes using liquid membranes

√ **Chapter 3** – Iono-molecular separations with Composite membranes

The present paper concludes with “**General conclusions. Personal contributions. Development perspectives**” where the main conclusions, their own contributions to new technologies and their development possibilities are addressed, presented, and supported. All these experimental results, research, analysis, and conclusions were published and presented in the specialized journals and conferences in the field.

The research topic addressed and studied included several milestones, namely:

1. Preparation and characterization of polysulphone and composite nanoparticles.

2. Separation of nitrophenolics by ultrafiltration with polysulphone and composite nanoparticles.

3. Nitrophenolic pervaporation by polysulphone composite membranes.

4. Separation of nitro-phenols with n-alkyl alcohols on liquid membrane support.

5. Separation of nitrophenolics by sulfated polyether ketone membranes on capillary polypropylene.

6. Neutralization with simultaneous separation of aluminum and copper ions from water condensed by capillary polypropylene and cellulose derivatives.

7. Pharmaceutical industry – wastewater treatment by electrocoagulation and micellar ultrafiltration.

8. Operational parameters pH and PCL in the separation of some metal ions with composite membranes of chitosan/sulphone (polyether ketone)/polypropylene from empty fibers.

3.8. pH and pCl Operational Parameters in Some Metallic Ions Separation with Composite Chitosan/Sulfonated Polyether Ether Ketone/Polypropylene Hollow Fibers Membranes

The development of new composite membranes is required by the need to separate chemical species from aggressive environments without using correction reagents. One such case is strongly hydrochloric mixtures (pH and PCL) containing metallic ions in the mixture.

One such case is that of copper, cadmium, zinc, and lead ions in the Cu-Zn and CD-Pb or quaternary binary mixture. This chapter presents the production of a chitosan (Chi) composite membrane - poly sulfonate (ether ketone) (sPEEK) - polypropylene tubular fiber (Chi/sPEEK/PPHF) and its use in the separation of binary or quaternary mixtures of copper, cadmium, zinc, and lead ions by nanofiltration and pertraction.

The obtained membranes were morphologically and structurally characterized: Scanning electron microscopy (SEM), high resolution SEM (HR-SEM), energy dispersion spectroscopy analysis (EDAX), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis, differential scanning calorimetry (TGA), but also in preliminary separation tests.

Using ion solutions in 3 mol/L hydrochloric acid, the separation of copper and zinc ions or cadmium and lead from binary mixtures was achieved. The results were superior to those obtained by nanofiltration both in terms of extraction efficiency and because the separated cation was simultaneously concentrated with an order of magnitude.

The mixture of the four cations was separated by nanofiltration (at 5 bar and with a $1m^2$ membrane) by varying two operational parameters: PH and PCL.

Cation retention can reach 95% by choosing the appropriate operational parameter values. In this chapter some recommendations are made for the use of chitosan (Chi) composite membranes - poly sulfonate (ether ketone) (sPEEK) - polypropylene tubular fiber (Chi/sPEEK/PPHF) so as to achieve the maximum possible retention of the target cation.

Metals with atomic number Z, higher than iron (Z=26) are known as "heavy metals" and their technical and economic importance was so high that their per capita consumption was an indicator of quality of life during the period of intensive industrial development [304].Of these metals, copper, cadmium, zinc, and lead have outstanding technical applications in electronics and electrotechnics, construction, transportation, automotive, dye and pesticide industries, agriculture, and telecommunications [305-307].

The map of the distribution of these metals around the globe has changed so much that areas with natural reserves hold less of these elements than the developed regions where they were brought for use [308].

The concentration of chemical species derived from these metals has dissipated globally, so that in the environment they appear as polluting elements in water, soil and even air [309-311]. It is not surprising that the various wastes containing copper, cadmium, zinc, and lead constitute an important resource of raw materials, and the recycled amount of these metals has become a symbol and indicator of environmental protection [312].

The rich natural deposits were exploited through highly developed technological techniques specific to metallurgy, but also chemistry, electrochemistry, and hydrometallurgy (flotation, precipitation-sedimentation, extraction, ionic exchange, electrolysis) [313-316].

Unfortunately, the recycling of industrial waste containing the metals considered is not completely solved both because of the complexity of the various sources and the different and very low concentrations [317].

The removal of heavy metal ions from various wastewater, up to the limits accepted by international standards [318] uses conventional techniques, but also the use of bio-adsorption [319], adsorption on various nanomaterials [320], iono-molecular flotation [321], magnetic separation [323] and various membranes and membrane processes [324].

Given the low concentration of metals considered in various waste and wastewater, their removal is often sufficient, but their greatest challenge is their recovery separation [325].

The requirements for regenerative separation technologies are both process (selectivity and productivity) and technical-economic and environmental (reduction of material consumption and operating costs) [326].

Membrane technologies respond well to process requirements but are still in the research-developed stage to ensure competitive costs [327].

Of the many membrane materials used in the study of the separation and recovery of heavy metals such as copper, cadmium, zinc and lead recent attention focuses on various nanoparticles [328], synthetic resins [329] and bio-sorbents [330].

Among polymeric membrane materials with ion groups polyetherterketone sulfonate has more and more applications [331], and among bio-sorbents, cellulose, and its derivatives, such as chitosan is increasingly used [332].

For increasing process performance, the design of membrane modules is of overwhelming importance and therefore, each time a specific separation is approached, research is conducted on flat, spiral, tubular and tubular fiber modules [333].

The amount of fluid and the concentration of metal ions in the supply can decide the type of module needed, but most of the time for the transition to the production level the tubular fiber modules are the preferred ones [334].

The specification of metals in the aqueous processing environment is another element that can determine the costs of a membrane process both in terms of the required membrane materials and the membrane configuration in the permeation module [335].

The characteristics of wastewater or solutions that are obtained by acid attack on industrial solid waste are dominated by two restrictive parameters pH and PCL, and the intervention with reagents regulating these parameters should be as economical as possible (number and low concentration of reagents) [336-338].

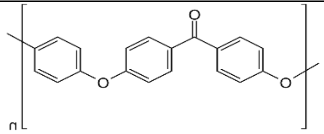
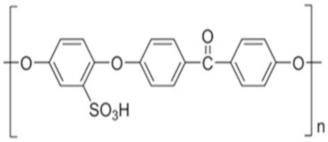
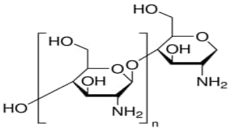
This chapter examines the regenerative separation of copper, cadmium, zinc, and lead from synthetic solutions using chitosan/polyetherterketone sulfated/polypropylene composite membranes from empty fibers using pH and PCL as operational parameters.

$CuSO_4 \cdot 5H_2O$, $CdSO_4$, $ZnSO_4$, $Pb(NO_3)_2$, NaCl, Chitosan and glacial acetic acid (analytical grade, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) have been used in studies. Granules of NaOH, H2SO4 (96%), HCI 35% overlay and NH4OH 25% (analytical grade) were purchased from Merck KGaA Darmstadt, Germany.

Ultra-fast water was used to prepare food solutions.

The characteristics of the polymer compounds and derivatives used in the study are shown in Table 3.8.1.

Table 3.8.1. Characteristics of the polymer compounds and derivatives used

Polymer compounds	Symbol	Molar mass (Da)	Solubility	pKa*)
	PEEK	30.000	Sulfuric Acid	-
	sPEEK		Organic polar solvents	1.9
	Chi		Acidulated water	6.5

*) [339-341]

Place 300 ml of 96 % H2SO4 in a 500 ml glass bottle with a sealing cap, then gradually add 25 g of polymer (PEEK), shaking continuously by hand to avoid polymer clumping. After about 2 hours of agitation, the polymer solution phial is stored without agitation for up to 24 hours to promote complete dissolution of the polymer into the acid. This time interval should not be exceeded as additional sulphonation of the polymer [342-343] occurs. Obtain a clear light orange solution of 4.4 % poly(ether ketone) sulphonated concentration (sPEEK).

After the same method, prepare a solution of 30 g of peek and 300 ml of 96% sulfuric acid. A solution of 5.2% sPEEK concentration is obtained, with varying degrees of sulphonation depending on the time of storage of the solution. The colours of the solutions vary from light orange to brown, indicating the different degree of sulfonating (Fig. 3.8.1).

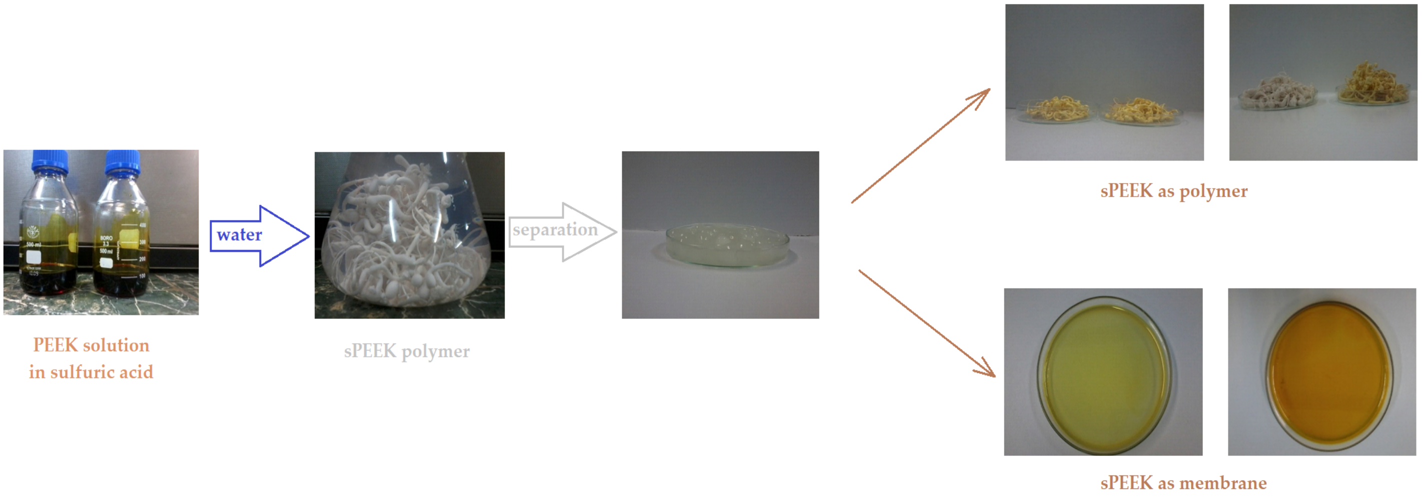


Fig. 3.8.1. Scheme for obtaining sulfonated poly (ether ether ketone) sPEEK as a polymer and as a membrane from the solution of poly (ether ether ketone) (PEEK) in sulfuric acid.

The solution of poly sulfonate (ether ketone) (sPEEK) is used as such for impregnating polypropylene tubular fiber membranes using the impregnation method [344].

Poly sulphonated composite membranes (ether ketone)/empty polypropylene PEEK/HFPP fibers may be conditioned either by drying or by immersion in water or aqueous solutions. To obtain the chitosan/poly sulphonate composite membrane (ether ketone)/polypropylene Chi/sPEEK/PPHF hollow fiber the poly sulfonate composite membrane (ether ketone)/polypropylene tubular fiber sPEEK/PPHF is immersed in a 3% chitosan solution in 3% acetic acid [345-349]. Each type of membrane is washed with water and vacuum dried for 24 hours at 50°C.

Membrane materials are characterized for the determination of porosity [350], morphology [351], thermal characteristics [352], ion exchange capacity and ion retention capacity of heavy metals [353].

Separation tests shall be carried out with equimolar solutions of $CuSO_4 \cdot 5H_2O$, $CdSO_4$, $ZnSO_4$, $Pb(NO_3)_2$, obtained in ultra-high water [354].

For the performance of the tests, experiments of nanofiltration and pertraction are carried out in installations with the tubular configuration module [355-358], presented in Figure 3.8.2. And 3.8.3 the volume of solution subjected to the experiments is 10 L, and the concentration of ions in the range 10^{-6}-10^{-4} mol/L. The operational parameters chosen are pH and PCL, the variation of which is achieved with hydrochloric acid, sodium hydroxide or ammonia and sodium chloride.

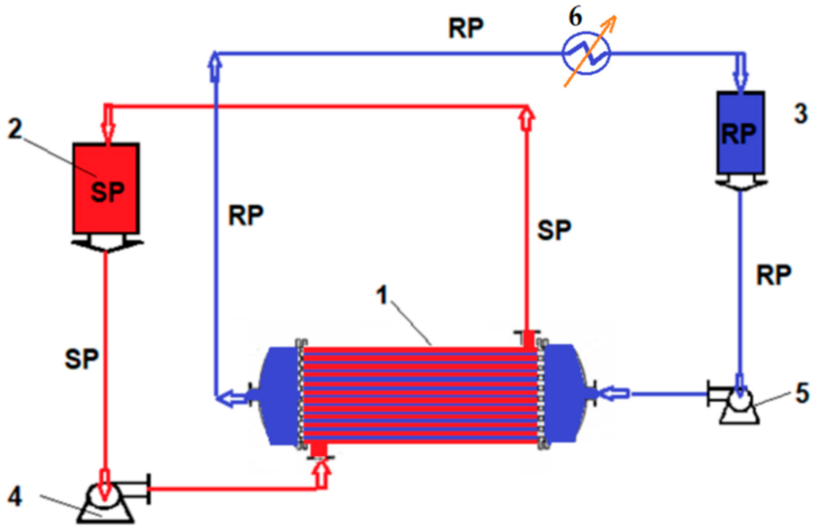


Fig. 3.8.2. Schematic of the installation for pertraction: SP—source phase, RS—receiving phase. 1. Hollow-fiber pertraction module; 2. SP reservoirs; 3. RP reservoirs; 4. SP pump; 5. RP pump; 6. Thermostat.

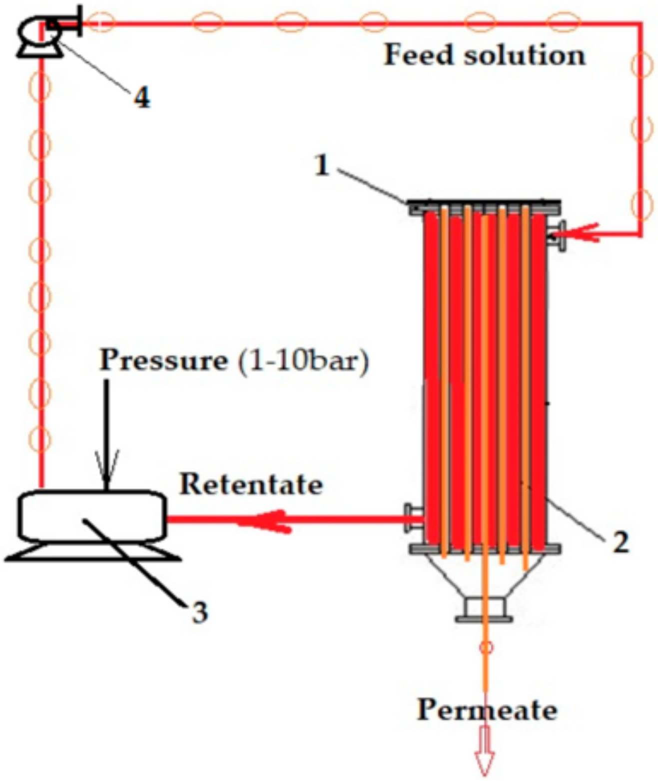


Fig. 3.8.3. Schematic of the installation for nanofiltration: 1. Hollow fiber pertraction module. 2. Composite membranes; 3. Pressure reservoir; 4. Recycling pump.

The flows in the source phase [359] were determined relative to the mass of permeate measured over a specified time interval, applying the following equation:

$$J=M/ (S \cdot t) \ (g / (m^2 \ h)) \ (1)$$

Where: M = permeat weight (g),

S = the effective surface of the membrane (m^2),

t = the time required to collect the volume of permeate (h).

The extraction efficiency (EE%) in the process of separation or retention or retention in the process of nanofiltration of the analytes calculated using the concentration or absorbance of the solutions [360-364] are:

$$EE\ (\%) \text{ or } R\ (\%) = ((c_0-c_f)) /c_0 \cdot 100 \ (2)$$

Where: c_f - is the final concentration of the solute (metallic aluminum ions),

c_o - initial concentration of solute (aluminum).

$$EE\ (\%) \text{ or } R\ (\%) = (A_0- A_s)/A_0 \cdot 100 \ (3)$$

Where: A_0 - initial absorbance of the sample solution,

A_s - absorbance of the current sample.

Scanning microscopy, SEM and HR-SEM investigations were conducted on a Hitachi S4500 (Hitachi High– technologies Europe GmbH, Mannheim, Germany) system [365].

Thermal analysis (TG-DSC) was carried out with A STA 449°C Jupiter apparatus from Netzsch (NETZSCH-Gerätebau GmbH, Selb, Germany). Each sample weighed approximately 10 mg. the samples were placed in an open alumina crucible and heated to 900°C at a rate of 10 K min^{-1}, under a flow of 50 ml min^{-1} of dry air. As a reference, I used an empty alumina crucible. The released gases were analysed with a Bruker FTIR Tensor 27 (Bruker Co., Ettlingen, Germany) equipped with a thermostat gas cell [366]. UV-VIS analysis of the solutions was carried out on a CamSpec M550 spectrophotometer (Spectronic CamSpec Ltd., Leeds, UK) [367].

Electrochemical processes were tracked with a PARSTAT 2273 potentiostat (Princeton applied Research, AMETEK Inc., Berwyn, Pennsylvania, USA). A glass cell with three configured electrodes was used. [368].

The pH and PCL of the environment were tracked with a combined selective electrode (Hi 4107, Hanna instruments Ltd, Leighton Buzzard, UK) and a multi-parameter system (Hi 5522, Hanna instruments Ltd., Leighton Buzzard, UK) [369].

To evaluate and validate the metal ion content, Aanalyst 400 AA spectrometer atomic absorption spectrometer (Perkin Elmer Inc., Shelton, Connecticut, USA) was used with a single-element hollow cathode lamp, led by WinLab 32–Aa software (Perkin Elmer Inc., Shelton, Connecticut, USA) [370-372].

The separation of low-concentration ions from various complex aqueous systems is an important objective of the membrane domain and membrane processes. Ion-poor systems of heavy metals have been treated through various membrane processes including reverse osmosis, direct osmosis, nanofiltration, dialysis, electrodialysis, or liquid membranes, but the need for a reduced amount of reagents and regenerative separation further encourages research.

In this chapter, synthetic solutions are used that adequately simulate aqueous solutions that come from the recovery of waste from electronics and electrotechnics, especially those coming from the Cu-Zn and Pb-CD. Such solution contains, for example, in concentrations of 10-6-10-4 mol/L copper ions, cadmium, zinc and lead in the mixture.

The aqueous system separation is studied in hollow fiber modules with polysulphone composite membranes (ether ketone) (sPEEK) – hollow fiber polypropylene (sPEEK/PPHF) or chitosan (Chi) – polysulfonated (ether ketone) (sPEEK) – hollow fiber polypropylene (Chi/speek/PPHF).

The use of operational parameters pH and PCL is based on balances (4-7) that are established in hydrochloric supply solutions:

$CuCl_2 + 2Cl^- \rightleftharpoons [CuCl_4]^{2-}_{(aq)}$ (4)

$PbCl_{2(s)} + 2\,Cl^- \rightleftharpoons [PbCl_4]^{2-}_{(aq)}$ (6)

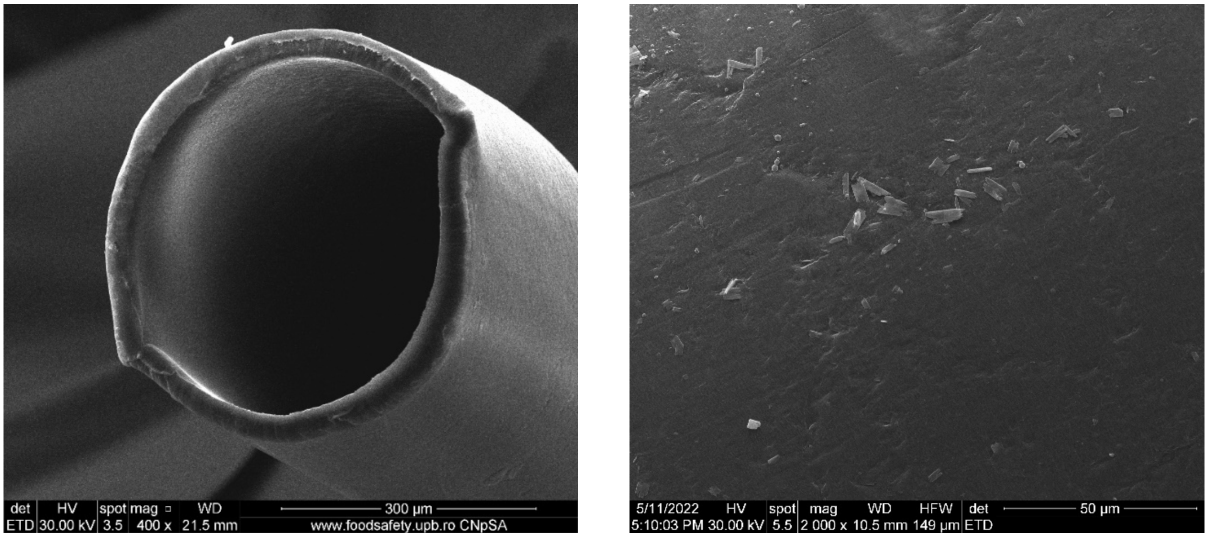
$ZnCl_2 + 2Cl^- \rightleftharpoons [ZnCl_4]^{2-}_{(aq)}$ (5)

$CdCl_2 + 2\,Cl^- \rightleftharpoons [CdCl_4]^{2-}_{(aq)}$ (7)

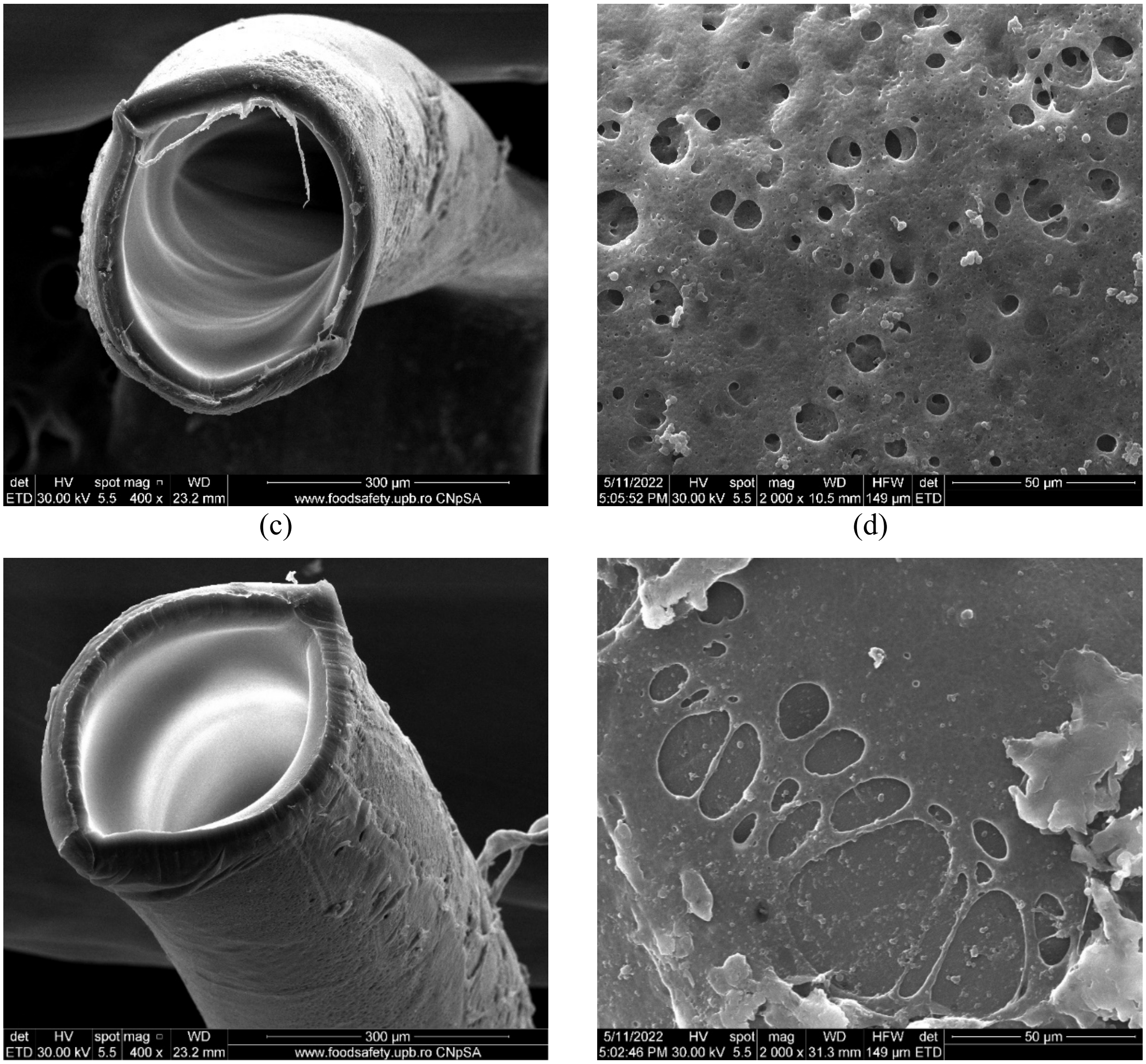
These balances have been intensively studied [373], and chemical speciation plays a primordial role in the membrane separation processes addressed.

The morphology obtained by electronic balayage microscopy provides important information for both the operation and conditioning of the membranes in the permeation modules. Figure 3.8.4 shows sections and details of the obtained composite membranes. It is observed that polypropylene hollow fiber membranes (PPHF) (Fig. 3.8.4 a and b, Fig. 3.8.5) have an inner diameter of approx. 300 µm and a membrane wall thickness of about 20 µm (Fig. 3.8.4 a Fig. 3.8.5) and a relatively smooth surface (Fig. 3.8.4 b).

By depositing the polysulphone layer (ether ketone) on the polypropylene support, a composite membrane (sSPEEK-PPHF) is obtained (Fig. 3.8.4 c and d, Fig. 3.8.5) in which the polysulphone layer (ether ketone) is approximately 10 µm thick (Fig. 3.8.4 c, Fig. 3.8.5), And the surface of the membrane has pores and micropores specific to ultrafiltration membranes [374], the subsequent deposition of chitosan for obtaining the chitosan (Chi) composite membrane - polysulphone (ether ketone) (sPEEK) - polypropylene of empty fibers (Chi/sPEEK/HFPP) does not significantly increase the thickness of the membrane wall (Fig. 3.8.4 e), but significantly changes the appearance of the composite fibers (Fig. 3.8.4 f).



(a) (b)



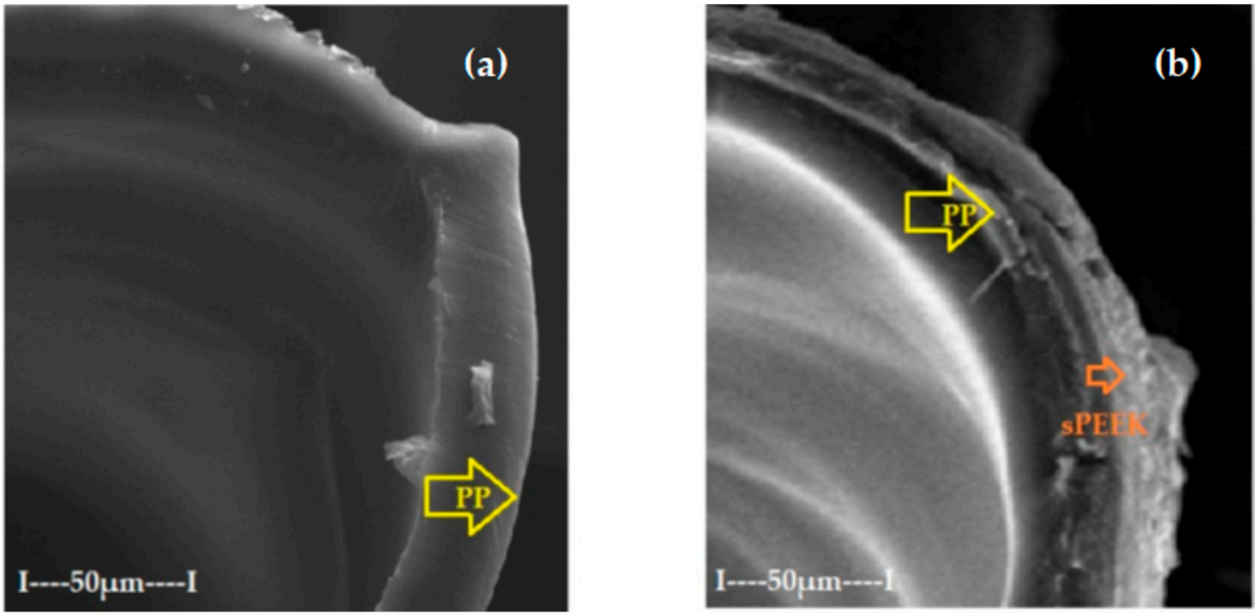
(c) (d)

(e) (f)

Fig. 3.8.5. Scanning Electron Microscopy (SEM) on: (a) polypropylene hollow-fiber membrane (PPHF); (b) detail on surface; (c) sulfonated poly (ether ether ketone) (sPEEK)-polypropylene hollow fiber (sPEEK/PPHF); (d) detail on surface; (e) chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)– polypropylene hollow fiber (Chi/sPEEK/PPHF); (f) detail on surface.

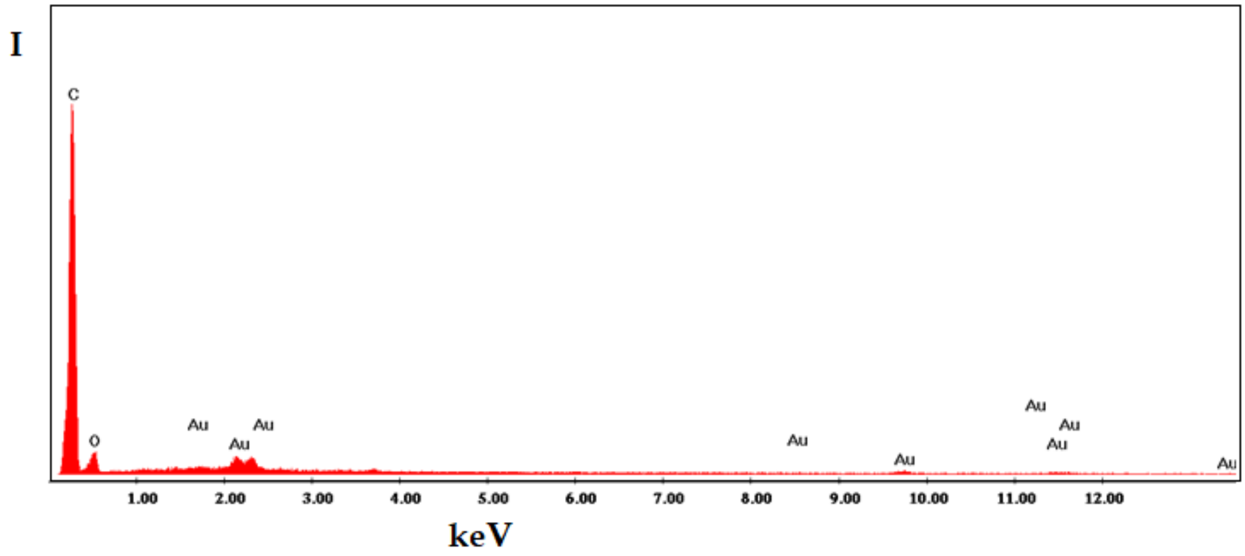
It is interesting that Energy Dispersive X-ray analysis (EADX) (Fig. 3.8.6) highlights the change in surface composition. Thus, if only carbon and oxygen atoms appear in the polypropylene support (Fig. 3.8.6 a), the composite membranes change both the atomic ratio C:O and the composition by the appearance of sulfur atoms (Fig. 3.8.6 b and c). Although it is a strictly local

Energy Dispersive X-ray analysis (EADX) it is very useful to track the quality of the membrane formation process as well as the process of separation of the complex system.



(a) (b)

Fig. 3.8.5. Scanning Electron Microscopy (SEM) details on polypropylene hollow-fiber membranes (PPHF) (a); and composite membranes (b).



(a)

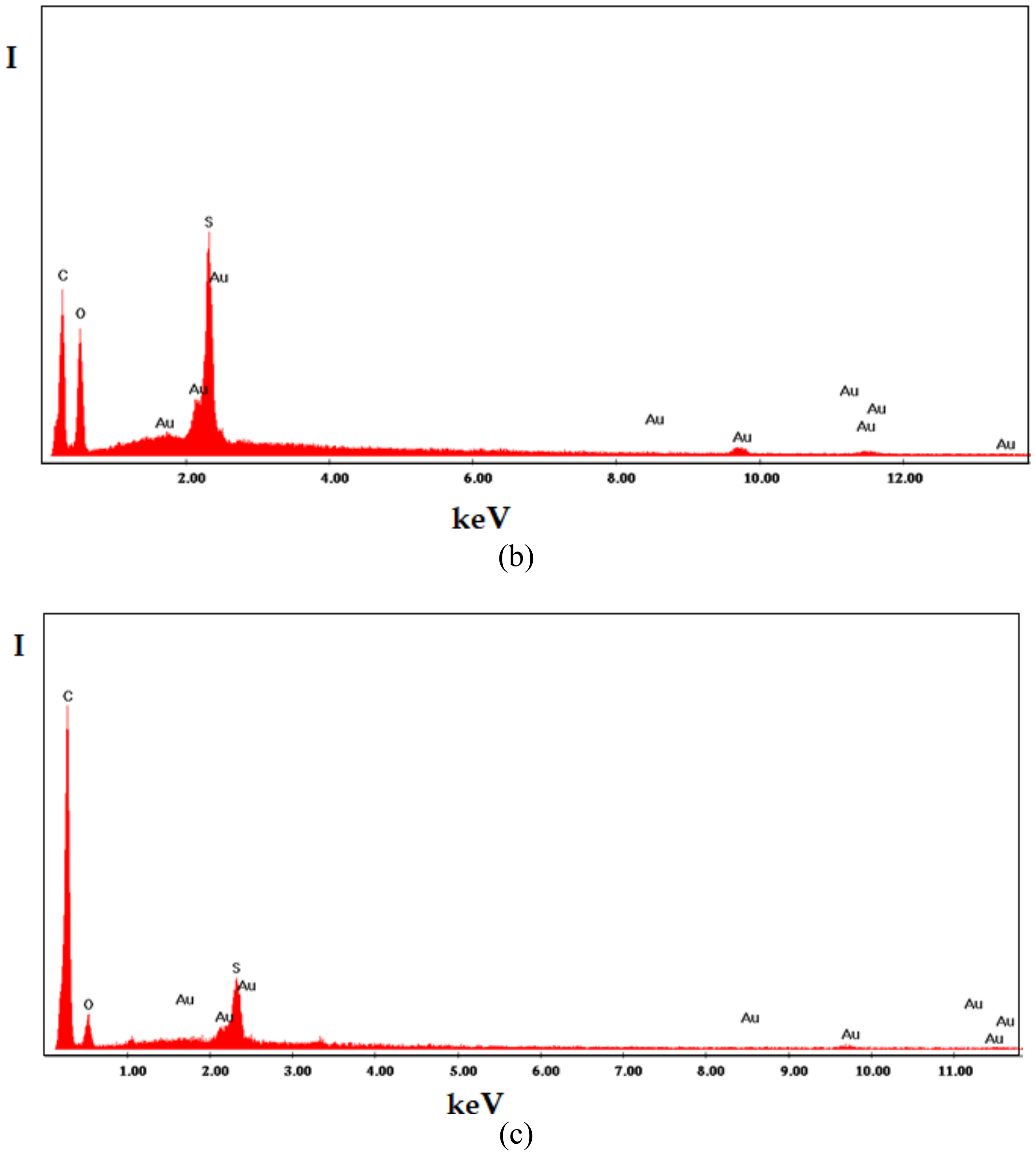


Fig. 3.8.6. Energy dispersive X-ray analysis (EADX) on: (a) polypropylene hollow-fiber membrane (PPHF); (b) sulfonated polyether ether ketone (sPEEK)–polypropylene hollow fiber (sPEEK/PPHF) and (c) chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF).

The studied membranes have structurally specific functions that can be highlighted by Fourier Tansform Infrared (FTIR) spectral analysis (Fig. 3.8.7). At the same time, the UV-VIS spectrum may indicate significant differences (Fig. 3.8.8).

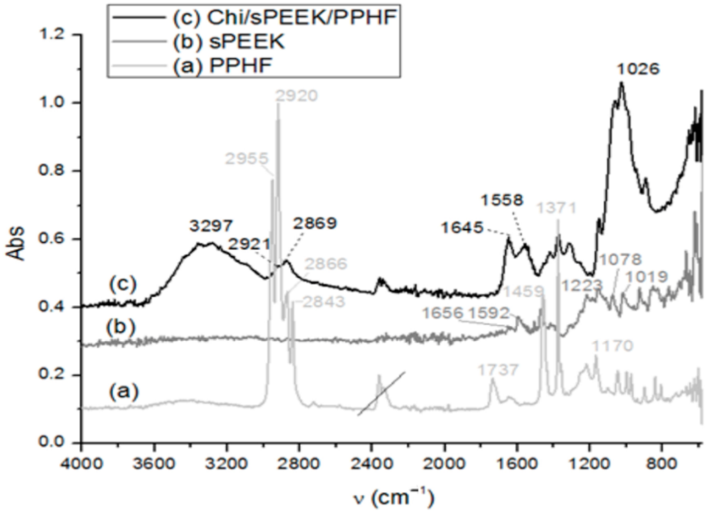


Fig. 3.8.7. Fourier Transform InfraRed (FTIR) on (a) polypropylene hollow-fiber membrane (PPHF); (b) sulfonated poly (ether ether ketone) (sPEEK); and (c) chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF).

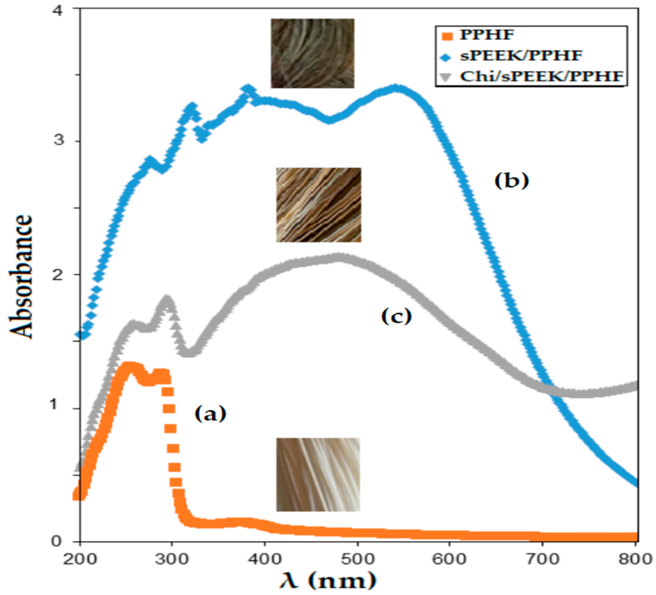


Fig. 3.8.8. UV-Vis spectrometry on (a) polypropylene hollow-fiber membrane (PPHF); (b) sulfonated poly (ether ether ketone) (sPEEK)-polypropylene hollow fiber (sPEEK/PPHF); and (c) chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF

Thermal analysis, TG-DSC (thermogravimetry and differential calorimetric scanning), was performed with a NETZSCH STA 449C F3 (Selb, Germany), between 20-900°C, in dynamic air atmosphere (50 ml/min). The released gases were analysed with a Bruker FTIR Tensor 27 (Bruker Co., Ettlingen, Germany) equipped with a thermostatic gas cell.

The diagram of the three basic materials for the production of composite membranes is presented as an assembly in Fig. 3.8.9.

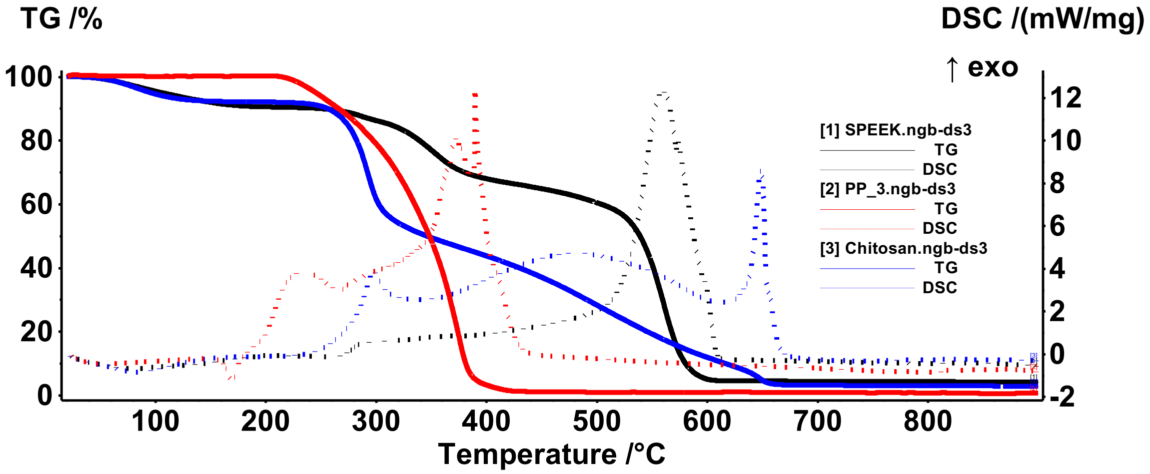


Fig. 3.8.9. Comparative thermal diagrams of the three membranes

The speek sample (Fig. 3.8.10) loses 9,38% of the initial mass in the RT-200°C range in an endothermic process with a minimum of 79.2°C. This can be attributed to the removal of some water molecules. The presence of adsorbed water in sPEEK is a natural phenomenon because it is a polymer with sulfonic groups.

As such, it speaks of a hydrophilic compound in which water is rather bound, and therefore a higher temperature is required to remove it. Between 200-420°C the samples lose 23,89%, the process being associated with an endothermic effect with a minimum of 261.9°C. This can be attributed to the desulfurization process of sPEEK and the poor oxidation processes that follow. The breakdown of the polymer spine and complete oxidation occurs between 420-600°C, with a strong exothermic effect associated with the maximum at 559.4°C.

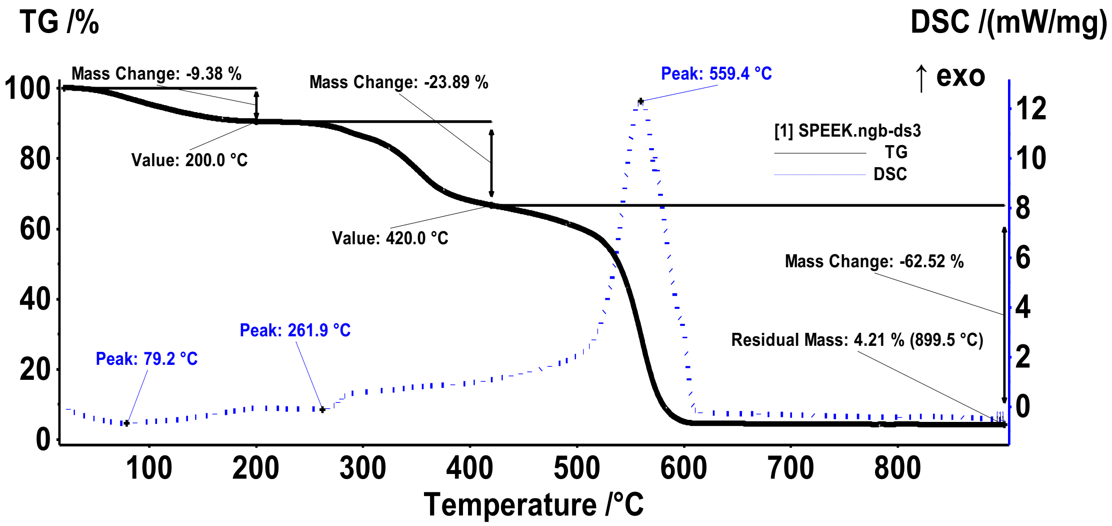
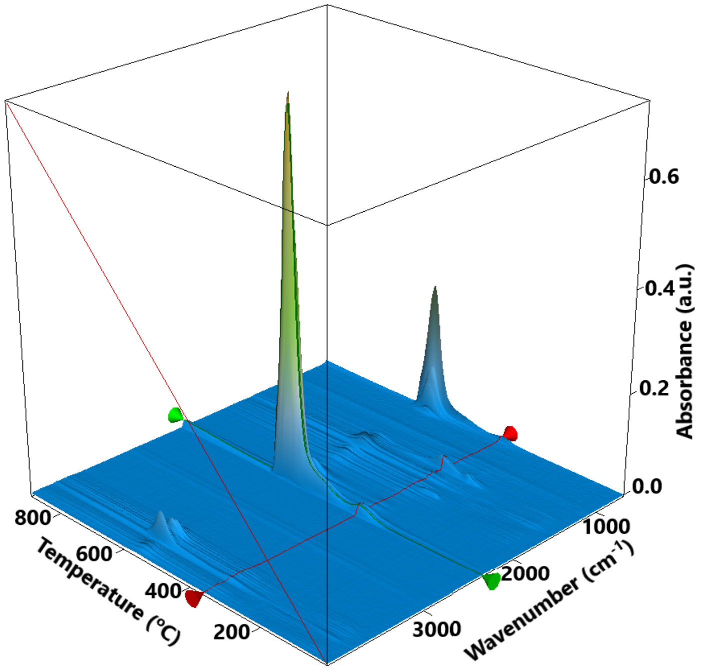
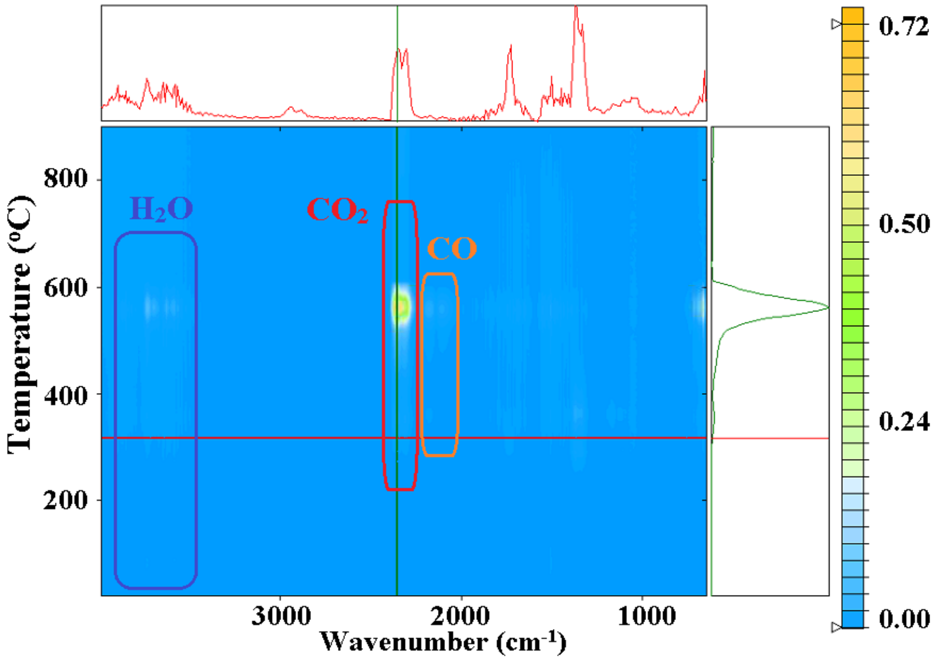


Fig. 3.8.10. Detailed thermal diagram of polysulfone (ether ketone) (sPEEK)

The 3D FTIR graph (Figure 3.8.11 a) shows the evolution of the FTIR spectrum according to temperature. By designing this map in 2D space (wave number vs temperature) we can easily identify components and temperature ranges when removed from the sample (Figure 3.8.11 b).



(a)



(b)

Fig. 3.8.11. FTIR 3D evolved gas diagram for the SPEEK sample (a) and its 2D projection with assigned identification/temperature ranges (b)

The FTIR spectra recorded for the released gases indicate the presence of carbon dioxide and water molecules mainly in the range 500-600°C, but also traces of carbon monoxide. The presence of sulfated hydrocarbon fragments can also be identified around 300-400°C.

The PPHF sample (Figure 3.8.12) is stable up to 210°C with a negligible mass loss of 0,26%. On the DSC curve, an endothermic effect with onset at 160.3°C corresponds to the melting process of PP. The sample begins to degrade between 210-440°C, when virtually all mass is lost (99,53%). The process is accompanied by a series of endo-thermal effects (268.1°C) and exotherms (233,1 and 372.8°C), corresponding to the breaking of polymer chains and the oxidation of fragments. The last strong exo-thermal effect from 389.6°C corresponds to the burning of residual carbon mass.

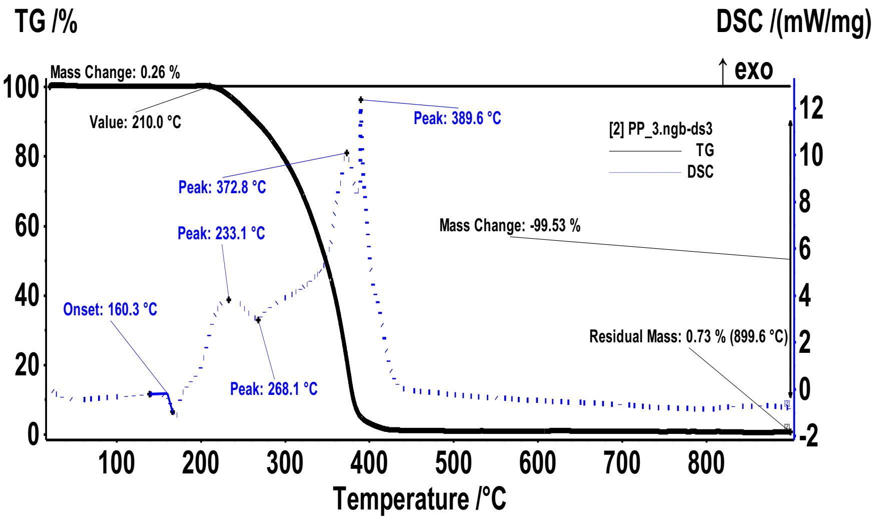
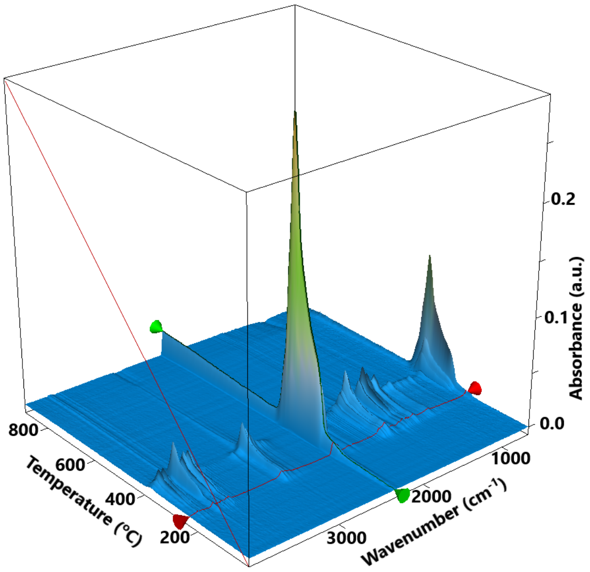
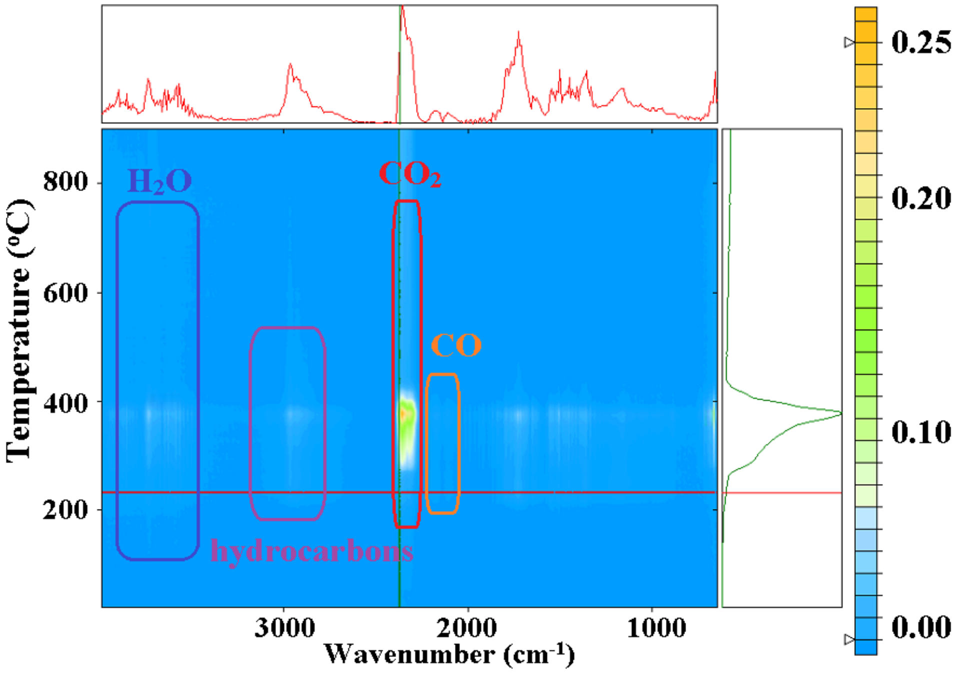


Fig. 3.8.12. Detailed thermal diagram of the hollow polypropylene fiber membrane (PPHF).

The 3D FTIR graph (Figure 3.8.13 a) shows the evolution of the FTIR spectrum according to temperature. By designing this map in 2D space (wave number vs temperature) we can easily identify components and temperature ranges when removed from the sample (Figure 3.8.13 b). FTIR spectra recorded for the released gases indicate the presence of water and carbon dioxide molecules mainly, but also some traces of carbon monoxide and hydrocarbon fragments can be identified between 200-400^{o}C.



(a)



(b)

Fig. 3.8.13. FTIR 3D diagram of evolved gases for PPHF sample (a) and its 2D projection with assigned identification/temperature ranges (b)

The chitosan sample (Figure 3.8.14) shows a three-stage thermal degradation process. The sample loses 8,16% of its mass up to 230°C. This process can be attributed to the removal of water molecules since the associated effect on the DSC curve is endothermic with a minimum of 83.6°C. In the second stage, between 230-320°C the sample loses 37,64% of its mass, the process being associated with an exothermic effect of maximum at 297.5°C. This process can be attributed to the breaking of polysaccharide chains and the oxidation of smaller fragments.

The FTIR spectra of the released gases allow the identification of water, CO_2, and hydrocarbon fragments within this temperature range. The third stage is a continuous slow oxidation, in which the sample loses 45,75% between 320-630°C. The process is associated with a large exothermic effect on the DSC curve with a maximum of 482.1°C. The residual carbon mass is burned after 630°C, with the corresponding exothermic effect showing a maximum of 648,5°C.

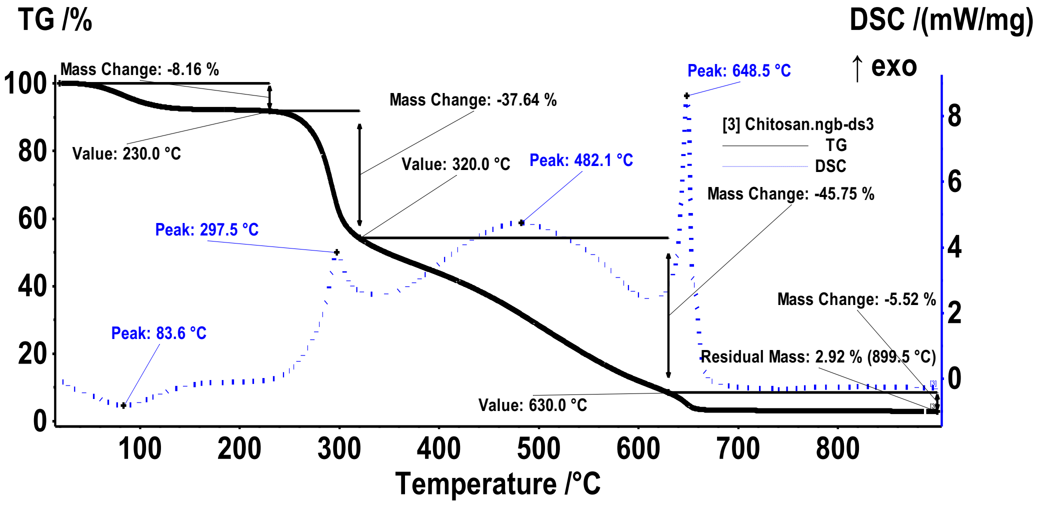
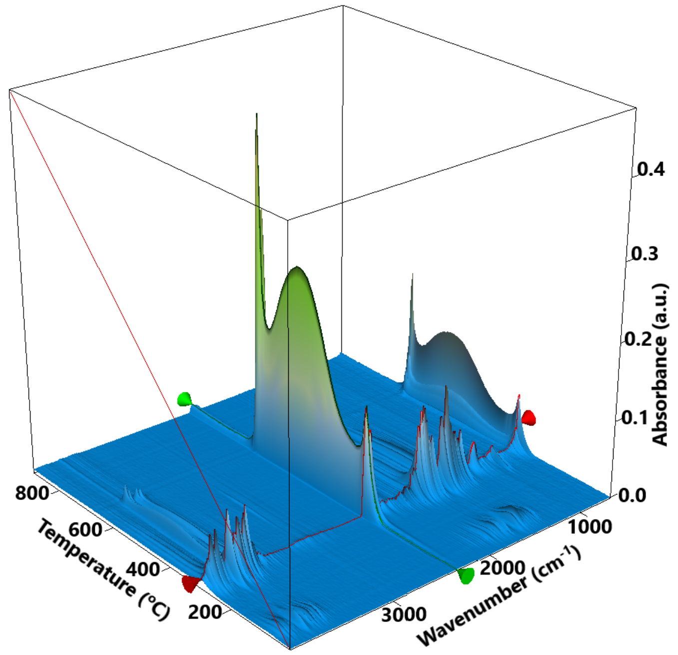
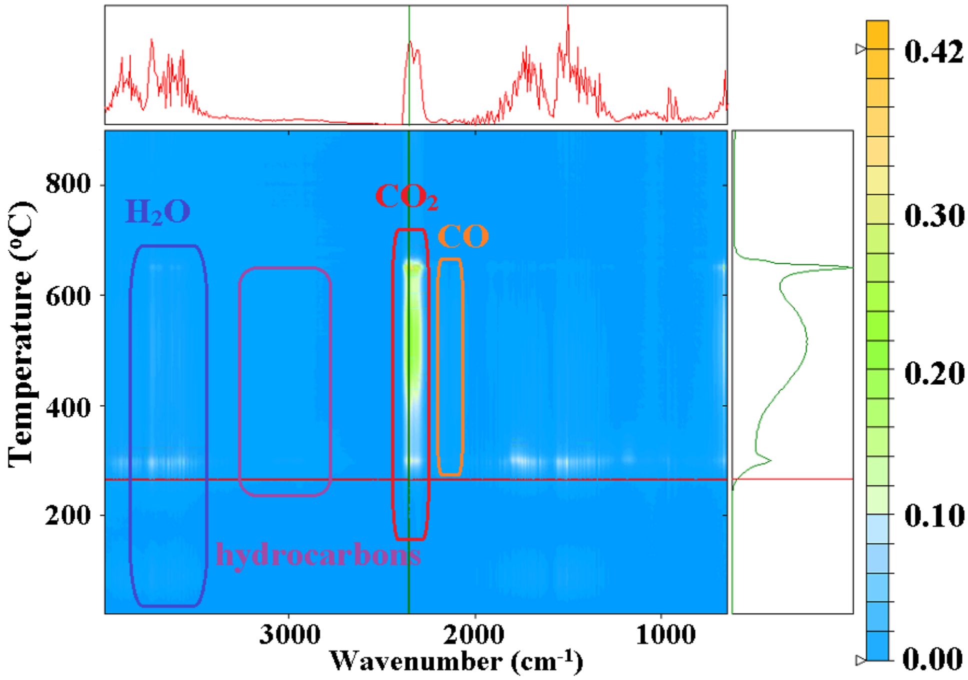


Fig. 3.8.14. Detailed thermal diagrams of the composite membranes

The 3D FTIR graph (Figure 3.8.15 a) shows the evolution of the FTIR spectrum according to temperature. By designing this map in 2D space (wave number vs temperature) we can easily identify components and temperature ranges when removed from the sample (Figure 3.8.15 b).



(a)



(b)

Fig. 3.8.15. The evolved gases FTIR 3D diagram for the PCS sample (a) and its 2D projection with assigned identification / temperature intervals (b)

FTIR spectra recorded for the released gases indicate the presence of water and carbon dioxide molecules mainly, but also traces of carbon monoxide. The hydrocarbon fragments can be identified from 250°C.

The recuperative separation of copper, cadmium, zinc, and lead ions is studied by two membrane processes: nanofiltration and pertraction (Figure 3.8.15 a and b), using binary systems: copper–zinc and lead-cadmium, as well as quaternary systems: copper, cadmium, zinc, and lead.

The nanofiltration or pertraction module has a usable membrane area of 1m^2, the difference in behaviour of the membranes being imposed by the forced circulation un-der pressure (nanofiltration) or flow through the outside of the membrane of the source phase with the capture of the ions transported in the receiving phase inside the membrane (pertraction) (Figure 3.8.15).

The operation in the nanofiltration process is performed under a pressure of 4-6 bar, with a recirculation flow rate of 0.1–1 L/min for the source phase through the exterior of composite the hollow fiber membrane.

In the case of pertraction, the module plays the role of the contactor. The source phase circulates through the outside of the composite hollow fiber membrane at a flow rate of 0.1–1 L/min, and inside them the receiving phase has a flow rate of 0.10–0.100 L/min (Figure 2).

The membranes used in the separation modules are chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF), but comparative tests were also performed with sulfonated polyether ether ketone (sPEEK)-polypropylene hollow fiber (sPEEK/PPHF), at the same time or alternately.

The variable operational parameters are pH and pCl, trying to use as few reagents as possible, considering the supply with a strong acidic solution that also contains ex-cess chloride ions (coming from both hydrochloric acid and sodium chloride).

The pH is adjusted either with sodium hydroxide solution or with ammonia, which is also formed in elution systems.

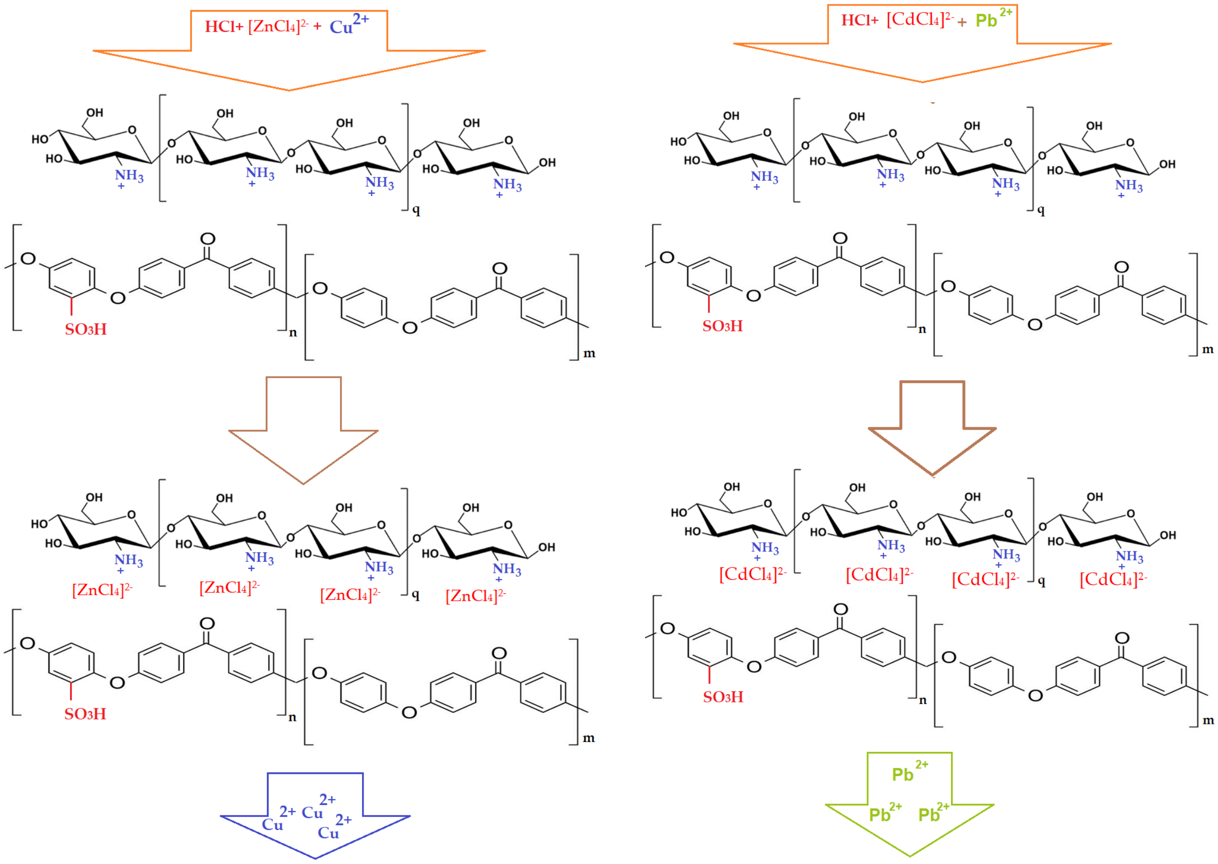
The first system studied consisted of a 3 mol/L hydrochloric acid solution containing copper and zinc ions in an equimolar mixture of 10^{-4} mol/L concentration. This system can be separated with chitosan membranes (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF), since sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (sPEEK/PPHF) are unable to interact with $[MCl_4]^{2-}$ anions.

Copper and zinc form with hydrochloric acid complex combinations of different stabilities depending on its concentration equilibria (4) and (5). Because in the presence of 3 M HCl zinc forms a complex $[ZnCl_4]^{2-}$ anion, while copper remains in the form of Cu2+ cations or less stable complexes, the two ions can be separated by passing through a module with a membrane of chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF). The complex anion $[ZnCl_4]^{2-}$ will be retained on the membrane while Cu^{2+} will pass through the module without being retained, the tetra chloro cupper complex being much less stable [82].

Elution of Zn2+ from the module is done in the presence of HCl 3□10-2 M, which no longer provides conditions for the existence of complex anions and Zn2+ cations will leave the membrane (Figure 3.8.16). The scheme shown in Figure 3.8.16 a is specific to the nanofiltration of chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF) membrane.

The second system studied consisted of a 3 mol/L hydrochloric acid solution containing lead and cadmium ions in equimolar mixture, of 10-4 mol/L concentration.

The lead chloride is insoluble and that of cadmium is very weakly dissociated, but in strongly hydrochloric solution (3 mol/L HCl) and at a temperature of 50°C, by nano-filtration through chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF) membranes, the cadmium as anion $[CdCl_4]^{2-}$ is retained while the lead passes into the permeate as lead cations (Figure 3.8.16 b).



(a) **(b)**

Fig. 3.8.16. Separation of the mixture of copper and zinc ions or cadmium and lead with strong acid solution (3 mol/L hydrochloric acid) by nanofiltration copper and zinc ions (a); and cadmium and lead ions (b).

The appearance of the retention–elution curves in the case of nanofiltration (5 bars and 200 mL/min feed solution flow) indicates lower performance when separating lead and copper ions compared to that of cadmium and zinc ions (Figure 3.8.17). The recuperative separation of zinc and cadmium ions, which form more stable tetra-chloro-complexes, after 4 hours of operation, exceeds 70%, while for copper and especially lead ions, it does not reach 40%. One explanation for these results would be that the membrane, however, retains some of the lead or copper ions either in the form of ani-on-complexes or expels them (does not allow passage through the membrane) as positive ions.

The results in a single separation stage are promising, especially since the concentration of test ions in the feed is relatively high, 10^{-4} mol/L.

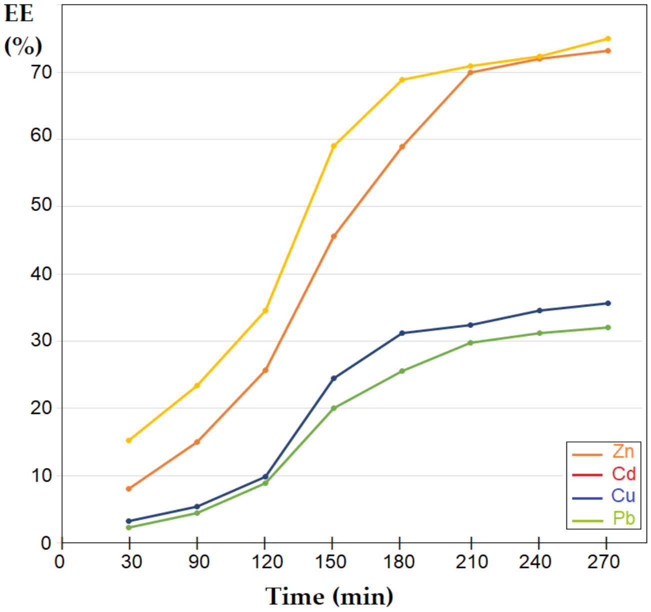


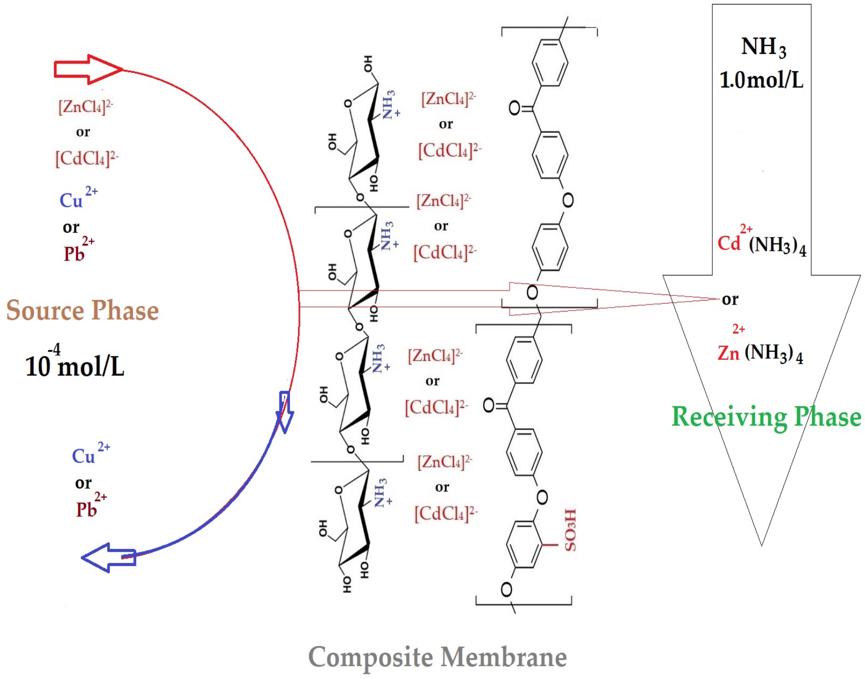
Fig. 3.8.17. Retention-elution curves when separating the ion mixture with strongly acid solution (3 mol/L hydrochloric acid) by nanofiltration (5 bars and 200 mL/min feed solution flow), for the copper–zinc system and the lead–cadmium system from equimolar 10^{-4} mol/L solution.

Figure 3.8.18 a show the separation of the copper-zinc system of equimolar concentration 10^{-4} mol/L through membranes of chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF), in the pertraction module in which 1.0 mol/L ammonia receptor solution flows through the fibers, which con-tributes to the fixation of zinc ions as tetra-ammonia ion. The process control is performed by monitoring the concentration of zinc ions in the receiving phase, the end of the process being considered when reaching the degree of recovery of 90% of zinc. Un-like nanofiltration, in this process the tetra-chloro-zincate ion passes through the membrane, and the cupric ion remains mostly in the supply.

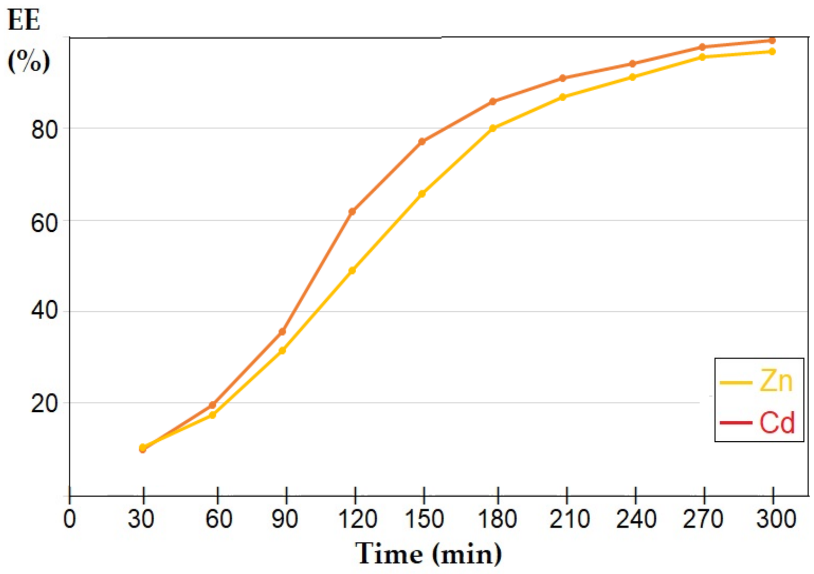
On one hand, this behaviour is justified by the particular mechanism of pertraction, in which the cationic groups of chitosan in the strongly acidic environment favour the transport of the more stable anion, $ZnCl_4^{2-}$, but also the fact that copper ions, Cu^{2+}, reaching the interface with the basic ammonia solution are retained by the membrane which, in that section, will have the free amino groups.

The lead-cadmium system behaves in the same way (Figure 3.8.18 a), thus confirming the proposed transport mechanism (Figure 3.8.18 b). After four hours of operation, the recovery of the two ions in the receiving solution exceeds 90%. It is noteworthy that the cadmium ion separates with noticeably better efficiency from its lead system than the zinc ion from the zinc-copper system.

The advantage of the extraction process, from the point of view of the higher ex-traction efficiency, is doubled by the fact that the receiving solution being 10 times smaller in volume than the receiving solution (1L NH_3 aqueous solution 1.0 mol/L), leads to the concentration of the separate chemical species. An important disadvantage of extraction is the additional consumption of reagents (ammonia).



(a)



(b)

Fig. 3.8.18. Separation of the mixture of equimolar concentration of 10^{-4} mol/L of the copper and zinc ions, or lead and cadmium ions, from the strongly acidic source phase (3 mol/L hydrochloric acid) by pertraction in the ammonia receiving phase (NH_3 aqueous solution 1.0 mol/L): **(a)** trans-membrane transport scheme; **(b)** the efficiency of cadmium or zinc ion extraction.

If the source of the aqueous solution from which the copper, zinc, cadmium, and lead ions are to be recovered has a pH that falls within the normal pH scale, as is the case for surface waters contaminated with the ions considered, the use of nanofiltration through the prepared composite membranes can have as operational parameters both the pH of the feed and the pCl (salinity induced with sodium chloride).

Table 3.8.2 presents the main parameters of copper, zinc, cadmium, and lead ions in aqueous solutions [82,83] of variable pH and pCl considered in establishing the operating parameters for nanofiltration of solutions containing the mixture of these ions.

These parameters must be correlated with the ionic charge of the functional groups of the composite membrane (Table 3.8.2), depending on the pH of the aqueous environment in which it operates, as follows: at pH up to 1.9 the functional groups are in the form $–SO_3H$ and $–NH^{3+}$, between 2 and 6.4 are found $–SO^{3-}$ and $–NH^{3+}$, and after pH 6.5 the groups become $–SO^{3-}$ and NH_2.

Table 3.8.2. The characteristics of the tested metallic ions in aquatic solution

Metallic ion	**Ionic Radius (Å)**	**$[MCl_4]^{2-}$ pK $_{instability}$**	**pH**	**MCl_2 Solubility in water (g/100mL)**	**K_s $M(OH)_2$**
Cu^{2+}	1.96	5.30	4.4	75.7	$1\cdot10^{-20}$
Zn^{2+}	0.83	0.15	6.8	432.0	$5\cdot10^{-17}$
Cd^{2+}	0.94	2.46	4.5	119.6	$1\cdot10^{-14}$
Pb^{2+}	1.81	13.22	4.2	0.99	$3\cdot10^{-16}$

At the same time, the way in which the pH variation is achieved can influence the efficiency of the separation (retention) of the four cations in the nanofiltration process of 10L equimolar solution 10^{-4} mol/L ions of copper, zinc, cadmium, and lead, at 5 bars with chitosan (Chi)–sulfonated polyether ether ketone (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF) composite membranes with active surface of 1 m^2, at a recirculation rate of 0.20 L/min.

The pH variation can be achieved by neutralizing the initial stock solution of zero pH (1 mol/L HCl solution) with solid sodium hydroxide or using only hydrochloric acid. In the first case the pH varies from 0 to 8, and pCl remains identical, and in the second case both pH and pCl have identical values (Table 3.8.3).

The pH variation can be achieved by neutralizing the initial stock solution of zero pH (1 mol/L HCl solution) with solid sodium hydroxide or using only hydrochloric acid. In the first case the pH varies from 0 to 8, and pCl remains identical, and in the second case both pH and pCl have identical values (Table 3.8.3).

The obtained results showed that the ion retention depended on both pH and pCl, because in the aqueous solution there were competitive equilibria of formation of chlorides (MCl_2), tetra-chloro-complexes ($[MCl_4]_2^-$), hydroxides ($M(OH)_2$), or even aqua complexes and/or hydroxy complexes. The data in Table 3.8.2 are a good benchmark for justifying the retention values, but they are not enough because the interaction of each species with the membrane is complex and very different from case to case. This is also due to the fact that the tasks of the functional groups vary with the change of the pH of the supply solution.

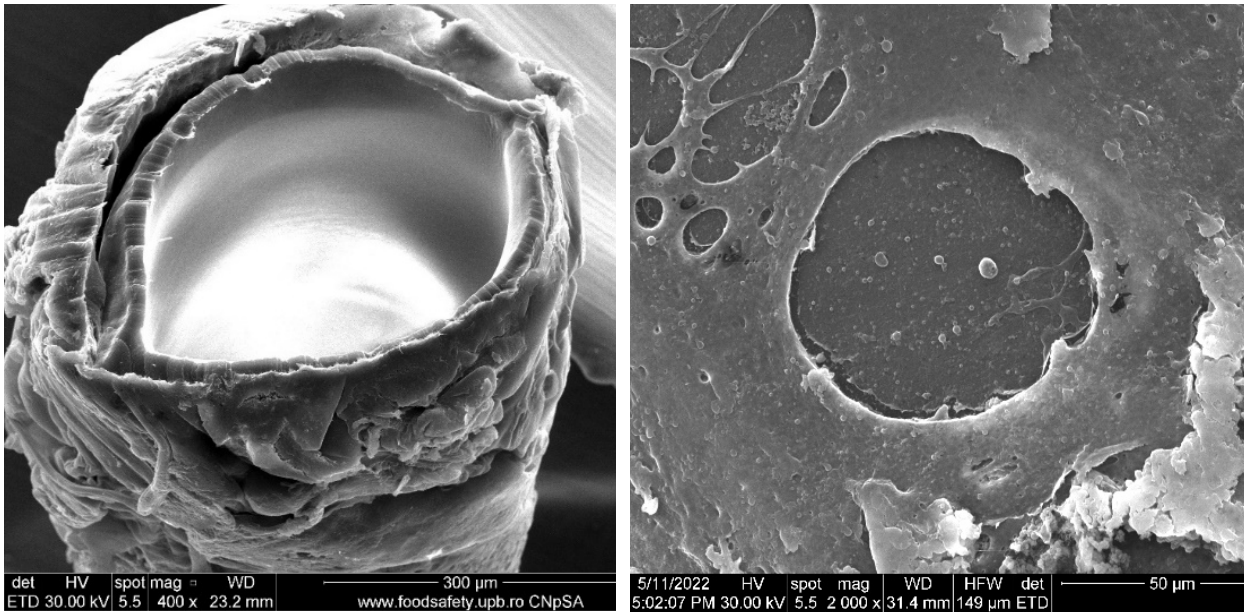
Tabel 3.8.3. Separation efficiency (retention) of copper, zinc, cadmium, and lead ions from aqueous solutions, depending on the pH and pCl

Feed Solution Characteristics		**Metallic Ion Retention R (%)**			
pH	**pCl**	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
0	0	23.12	75.33	74.67	87.58
1	0	29.34	62.42	70.84	89.23
4	0	48.90	45.20	54.08	92.00
6	0	79.85	40.48	59.65	90.23
8	0	93.32	64.84	61.20	70.05
1	1	18.56	60.32	65.44	85.00
4	4	68.26	49.86	51.62	60.88
6	6	90.45	62.95	74.32	50.08
8	8	95.18	78.59	80.51	48.82

Some recommendations regarding the separation of copper, zinc, cadmium, and lead ions from a mixture with membranes of chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF) can be as follows:

- √ The separation of zinc and cadmium ions is favored by high concentrations of chloride and hydronium ions (pCl and pH as low as possible).
- √ Copper separation is excellent at pCl and pH as high as possible.
- √ The separation of lead in environments with sufficiently low pCl is little influenced by the pH value. However, caution is advised when both pH and pCl are high.
- √ At high pH the separation of copper, zinc and cadmium ions is very good because it interacts with the membrane in both sulfonic and amino groups.

It should be noted that in repeated uses the membranes lose their qualities (retention decreases for all cations studied), most likely due to the detachment of the composite membrane from the support (Figure 3.8.19).



(a) **(b)**

Fig. 3.8.19. Scanning electron microscopy (SEM) for repeatedly used membranes: (a) section; (b) surface

The application of nanofiltration for the separation of the quaternary system must take into account the permeate flows of the composite membrane chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF), which were much lower than the polypropylene support (PPHF) or the sulfonated poly (ether ether ketone) (sPEEK) polypropylene hollow-fiber (sPEEK/PPHF) membrane (Table 3.8.4).

The support polypropylene membrane is a membrane specific to microfiltration and has relatively low water flows, being hydrophobic. Although the sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow-fiber (sPEEK/PPHF) membrane had the pores of the support covered, by increasing the pressure, specific ultrafiltration flows were obtained. However, it must be borne in mind that at the contact surface with the supply it had the hydrophilized layer of sulfonated polyether ether ketone (sPEEK). Finally, the composite membrane of chitosan (Chi)–sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollow fiber (Chi/sPEEK/PPHF) had specific nanofiltration flows, and the operation at 5 - 6 bar was performed only for technical and economic reasons (obtaining an acceptable flow at medium working pressure).

Tabel 3.8.4. Transmembranar water flows for the studies membranes.

Pressure (bar)	**Flux of Pure Water** (L/m^2·h)		
	PPHF	**sPEEK/PPHF**	**Chi/sPEEK/PPHF**
1.0	8.20	-	-
1.5	12.37	-	-
2.0	19.90	-	-
2.5	22.85	-	-
3.0	-	2.32	-
3.5	-	3.48	0.63
4.0	-	5.95	1.45
5.0	-	6.64	2.32
6.0	-	7.22	2.51

At this stage of the study, the increase in pressure above 6 bar was not taken into account both for energy consumption reasons but also because the composite membrane must be optimized by a possible crosslinking to avoid detachment from the support (Figure 3.8.19).

Among the objectives to be achieved by developing the study of this type of membrane, the following must be found:

√ Tracking the influence of the molecular weight of chitosan.
√ Degree of sulfonation of the poly-ether-ether-ketone.
√ Decreasing the thickness of the polymer membrane support layer.
√ Optimization of flow-retention under the imposed pressure limit conditions.

In this study, we presented the obtaining of a composite membrane of chitosan (Chi)-sulfonated poly (ether ether ketone) (sPEEK)–polypropylene hollowfibre (Chi/sPEEK/PPHF), which was characterized morphologically, structurally, and from the point of view of the separation performances of copper, cadmium, zinc, and lead ions, in either binary mixture (Cu–Zn and Cd–Pb) or quaternary mixtures, in the conditions of strongly hydrochloric systems (Very low pH and pCl). The separation of binary systems from solutions of hydrochloric acid 3 mol/L was performed both by nanofiltration and pertraction. The quaternary system was separated by nanofiltration under variable pH and pCl conditions.

The obtained membranes were morphologically and structurally characterized by scanning electron microscopy (SEM), high-resolution SEM (HR–SEM), energy dispersive spectroscopy analysis (EDAX), Fourier Transform InfraRed (FTIR) spectroscopy, thermal gravimetric analysis, and differential scanning calorimetry (TGA).

Preliminary separation tests showed that binary systems could be efficiently separated by both nanofiltration and pertraction. Extraction would be more advantageous in terms of separation efficiency (90% is reached), but also because the chemical species that is extracted is concentrated by almost an order of magnitude.

Nanofiltration has the advantage of a simpler operation and applicability to multiple systems, but the separation efficiency is strongly influenced by both pH and pCl.

Depending on the target cation and the pH and pCl conditions, retentions of over 90% (For Pb) and almost 95% (for Cu) could be obtained.

The study carried out here opens the perspective of obtaining and characterizing new chitosan (Chi)–sulfonated poly (ether ketone) (sPEEK)–polypropylene hollow-fiber (Chi/sPEEK/PPHF) composite membranes using different types of chitosan, but also sulfonated polymer compounds that improve not only the stability and lifetime of the membranes but also of the process performances.

4. General conclusions. Personal contributions. Prospects for development.

4.1. General conclusions

1. Membrane processes are the most widely used separation processes in industrial applications and belong to the class of advanced filtration processes. Filtration processes include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, which differ from conventional filtration due to the size of the particles retained on the membrane surface.

2. The barometric membrane process occupies the first position in the field of industrial applications. Reverse osmosis is therefore like filtration dehydration, ultrafiltration is like the techniques of concentration, purification, and fractionation of macromolecular or colloidal dispersion, and microfiltration is dedicated to the separation of suspensions. Almost any membrane process can be a viable alternative to other separation processes.

3. Liquid membranes in all practical applications (supported liquid membranes, emulsion liquid membranes, volume liquid membranes) offer multiple economic advantages such as: compact equipment, application of various motor forces (gradient of chemical potential, pressure or temperature between different compartments, electric fields, etc.) small losses of membrane solvent and/or conveyor, large membrane lifetime, continuous operation in one direction (source phase → receiving phase).

4. Composite membrane processes take precedence over simple membrane technologies, combining the advantages of polysulphone, polyaniline and polypropylene, and are widely used in most diverse fields.

5. Analysing on a narrow scale the iono-molecular separations with polysulphone composite membranes, polyether capillary polypropylene composite membranes and capillary polypropylene composite membranes and cellulose derivatives, special results were obtained considering the process operating parameters as well as the specific properties of the obtained membranes.

4.2. Personal contributions

---

1. The retention of copper ions and nitrophenolics is significantly superior in ultrafiltration with composite nanoparticles to polysulphone nanoparticles. The possibility of copper complexity by both nitrophenols and nanoparticle surfaces is likely to lead to more stable aggregates in the source phase, which can sufficiently justify the increase in retention. The retention of target chemical species shall comply in all tests carried out in the series:

R NP-PSf-PANI-M> R NP-PSf-PANI-E> R NP-PSf-PANI-P> R NP-PSf

2. Analysing the operational parameters of the nitrophenolic absorption process on polymer and composite nanoparticles by colloidal ultrafiltration on composite membranes (nitrophenol concentration, nanoparticle concentration, pH of the feed solution), the following were found:

√ permeate flow is optimal at a pressure of 5 atm.

√ the retention of nitrophenolics depends on their nature.

√ good results were obtained at pH=1-3, for polysulphone nanoparticles (NP).

√ excellent retention results were obtained at pH=1-3 and pH>7, respectively, for composite nanoparticles (NP-PSf-PANI).

√ o-nitrophenol rejection is superior to the other two nitrophenols in all experiments.

3. Tests carried out over 144 hours at a pressure of 100 mm Hg or 5 L/min air flow at 25°C and pH 7 of the supply solution show that vacuum pervaping is better than vacuum. The more advanced composite membranes are those with ionizers of polyether-ether sulfated cellulose (PSf-PEEK-S) and polyaniline (PSf-PANI). The results of air pervaporization show that the composite membranes (PSf-PEEK-S and PSf-PANI) show a marked flow difference for mono-nitrophenol isomers, which could also be found in a technically exploitable selectivity. Thus, in the case of the PSf-PEEK-S composite membrane, the mono-nitro-phenol flows decrease in the order:

$$m\text{-}C_6H_5NO_3 > o\text{-} C_6H_5NO_3 > p\text{-} C_6H_5NO_3,$$

While for the PSf-PANI composite membrane the order is:

$$o\text{-} C_6H_5NO_3 - C_6H_5NO_3 > p\text{-} C_6H_5NO_3.$$

At the same time, it is noted that the flow performance of the Psf-PEEK-S composite membrane is superior during operation but shows a more pronounced downward slope.

4. The results of the separation of nitrophenolics by composite capillary polymeric liquid membrane membranes (HFCLM) based on n-alkyl medium alcohols (C6, C8 and C10) on a well-characterized tubular polypropylene support of 5 mg/L concentration in the pH 4.8 source phase, Indicate the following optimal hydrodynamic, solvent and pH parameters:

√ source phase rate of 4.0 L/min, receiving phase rate of 0.3 L/min.

√ n-octanol, the membrane solvent.

√ pH of the receiving phase ensuring maximum separation efficiency between 10 and 11.

√ pH ensuring selective separation of O- and p-nitrophenol from m-nitrophenol between 8 and 10.

The efficiency of the separation of nitrophenolics by N-alcohols liquid membrane composite membranes on polymeric capillary polypropylene support reaches more than 90 % under the established working conditions, but operation below pH 12 should be considered in order not to cause instability of the membrane on the support.

5. The transfer of nitrophenolics through a membrane system consisting of porous polypropylene (PP) capillaries impregnated with sulphonated polyetherterketone (SPEEK) was carried out in a PP-SPEEK capillary membrane module, with a useful surface of 1 m2. The determinations made using a source phase with a flow rate through the module of 4 L/min, concentration 5 mg/L nitrophenols and pH 5 or pH 7, and the receiving phase of pH 12 and the flow rate through the module of 0,3 L/min, showed that:

√ o- and p-nitrophenol transfer much faster than m-nitrophenol (the flow is almost double).

√ the source phase of the system is concentrated in m-nitrophenol, and the receiving phase in o- and p-nitrophenols.

√ transfer data correlate with the greater water solubility of m-nitrophenol.

√ mono- and dinitrophenol transfer much faster than dinitrophenol, but both mono- and dinitrophenol flow decreases over time.

√ after 4-5 hours of work, the concentration of mononitrophenol triples in the receiving phase, while the concentration of 2,4 dinitrophenol doubles in the source phase.

6. Membrane processes can help avoid environmental problems generated by acidic waters with traces of aluminum and copper generated by boilers producing heat energy in condensation. The optimal operating parameters regarding the concomitant reduction of the condensation pH of thermal installations and the removal of aluminum and copper ions using permeability through polypropylene capillary membranes with carboxymethylcellulose inserts were determined: Flow rate, pH of the receiving phase and working time. It is interesting to note that after 4 hours of operation, the performance of the process, especially neutralization, decreases, suggesting an osmotic or retro-dialytic process, caused by a decrease in the pH gradient

7. Micellar electrocoagulation and ultra-filtration wastewater treatment in the pharmaceutical industry have the best yield at working pressures of at least 4 atm and with membranes with minimum 2% to 12% PSF/DMF. Given that the industry generates around 3 million tons of potentially toxic and hazardous waste worldwide, of which 200,000 tons of sludge in the pharmaceutical industry, it is justified to try electrocoagulation and micellar ultrafiltration treatment of this type of wastewater. In this respect, the following have been determined:

√ The evaluation of the performance of electrocoagulation and micellar ultrafiltration was analysed in terms of the influence of the main operational parameters: PH, current density, working pressure, nature and concentration of the surfactant, the nature of the anode and the nature of the composite membrane.

√ The best results for electrocoagulation were obtained under the following experimental conditions: PH = 5, I = 13.94 mA/cm2, anode material: Iron. In this combination it was possible to achieve an efficiency of colour/organic matter of about 99%.

√ The best performance for micellar ultrafiltration was achieved with: Membranes based on 12% polysulfone and 2% polyaniline in dimethylformamide, surfactant: SPAN 80 to 10-4 M at a pressure of at least 4 atm and pH = 9.2

8. Chitosan (Chi) - polysulfonated (ether ketone) (sPEEK) - polypropylene tubular fibers (Chi/sPEEK/PPHF) obtained were morphologically and structurally characterized by electronic scanning microscopy (SEM), high resolution SEM (HR-SEM), dispersive Energy Spectroscopy analysis (EDAX), Fourier transform Infrared Spectroscopy (FTIR) and thermal gravimetric analysis, Differential scanning calorimetry (TGA).

Preliminary separation tests show that binary systems can effectively separate by both nanofiltration and pertraction. Pertraction would be more advantageous in terms of separation efficiency (90%), but also because the chemical species that is extracted concentrates almost an order of magnitude. Nanofiltration has the advantage of simpler operation and is applicable to multiple systems, but separation efficiency is strongly influenced by both pH and PCL. Depending on the target cation and pH and PCL conditions, retention of more than 90% (for Pb) and almost 95% (for Cu) can be achieved.

4.3. Prospects for development

The experience gained in writing the doctoral thesis will help me develop my professional career by addressing similar topics in projects in the current job. New research on membrane and membrane processes will be presented and further research will be developed to extend the application areas of membrane processes (e.g., nitrophenol separation, water purification).

To valorise and scale application of nitrophenolic separation by ultrafiltration with polysulphone and composite nanoparticles, further research is needed on the influence of physico-chemical parameters: Temperature, variable flow regime, ionic strength, and nanoparticle morphology.

The separation and removal of nitrophenolics from aqueous effluents is primarily an environmental protection issue, but at the same time can be an important technological and technical-economic application.

The objectives of the doctoral thesis were subordinated to the need to improve the methods of removal of nitro-phenols by promoting membrane techniques and methods of separation and concentration. The removal and recovery separation of nitrophenolics is a permanent goal of the membrane scientists that will be intensively analysed, studied, and researched in future works.

The separation or removal of nitrophenolics from dilute aqueous solutions has been a permanent objective for environmental protection due to toxicity, but also for the concentration and revalorisation of these compounds of high technological interest for drugs, dyes, explosives, pesticides, and phenolic resins. The nitrophenolic removal experiments aimed at establishing optimal conditions for the composite membrane separation process (Psf-PANI), considering the influence of polymer nanoparticles (NP-Psf-PANI) and the coupling of the process with proton transfer reactions capable of providing induced separation.

Development of ecological technologies with composite membranes, iono-molecular separations with composite membranes, preparation and characterization of polysulphone and composite nanoparticles, neutralization with simultaneous separation of aluminum and copper ions from condensate water through polypropylene capillaries and cellulose derivatives, polysulphone-based membranes, there are some of the study points that will certainly be addressed by researchers in order to improve the performance of membranes and membrane processes.

Professional development opportunities are also pursued through postdoctoral courses that deepen the concepts involved in work by conducting original research.

5. Annexes

5.1. Articles published in the doctoral thesis topic

5.1.1 Iono-molecular Separation with Composite Membranes. II. Preparation and characterization of polysulphone and composite nanoparticles, Hussam Nadum Abdalraheem Al Ani, **Anca Maria Cimbru**, Corneliu Trisca-Rusu, Szidonia Katalin Tanczos, Adriana Cuciureanu, Aurelia Cristina Nechifor, Revista de Chimie, Volume 68, Issue 2, pg. 203 – 209, February 2017.

5.1.2. Iono-molecular Separation with Composite Membranes. III. Nitrophenols separation on polysulphone and composite nanoparticles ultrafiltration, Hussam Nadum Abdalraheem, **Anca Maria Cimbru**, Szidonia Katalin Tanczos, Ion Spiridon Din, Adriana Cuciureanu, Ion Marius Nafliu, Gheorghe Nechifor, Revista de Chimie, Volume 68, Issue 3, pg. 427-434, March 2017.

5.1.3. Iono-molecular Separation with Composite Membranes. IV. Mono-nitrophenol's pervaporation through polysulfone composite membranes, Hussam Nadum Abdalraheem Al Ani, **Anca Maria Cimbru**, Ion Spiridon Din, Szidonia Katalin Tanczos, Ion Marius Nafliu, Adriana Cuciureanu, Materiale Plastice, Volume 54, Issue 2, pg. 353 – 358, June 2017.

5.1.4. Iono-molecular Separation with Composite Membranes. V. Nitro-phenol separation on n-alkyl alcohols supported liquid membranes, Ion Spiridon Din, **Anca Maria Cimbru**, Hussam Nadum Abdalraheem Al Ani, Ion Marius Nafliu, Szidonia Katalin Tanczos, Gheorghe Nechifor, Revista de Chimie, Volume 69, Issue 5, pg. 1084 – 1088, Mai 2018.

5.1.5. Iono-molecular Separation with Composite Membranes. VI. Nitro-phenol separation through sulfonated polyether ether ketone on capillary polypropylene membranes, Ion Spiridon Din, **Anca Maria Cimbru**, Abbas Abdul Kadhim Klaif Rikabi, Szidonia Katalin Tanczos, Simona Ticu (Cotorcea), Gheorghe Nechifor, Revista de Chimie, Volume 69, Issue 7, pg. 1603 – 1607, July 2018.

5.1.6. Neutralization with Simultaneous Separation of Aluminum and Copper Ions from Condensed Water Through Capillary Polypropylene and Cellulose Derivatives, Alexandra Raluca Grosu (Miron), Ion Marius Nafliu, Ion Spiridon Din, **Anca Maria Cimbru**, Gheorghe Nechifor, U.P.B. Sci. Bull., Series B, Vol. 82, Issue 1, pg. 25 – 34, 2020.

5.1.7. Pharmaceutical Industry Wastewater Treatment by Electrocoagulation and Micellar Ultrafiltration, Paul Constantin Albu, Hussam Nadum Abdalraheem Al Ani, **Anca Maria Cimbru**, George Alexandru Popa, Alexandra Gabriela Niculae, Alexandra Raluca Miron, Revista de Chimie, Volume 67, Issue 4, pg. 813 – 820, April 2016.

5.1.8. pH and pCl Operational Parameters in some Metallic Ion's Separation with Composite Chitosan / Sulfonated (polyether ether ketone)/Polypropylene Hollow Fibers Membranes, **Anca Maria Cimbru**, Gheorghe Nechifor, Alexandra Raluca Grosu, Szidonia-Katalin Tanczos, Vlad-Alexandru Grosu, Simona Gabriela Bungău, Paul Constantin Albu, Aurelia Cristina Nechifor, Revista MEMBRANES, Volume 12, Issue 9, pg. 833 - 859, August 2022.

5.2. Scientific communications in the topic of the doctoral thesis

5.2.1. Neutralization with Simultaneous Separation of Metallic Ions from Condensed Water Through Capillary Polypropylene and Cellulose Derivatives - XVIth International Symposium "Priorities of Chemistry for a Sustainable Development" PRIOCHEM XVI, October 28-30, October 2020.

5.3. Other pebbled articles

5.3.1. Titanium Dioxide for Biomedical Uses I. The controlled production of nanoparticles by hidrothermal synthesis moderated by dimedone, Gavril Lucian Gheorghievici, Corneliu Trisca Rusu, Elena Voicila, Ion Marius Nafliu, **Anca Maria Cimbru**, Szidonia Katalin Tanczos, Revista de Chimie, Volume: 68, Issue: 1, pg. 11-15, January 2017.

5.3.2. Cr (VI) Ion Reduction Reaction on Nickel and Stainless-Steel Electrodes in Acid Medium, Ioana Maior, Gabriela Elena Badea, Anca Cojocaru, **Anca Maria Cimbru**, Simona Bungau, Laura Endres, Revista de Chimie, Volume 70, Issue 7, pg. 2321 – 2324, July 2019.

6. Selective Bibliography

---

[1]. Alashkar, A.; Al-Othman, A.; Tawalbeh, M.; Qasim, M. A Critical Review on the Use of Ionic Liquids in Proton Exchange Membrane Fuel Cells. Membranes 2022, 12, 178. https://doi.org/10.3390/membranes12020178

[2]. Maiz-Fernández, S.; Pérez-Álvarez, L.; Silván, U.; Vilas-Vilela, J.L.; Lanceros-Méndez, S. pH-Induced 3D Printable Chitosan Hydrogels for Soft Actuation. Polymers 2022, 14, 650. https://doi.org/10.3390/polym14030650

[3]. Nechifor, A.C.; Ruse, E.; Nechifor, G.; Serban, B. Membrane materials. II. Electrodialysis with membranes of chemically modified polyetherketones. Rev. Chim. (Bucharest) 2002, 53(6), 472-482

[4]. Baicea, C.; Nechifor, A.C .; Vaireanu, D.I.; Gales, O.; Trusca, R.; Voicu, S.I. Sulfonated poly (ether ether ketone)–activated polypyrrole composite membranes for fuel cells. Optoelectronics and Advanced Materials-Rapid Communications 2011, 5, 1181-1185.

[5]. Din, I.S.; Cimbru, A.M.; Rikabi, A.A.K.K.; Tanczos, S.K.; Ticu (Cotorcea), S.; Nechifor,G. Iono-molecular Separation with Composite Membranes VI. Nitro-phenol separation through sulfonated polyether ether ketone on capillary polypropylene membranes. Rev. Chim. (Bucharest) 2018, 69(7), 1603-1607

[6]. Nechifor, A.C.; Cotorcea, S.; Bungău, C.; Albu, P.C.; Pașcu, D.; Oprea, O.; Grosu, A.R.; Pîrțac, A.; Nechifor, G. Removing of the Sulfur Compounds by Impregnated Polypropylene Fibers with Silver Nanoparticles-Cellulose Derivatives for Air Odor Correction. Membranes 2021, 11, 256. https://doi.org/10.3390/membranes11040256

[7]. Xue, Y.; Fu, R.; Xu, T. (-03). Preparation of speek and speek/chitosan composite proton-exchange membranes for application in direct methanol fuel cells. Acta Polymerica Sinica (3) 2010, 03, 285-291. http://scholarbank.nus.edu.sg/handle/10635/64463

[8]. Palacio, L.; Pradanos, P.; Calvo, J.I.; Hernandez, A. Porosity measurements by a gas penetration method and other techniques applied to membrane characterization. Thin Solid Films 1999, 348(1-2), 22-29. https://doi.org/10.1016/S0040-6090(99)00197-2

[9]. Ramaswamy, S.; Greenberg, A.R.; Peterson, M.L. Non-invasive measurement of membrane morphology via UFDR: pore-size characterization. Journal of membrane science 2004, 239(1), 143-154. https://doi.org/10.1016/j.memsci.2003.08.030

[10]. Dimulescu, I.A.; Nechifor, A.C.; Bărdacă, C.; Oprea, O.; Paşcu, D.; Totu, E.E.; Albu, P.C.; Nechifor, G.; Bungău, S.G. Accessible Silver-Iron Oxide Nanoparticles as a Nanomaterial for Supported Liquid Membranes. Nanomaterials 2021, 11, 1204.

[11]. Nechifor, A.C.; Ruse, E.; Nechifor, G. Membrane materials. I. Polyetherketones. Rev. Chim. (Bucharest) 2001, 52 (10), 531-540

[12]. Gheorghe, E.; Barbu, L.; Nechifor, G.; Luca, C. The Pb2+ cations transport through liquid membrane with macro cycle benzo-18-crown-6. Rev. Chim. (Bucharest) 2006, 57, 940–944.

[13]. Batrinescu, G.; Scutariu, R.E.; Nechifor, G.; Ionescu, I.A.; Iancu, V.I. Comparative analysis of the processes of collagen concentration by ultrafiltration using different types of membranes. Journal of Applied Polymer Science 2021, 138(12). https://doi.org/10.1002/app.50055

[14]. Nechifor, G.; Totu, E.E.; Nechifor, A.C.; Constantin, L.; Constantin, A.M.; Cărăuşu, M. E.; Isildak, I. Added value recyclability of glass fiber waste as photo-oxidation catalyst for toxic cytostatic micropollutants. Sci. Rep. 2020, 136(10). https://doi.org/10.1038/s41598-019-56836-7

[15]. Nechifor, A.C.; Pîrțac, A.; Albu, P.C.; Grosu, A.R.; Dumitru, F.; Dimulescu (Nica), I.A.; Oprea, O.; Pașcu, D.; Nechifor, G.; Bungău, S.G. Recuperative Amino Acids Separation through Cellulose Derivative Membranes with Microporous Polypropylene Fiber Matrix. Membranes 2021, 11, 429. doi: 10.3390/membranes11060429

[16]. Nechifor, G.; Păncescu, F.M.; Grosu, A.R.; Albu, P.C.; Oprea, O.; Tanczos, S.-K.; Bungău, C.; Grosu, V.-A.; Pîrțac, A.; Nechifor, A.C. Osmium Nanoparticles-Polypropylene Hollow Fiber Membranes Applied in Redox Processes. Nanomaterials 2021, 11, 2526. https://doi.org/10.3390/nano11102526

[17]. Nechifor, G.; Eftimie Totu, E.; Nechifor, A.C.; Isildak, I.; Oprea, O.; Cristache, C.M. Non-Resorbable Nanocomposite Membranes for Guided Bone Regeneration Based on Polysulfone-Quartz Fiber Grafted with Nano-TiO2. Nanomaterials 2019, 9, 985. https://doi.org/10.3390/nano9070985

[18]. Nechifor, A.C.; Goran, A.; Grosu, V.-A.; Bungău, C.; Albu, P.C.; Grosu, A.R.; Oprea, O.; Păncescu, F.M.; Nechifor, G. Improving the Performance of Composite Hollow Fiber Membranes with Magnetic Field Generated Convection Application on pH Correction. Membranes 2021, 11, 445. https://doi.org/10.3390/membranes11060445

[19]. Gill, N.S.; Taylor, F. B. Tetrahalo Complexes of Dipositive Metals in the First Transition Series. Inorganic Syntheses. 1967, 9, 136–142. doi:10.1002/9780470132401.ch37

[20]. Liddell, K.C.; Bautista, R.G. Equilibrium species concentrations in the aqueous HCl-NaCl-ZnCl2 and HCl-NaCl-CdCl2 systems: The effect of ionic strength. Hydrometallurgy, 1988, 21(1), 113-124. https://doi.org/10.1016/0304-386X(88)90020-5

[21]. Szczepański, P.; Guo, H.; Dzieszkowski, K.; Rafiński, Z.; Wolan, A.; Fatyeyeva, K.; Kujawa, J.; Kujawski, W. New reactive ionic liquids as carriers in polymer inclusion membranes for transport and separation of Cd (II), Cu (II), Pb (II), and Zn (II) ions from chloride aqueous solutions. Journal of Membrane Science 2021, 638, p.119674.

[22]. Suhalim, N.S.; Kasim, N.; Mahmoudi, E.; Shamsudin, I.J.; Mohammad, A.W.; Mohamed Zuki, F.; Jamari, N.L.-A. Rejection Mechanism of Ionic Solute Removal by Nanofiltration Membranes: An Overview. Nanomaterials 2022, 12, 437. https://doi.org/10.3390/nano12030437

[23]. Zhu, D.; Yang, Y.; Ma, T. Evaluation the Resistance Growth of Aged Vehicular Proton Exchange Membrane Fuel Cell Stack by Distribution of Relaxation Times. Sustainability 2022, 14, 5677. https://doi.org/10.3390/su14095677

[24]. Fedorov, V.A.; Kuznechikhina, M.A.; Kanarsh, I.V.; Kirnyuk, G.M.; Chernikova, G.E., Sov. J. Coord. Chem., 1978, 4,33-38

[25]. Martell, A.E.; Smith, R.M., 1982. Critical Stability Constants, Vol. 5: First Supplement, Plenum Press, New York, NY, p. 419.

[26]. Batrinescu, G.; Scutariu, R.E.; Nechifor, G.; Ionescu, I.A.; Iancu, V.I. Comparative analysis of the processes of collagen concentration by ultrafiltration using different types of membranes. J. Appl. Polym. Sci. 2021, 138, 50055.

[27]. Nechifor, G.; Totu, E.E.; Nechifor, A.C.; Constantin, L.; Constantin, A.M.; Carausu, M.E.; Isildak, I. Added value recyclability of glass fiber waste as photo-oxidation catalyst for toxic cytostatic micropollutants. Sci. Rep. 2020, 10, 136.

[28]. Nechifor, A.C.; Pîrtac, A.; Albu, P.C.; Grosu, A.R.; Dumitru, F.; Dimulescu (Nica), I.A.; Oprea, O.; Pascu, D.; Nechifor, G.; Bungau, S.G. Recuperative Amino Acids Separation through Cellulose Derivative Membranes with Microporous Polypropylene Fiber Matrix. Membranes 2021, 11, 429.

[29]. 68. Nechifor, G.; Pancescu, F.M.; Grosu, A.R.; Albu, P.C.; Oprea, O.; Tanczos, S.-K.; Bungau, C.; Grosu, V.-A.; Pîrtac, A.; Nechifor,

[30]. A.C. Osmium Nanoparticles-Polypropylene Hollow Fiber Membranes Applied in Redox Processes. Nanomaterials 2021, 11, 2526.