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POLITEHNICA Bucharest
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Chemical Engineering Field

Abstract PhD Thesis

Contributions to experimental studies on the rejection of trace nitrate anion from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes

Contribuții la studiile experimentale privind rejectia anionului nitrat în urme din apă și recuperarea toriului din matrici metalice utilizând membrane compozite de nanofiltrare

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INTRODUCTION

The PhD thesis: Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes represents an original, experimental contribution to the use of composite membranes in various and important separations, purifications and concentrations of chemical species.

The doctoral thesis has as development arguments the need to obtain pure chemical species through membrane processes or/and the removal of traces of unwanted dissolved substances found in aqueous solutions.

In particular, this doctoral thesis aimed to treat waters containing nitrate ions and the recuperative separation of thorium from various wastes after bringing them into solution.

If the removal of nitrate ions from aqueous solutions is a medical necessity in the event of their appearance in drinking water (harmful effect on young children), the separation of thorium from various wastes has a double importance: the treatment of waters that may come into contact with thorium-containing wastes and its recovery, which is important for fusion-based nuclear power plant technology.

The topic of the doctoral thesis: **Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes** falls entirely within the use of chemical process engineering in various branches of production through ecological processes, such as membrane ones, but also greening, which involve the removal, through membranes, of various contaminating chemical species from effluents.

The priorities of the research undertaken and presented in the doctoral thesis, composite membranes and nanofiltration of nitrate or thorium solutions, are fully validated by articles in specialized journals, three of which in high impact publications (Q1 or Q2).

The studies had as a premise that membrane processes can be developed both in the direction of treating effluents with a given composition and the recuperative separation of chemical species of high importance of application interest.

The basic questions that were raised in the approach of the present studies were the following:

- can composite membranes for nanofiltration be obtained, specific to trace chemical species?
- can the rejection (removal) of nitrate ion be achieved by membranes dedicated to the nanofiltration process?
- can thorium be recuperatively separated from various wastes by membrane processes?
- is the development of nanofiltration as a process, of known technical and economic efficiency, suitable for the concrete applications required in the doctoral thesis?

The doctoral thesis: **Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes** had as its central objective the obtaining of composite membranes and their application in separation, removal and recuperative separation processes.

Specifically, the doctoral thesis presents the results of research towards solving the following specific objectives:

1. obtaining polymer - polymer composite membranes
2. synthesis of polymer - complexant composite membranes
3. preparation of polymer - nanoparticle - specific complexant composite membranes
4. characterization of membranes made by high-performance techniques
5. application of nanofiltration, using the prepared membranes, to the removal (rejection) of nitrate ion from dilute aqueous solutions

6. recuperative separation of thorium from various wastes by nanofiltration and electrolysis
- The research methodology adopted for each specific objective:

1. The polymer-polymer membranes were made by the phase inversion method of a diluted polymer solution (cellulose acetate-AC, chitosan-Chi) in the pores of a capillary membrane (hollow fiber) made of propylene.

2. The polymer-complexing agent composite membranes involved the preparation of a diluted solution of polymer (poly-ether-ether-ketone-sulfonated-sPEEK) and crown ether (4-amino-benzo-15-crown-5 ether ABCE) followed by the phase inversion of the solution containing the crown ether.

3. The polymer-nanoparticle-complexing agent membranes were made by the phase inversion of cellulose acetate or polysulfone solutions. Silver nanoparticles obtained by in situ reduction and addition of nitron were dispersed in the polymer solution, as a complexing agent.

4. Membrane characterization was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravity analysis (TG), differential scanning calorimetry (DSC), Fourier transform infrared spectrometry (FTIR), infrared microscopy (MIR), energy dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS) – and dedicated process determinations.

5. Nanofiltration of dilute nitrate ion solutions was performed in a stirred vessel under inert gas pressure, for flat disc-cut membranes.

6. Nanofiltration of thorium-containing solutions was performed in a separator with a capillary fiber bundle, by introducing the solution to be separated through the membranes.

The five chapters of the doctoral thesis are:

Chapter 1. Membranes and membrane processes, presents a synthesis of the specialized literature

Chapter 2. Polymer nanocomposite membranes/Ag and nitron nanoparticles for the rejection (removal) of nitrate anion from aqueous solutions, illustrates the obtaining of planar membranes of cellulose acetate and polysulfone with silver nanoparticles or silver and nitron nanoparticles, for the rejection of nitrate anion from water.

Chapter 3. Recuperative separation of thorium and tungsten by membrane electrolysis and nanofiltration, shows how to recover thorium (minority) and tungsten (majority) from high-temperature welding electrodes by membrane processes

Chapter 4. Recuperative separation with composite membranes of thorium, tungsten and aluminum by membrane electrolysis and nanofiltration, emphasizes the possibility of separating and recovering some elements from high-temperature welding electrodes by membrane processes

Chapter 5. Recovery of thorium from dilute aqueous solutions by nanofiltration with polymer-crown ether composite membranes, shows how sPEEEK and sPEEK-ABCE membranes are prepared and used for the recovery (rejection) of thorium from water.

The doctoral thesis **Contributions to experimental studies on the rejection of trace nitrate anion from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes** contains 172 pages, 63 figures, 13 tables, and 271 bibliographic references.

PART A. SYNTHESIS OF SPECIALTY LITERATURE

Chapter 1. MEMBRANE AND MEMBRANE PROCESSES

If we focus on membrane processes, it can be stated that the membrane is a window of a multicomponent system (Figure 1), with selective permeability for the chemical species of the system [5].

The selectivity of the system can be ensured both by adjusting the window parameters and by the appropriate choice of the driving force that drives the process [6].

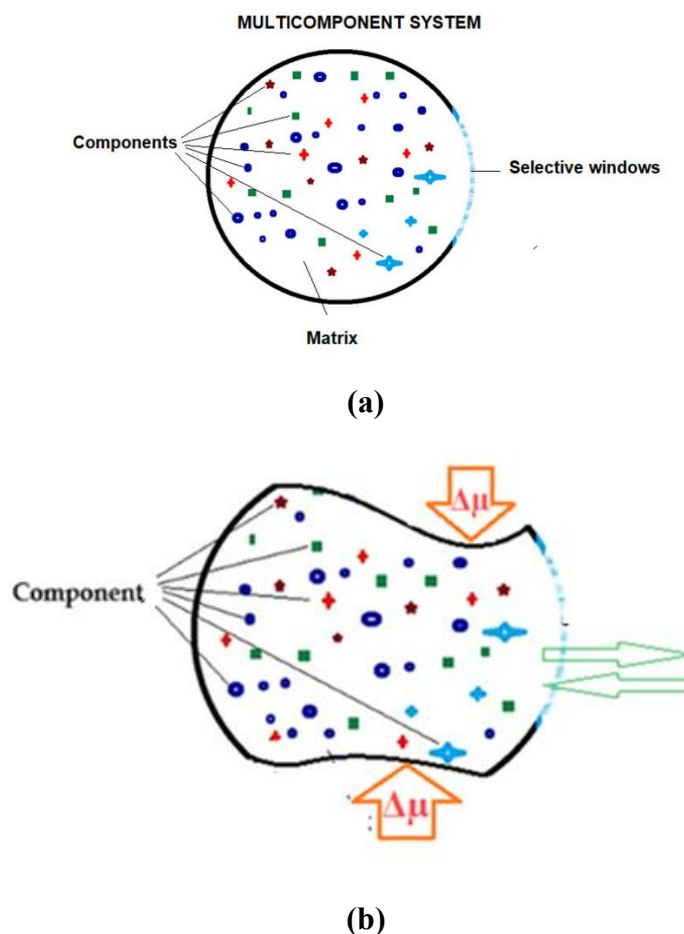


Figure 1. Multicomponent system bounded by a selective window: ions, small molecules, macromolecules, nanoparticles, microparticles, microorganisms and viruses, suspended particles: (a) system in equilibrium; (b) system subjected to a different electrochemical potential ($\Delta\mu$) [6].

This membrane allows the separation of the complex system formed by a solvent in which some ionic chemical species, molecules, macromolecules and some dispersed macromolecules or/and molecular aggregates and particles are dissolved.

In order for the membrane separation process to proceed, the system must be under a constraint or a difference in electrochemical potential or driving force ($\Delta\mu$) (Figure 1b).

PART B. ORIGINAL CONTRIBUTIONS

Chapter 2. POLYMER/AG AND NITRON NANOCOMPOSITE MEMBRANES FOR REJECTION (REMOVAL) OF NITRATE AION FROM AQUEOUS SOLUTIONS

*Chapter 2 includes the results presented in the publication reported only by the doctoral student: Razvan, A., **Man, G. T.**, Dumitru, F. *, Pandeale, M., Trusca, R., Motelica, L., ... & Nechifor, G.* (2024). Nanocomposite membranes prepared from cellulose acetate or polysulfone with Ag0 nanoparticles and nitron reagent for nitrate ion removal. *Desalination and Water Treatment*, 318, 100400. <https://doi.org/10.1016/j.dwt.2024.100400>*

The specific objectives addressed in this chapter are:

- obtaining asymmetric membrane from polysulfone by phase inversion (Psf)
- preparation of asymmetric membrane from cellulose acetate (CA)
- synthesis of composite membrane Psf and CA with silver nanoparticles
- synthesis of composite membrane containing polymer/silver nanoparticles and nitrone
- nanofiltration of aqueous solutions containing nitrate anions with the prepared composite membranes
- proposal of a mechanism for the removal, by nanofiltration, of nitrate anions

2.1. Introduction

Due to their high solubility in water, nitrates and nitrites are common water pollutants when used in nitrogen-containing fertilizers [51].

In Europe, the Nitrates Directive (91/676/EEC) and the Drinking Water Directive (98/83/EC) [52, 53] aim to control nitrogen pollution and establish a maximum allowable nitrate concentration of 50 mg/L in surface or groundwater as drinking water sources.

This chapter reports on the first use of nitrone as a complexing agent in nanocomposite membranes designed for nanofiltration. Knowing that nanofiltration membranes are ineffective in rejecting the monovalent nitrate ion, we considered the preparation of polysulfone cellulose acetate membranes functionalized with the nitrate-selective reagent nitrone, a heterocyclic compound that has been used for over 100 years as a reagent for the gravimetric determination of nitrate [88].

Given recent discoveries in nitrone chemistry, namely the knowledge about the formation of highly stable complexes with fabrication metals [89–92], we exploited this fact to facilitate the

anchoring of nitrene ligands on the membrane surface of Ag⁰ nanoparticles. To capitalize on the benefits brought by both Ag⁰ and nitrene nanoparticles in membranes, we synthesized new membranes based on cellulose acetate (CA) and polysulfone (Psf): M1 (CA 20%), M2 (CA 20% + Ag⁰ nanoparticles), M3 (CA 20% + Ag⁰ nanoparticles, impregnated with nitrene), M4 (CA 20% + Ag⁺: nitrene complex, molar ratio 1:1), M5 (Psf 15%), M6 (Psf 15% + Ag⁰ nanoparticles), M7 (Psf 15% + Ag⁰ nanoparticles, impregnated with nitrene) and M8 (Psf 15% + Ag⁺: nitrene complex, molar ratio 1:1), suitable for the nanofiltration process and capable of removing nitrate ions "by precipitation" on the membrane surface.

2.2. Results and Discussion

2.2.1. FTIR spectra and IR microscopy mapping of membranes

To obtain information on the structure and morphology of the membranes, FTIR microscopy analysis and IR mapping of the membranes were performed (Figure 2)

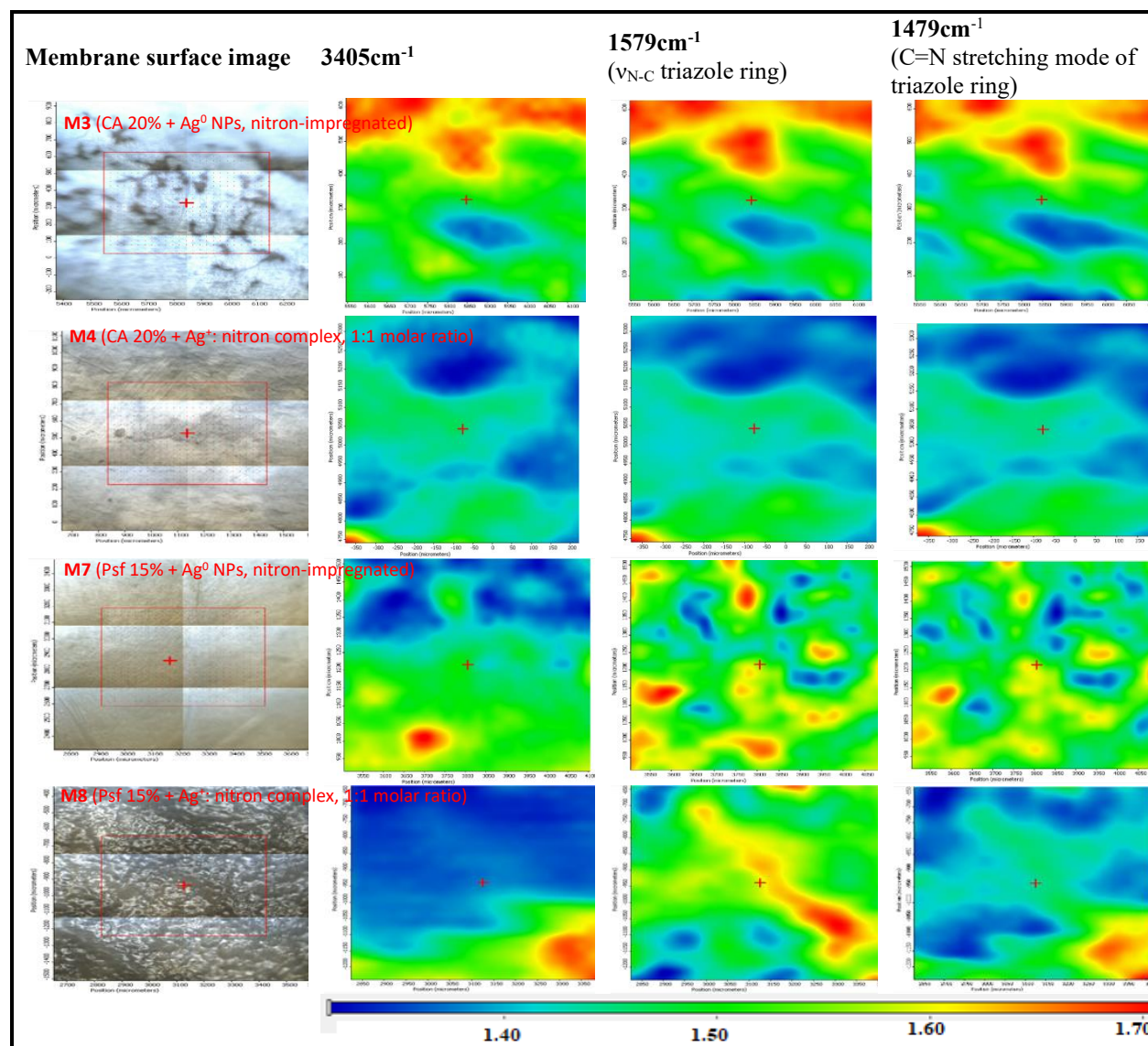


Figure 2. FTIR microscopy images recorded on membranes M3 (CA 20% + Ag0 NP, impregnated with nitron), M4 (CA 20% + Ag⁺: nitron complex, molar ratio 1:1), M7 (Psf 15% + Ag0 NP, impregnated with nitron) and M8 (Psf 15% + Ag⁺: nitron complex, molar ratio 1:1); the maps are color-coded according to the intensity of the peak heights (low intensities are coded in blue, high intensities in red, intermediate intensities in green, yellow and orange).

Water permeability experiments (Figure 3) showed that the M1-M8 membranes are suitable for use in the nanofiltration process, with water flux values ranging from 86.78-123.4 L/m²·h for the cellulose acetate-based membranes, M1-M4, and from 23.44-37.87 L/m²·h for the polysulfone-based membranes, M5-M8, in dead-end filtration experiments at a pressure of 1000 mbar. As shown in Figure 2.10, water permeability measurements showed a slight increase in the flux of pure water through the M6 (Psf 15% + Ag0 NPs), M7 (Psf 15% + Ag0 NPs, impregnated with nitron) and M8 (Psf 15% + Ag⁺: nitron complex, ratio 1:1) membranes compared to the M5 (Psf 15%) membrane, used as a reference. Regarding the permeability of M6-M8, the increase in water flux through the membranes can be correlated with the higher hydrophilicities brought by the incorporation of Ag0 nanoparticles into these membranes [83] and also with the silver-induced changes in the membrane morphologies. In the feed solutions, the NO₃⁻ concentration of 100 mg/L was kept constant for all pH values.

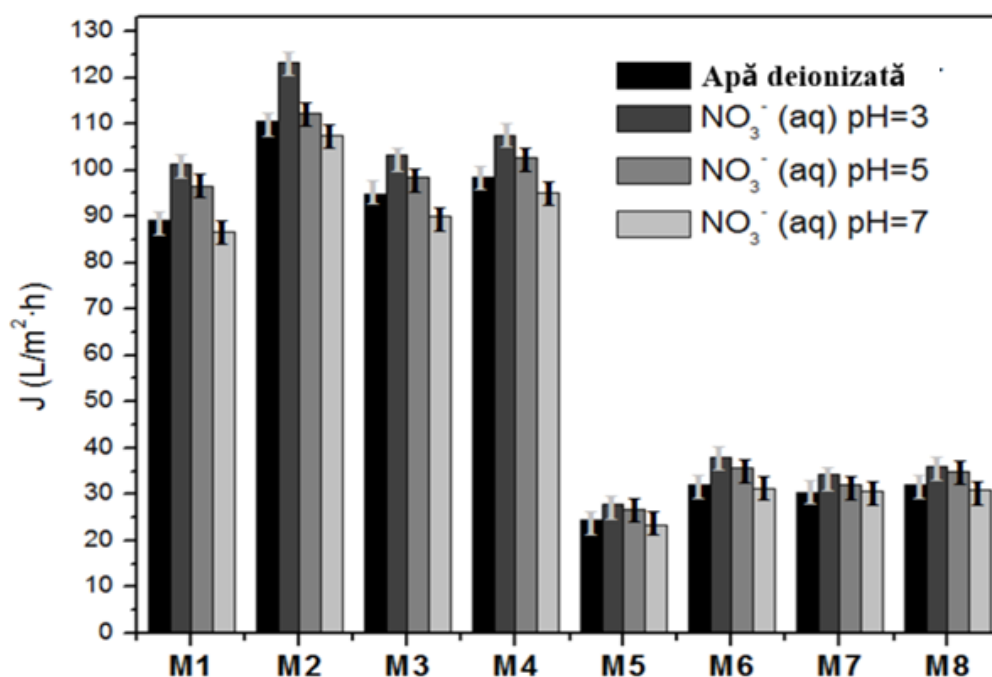


Figure 3. Water flux values for membranes M1-M8 in end-to-end nanofiltration experiments.

Table 1. Nitrate retention values for membranes M1-M8 in end-to-end nanofiltration experiments. The experiments were repeated three times, and the results presented are mean values, s.d. = ±3%

Membrane	R (%) NO ₃ ⁻ (aq) pH=3	R (%) NO ₃ ⁻ (aq) pH=5	R (%) NO ₃ ⁻ (aq) pH=7
M1	13,10	15,75	18,00
M2	42,30	59,48	73,,78
M3	69,54	87,82	94,40
M4	55,68	76,45	87,21
M5	8,20	11,04	13,15
M6	23,48	28,63	32,20
M7	34,20	38,96	43,44
M8	30,15	33,65	40,08

Chapter 3. RECUPERATIVE SEPARATION OF THORIUM AND TUNGSTEN BY MEMBRANE ELECTROLYSIS AND NANOFILTRATION

Chapter 3 includes the results presented in the publication reported only by the doctoral student:

Man, G. T., Albu, P. C., Popescu, D. I., Marinescu, V.E. & Nechifor, A. C. (2024). Thorium Recovery from the Tungsten Welding Electrodes by Electrolysis and Nanofiltration. *U.P.B. Sci. Bull., Series B*, 86(2), pp.81-92

De asemenea **capitolul 3** include o parte din publicația raportată doar de doctorand:

Man, G. T., Iordache, A. M., Popescu, D. I., Zgavarogea, I. R., & Șuțan, N. A. (2026). Thorium Valorization at the Interface of Technology, Risk, and Sustainability. *Toxics*, 14(3), 193. <https://doi.org/10.3390/toxics14030193>

The specific objectives addressed in this chapter are:

- preparation by nanofiltration of composite membranes of polypropylene tubular fibers with chitosan (Chi/PPHFM)
- obtaining by nanofiltration of composite membranes of polypropylene tubular fibers with ethylene-propylene-diene sulfonate terpolymer (sEPDM/PPHFM)
- electrolysis of high-temperature welding electrodes through membranes
- nanofiltration of thorium and tungsten solutions from the two compartments of the membrane electrolyzer
- interpretation of thorium and tungsten separation by Pourbaix diagrams of the obtained results

3.1. Introduction

The occurrence of thorium in waste electrical and electronic equipment (WEEE) is surprising, but also undesirable [103, 104]. The presence of thorium among WEEE is caused by its multiple domestic applications (crucibles, electrical jackets, refractory bricks, opto-electronic devices) [105, 106]. Thorium is also used to make high-temperature welding electrodes [107, 108]. The concentration of thorium in tungsten welding electrodes is between 1.0 and 7.0%, which requires its recuperative separation [110].

3.2. Results and Discussions

Nanofiltration of thorium dioxide dispersions is performed, at a pressure of 5 to 9 atmospheres, through the two types of membranes prepared in a module (Figure 4) in which the dispersion is the feed solution, the concentrate contains thorium dioxide, and the permeate is an aqueous solution of imposed pH.

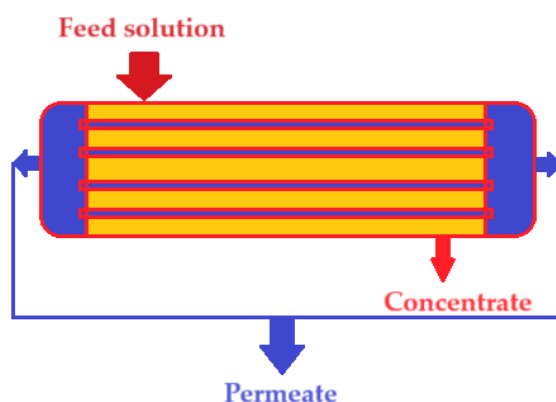


Figure 4. Nanofiltration of thorium dioxide dispersions in solutions of imposed pH

After two hours of electrolysis, the electrode surface is analyzed (Figure 5), observing, in the selected area (Figure 5b), the removal of thorium from the tungsten electrode matrix. In this case, the composition determined by EDAX reveals W 94.3 and O 5.7.

The results obtained were interpreted using Pourbaix diagrams (Figure 6).

The hydrodynamic performances, permeate fluxes, were monitored by varying the working pressure (Figure 7).

Separation (recovery) efficiency (EE) of acidic and alkaline nanodispersions, respectively, as a function of the pressure in the nanofiltration module (Figure 8).

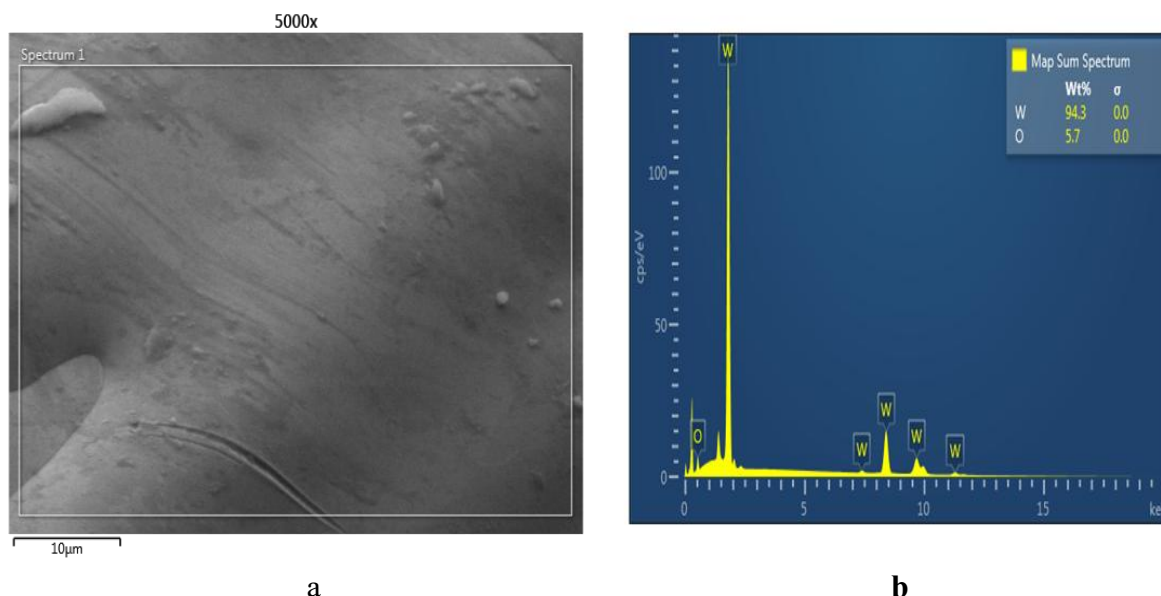


Figure 5. Microstructure of the electrode area after anodic dissolution of thorium (a) and EDX analysis of the selected area (b)

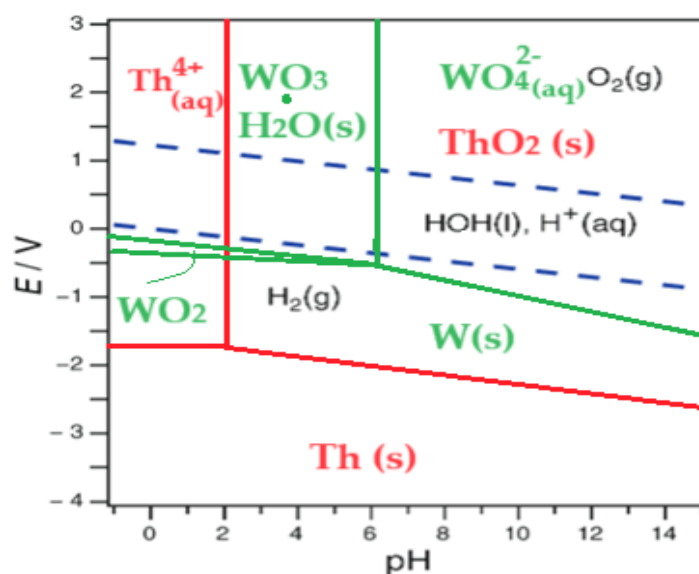


Figure 6. Superimposed Pourbaix diagrams of thorium (red) and tungsten (green) and the stability domain of water (blue parallels)

The results obtained are in good correlation with the results presented in the literature [136].

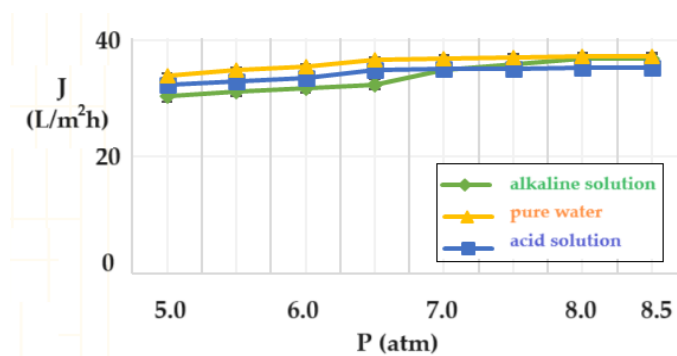


Figure 7. Variation of the fluxes (J) of pure water, acidic and alkaline nanodispersion, respectively, as a function of the pressure in the nanofiltration module

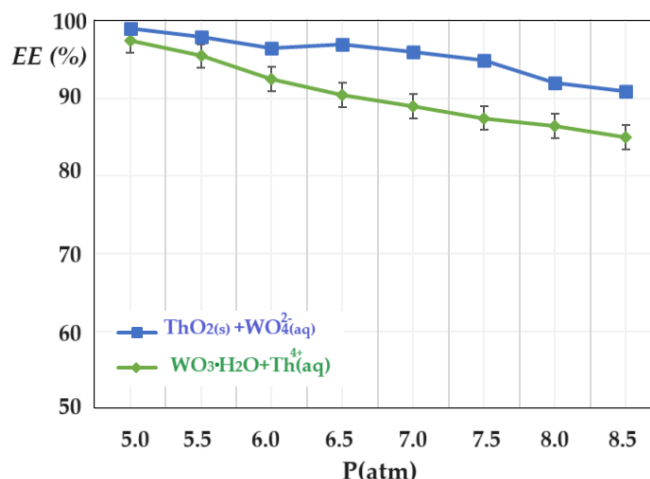


Figure 8. Variation of separation (recovery) efficiency (EE) of acidic and alkaline nanodispersions, respectively, as a function of the pressure in the nanofiltration module

Chapter 4. RECUPERATIVE SEPARATION OF THORIUM, TUNGSTEN AND ALUMINUM WITH COMPOSITE MEMBRANES BY MEMBRANE ELECTROLYSIS AND NANOFILTRATION

Chapter 4 includes the results presented in the publication reported only by the doctoral student:

Man, G. T., Albu, P. C., Nechifor, A. C., Grosu, A. R., Popescu, D. I., Grosu, V.-A., Marinescu, V. E., & Nechifor, G.* (2024). Simultaneously Recovery of Thorium and Tungsten through Hybrid Electrolysis–Nanofiltration Processes. *Toxics*, 12(2), 103. <https://doi.org/10.3390/toxics12020103>

Chapter 4 also includes a part of the publication reported only by the doctoral student:

Man, G. T., Iordache, A. M., Popescu, D. I., Zgavarogea, I. R., & Şuţan, N. A. (2026). Thorium Valorization at the Interface of Technology, Risk, and Sustainability. *Toxics*, 14(3), 193. <https://doi.org/10.3390/toxics14030193>

The specific objectives addressed in this chapter are:

- Preparation of flat membranes from sulfonated polyether-ether-ketone
- Obtaining composite membranes from tubular polypropylene membranes, as support (PHF-M), and high molecular weight chitosan as active, selective layer, (C-PHF-M)
- Membrane electrolysis of high temperature welding electrodes (W/Th/Al)
- Nanofiltration of colloidal systems from membrane electrolysis, which include tungsten, thorium and aluminum compounds
- Interpretation of electrolysis results by Pourbaix diagrams

4.1. Introduction

The development of technologies for recovering metals from municipal waste requires sound arguments regarding the value of the separated metals or the negative environmental impact if they are not separated and recycled [146-148]. A special case, recently reported [149], shows that metals such as thorium or tungsten originating from electrical and electronic equipment or construction materials can occur in municipal waste [150,151].

4.2. Results and discussions

The interest in the element thorium is justified both because it is a material with immense potential for energy generation, including nuclear energy, but also because, although it is radioactive, it is the subject of domestic applications that capitalize on the high-temperature resistance of thorium dioxide (lamps, protective jackets, crucibles, welding electrodes) or for its special refractive index (lenses, glasses, high-resolution opto-electronic equipment).

4.2.1. Membrane characteristics

Energy dispersive X-ray spectroscopy of the membrane after holding in the calcium hydroxide bath (Figure 9) provided the elemental composition.

4.2.2. Electrolysis of tungsten electrodes for thorium and tungsten recovery

The raw material required for the hybrid thorium recovery process is the scraps and ends of high-temperature welding electrodes. These materials can be selectively collected on construction sites or industrial production halls and subjected to membrane electrolysis followed by nanofiltration where thorium is recovered as thorium dioxide and tungsten as tungstate solution.

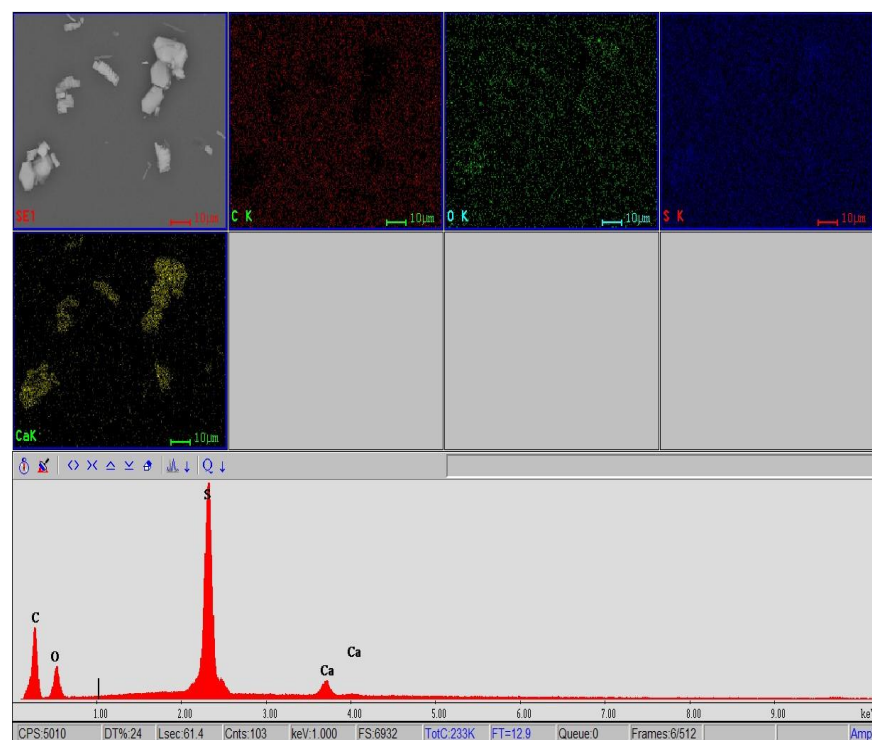


Figure 9. Energy dispersive X-ray spectroscopy of the membrane after holding in the calcium hydroxide bath.

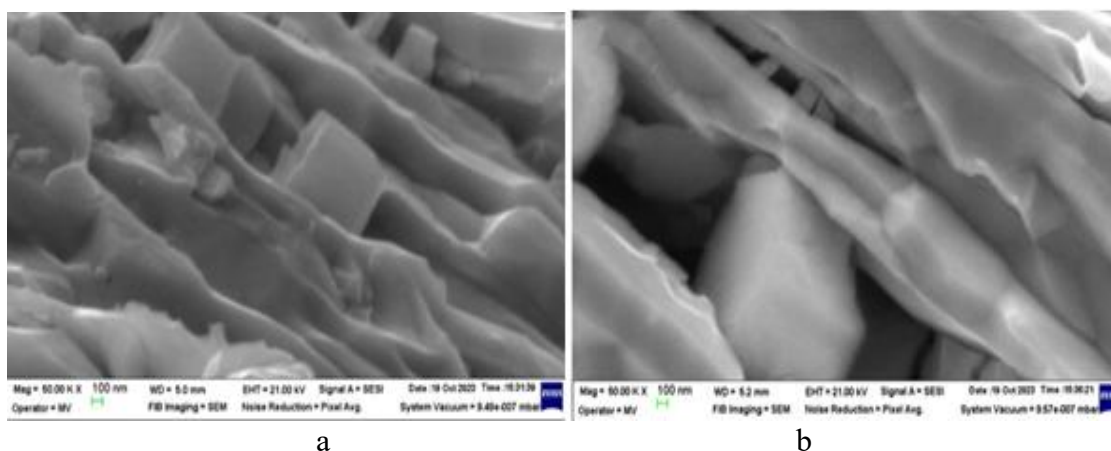


Figure 10. Scanning electron microscopy image for: a) electrode section 20,000X, detail of electrode section 50,000X

The elemental distribution (Figure 11 a,b) confirms the assumption that tungsten forms filaments and platelets that are joined by nanometric cubes of thorium dioxide. Aluminum, which is distributed over the entire surface of the electrode fracture (Figure 10), mainly covers the tungsten filaments and platelets, suggesting that it is an element with a binding role. The quantitative composition of the surface (Figure 11a) is shown in figure 11 b: W 89.4%; thorium 7.1%; oxygen 2.5% and aluminum 1.0%.

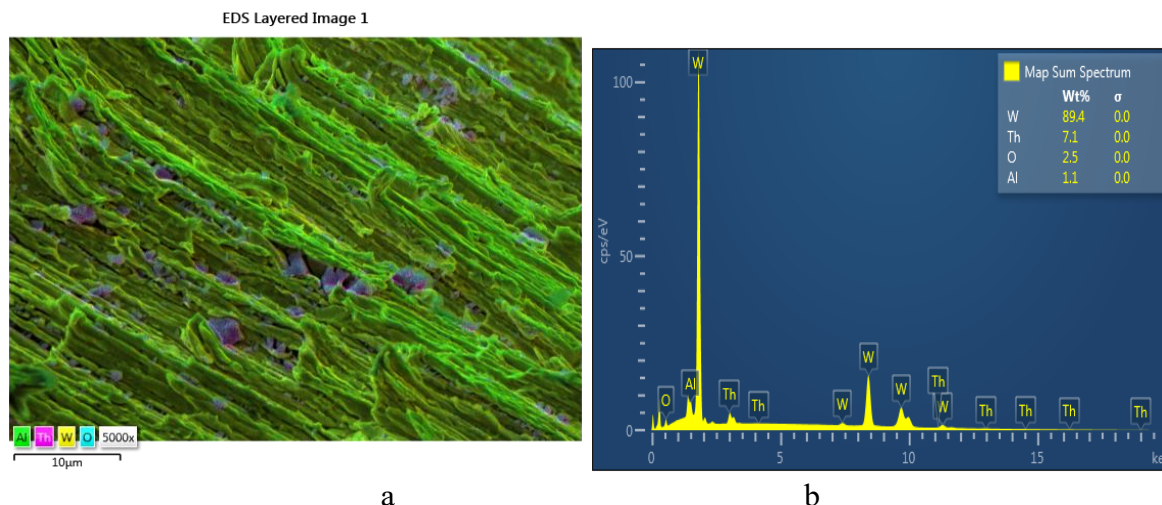


Figure 11. The quantitative composition of the surface (a) is shown in part (b)

The schematic of the hybrid membrane electrolysis and tungsten electrode nanofiltration plant is shown in figure 12.

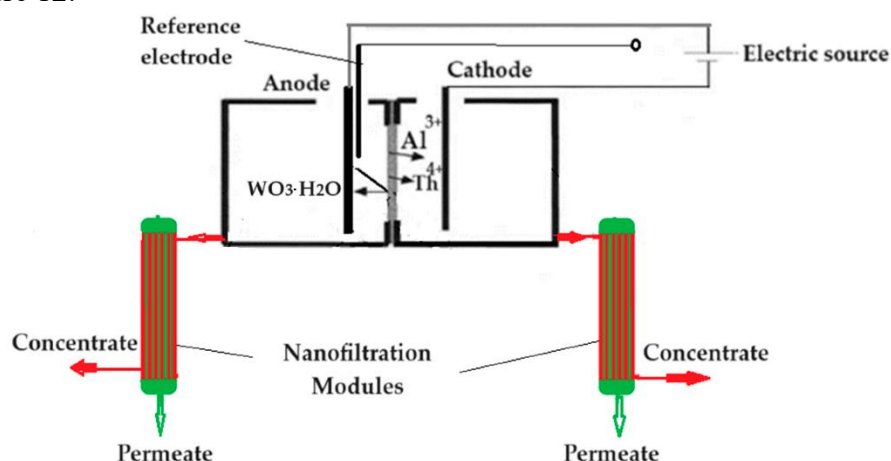


Figure 12. Schematic of the hybrid membrane electrolysis and nanofiltration installation of tungsten electrodes

The interpretation of the results was carried out by superimposing the Pourbaix diagrams [197-200] of the three elements (Figure 13) and it is possible to specify, at constant potential, the chemical species for each pH in the anodic space (Table 2).

At a potential of 20.0 V and zero pH in the anodic space and pH 13 in the cathodic space, following electrolysis, tungsten will be found in the form of tungstic acid $WO_3 \cdot H_2O$ (s), thorium as Th^{4+} (aq), and aluminum as Al^{3+} (aq) (Figure 13). The two cations, Th^{4+} and Al^{3+} , will migrate to the cathode, and the tungstic acid will remain in the anodic space. The tungsten in the anodic space will be recovered by nanofiltration through the module attached to this space. The thorium will be immobilized as a solid in the cathode space in the form of thorium dioxide (ThO_2), and the aluminum ion will pass into soluble sodium aluminate (AlO_2^-). By nanofiltration [201-203] of the

solution in the cathode space through the module attached to this space, the thorium dioxide will be retained on the membrane (concentrated) and the aluminate ion as permeate.

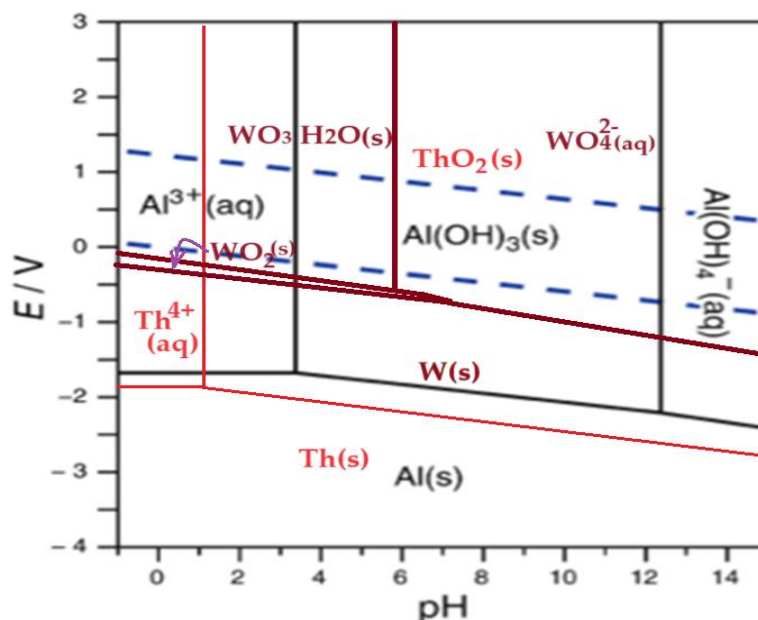


Figure 13. Overlaid Pourbaix diagrams of tungsten (purple), thorium (red), aluminum (black) and the blue dotted lines delimiting the water stability range.

Table 2. Speciation of tungsten, thorium and aluminum elements as a function of potential and pH in the anodic space and pH 13 in the cathodic space

Metallic Element or Membrane Reactive Group	Metal Element Speciation at Variable pH in the Anodic Space, at pH 13 in the Cathodic Space and 20.0 V Anodic Potential				
	0–1	1–3	3–6	6–12	>12
Wolfram	WO ₃ ·H ₂ O(s)	WO ₃ ·H ₂ O(s)	WO ₃ ·H ₂ O(s)	WO ₄ ²⁻ (aq)	WO ₄ ²⁻ (aq)
Thorium	Th ⁴⁺ (aq)	ThO ₂ (s)	ThO ₂ (s)	ThO ₂ (s)	ThO ₂ (s)
Aluminum	Al ³⁺ (aq)	Al ³⁺ (aq)	Al(OH) ₃ (s)	Al(OH) ₃ (s)	AlO ₂ ⁻ (aq)
sPEEK–M *	HSO ₃ –Ar	HSO ₃ –Ar	⁻ SO ₃ –Ar	⁻ SO ₃ –Ar	⁻ SO ₃ –Ar
C–PHF–M **	⁺ H ₃ N–R	⁺ H ₃ N–R	⁺ H ₃ N–R	H ₂ N–R	H ₂ N–R

* Ar—aromatic group; ** R—alkyl group.

Variation of thorium concentration in the permeate during nanofiltration of thorium dioxide nanodispersion as a function of pH: blue thorium dioxide obtained from the electrolysis process

of the welding electrode, and green thorium dioxide obtained by precipitation from solution (Figure 14)

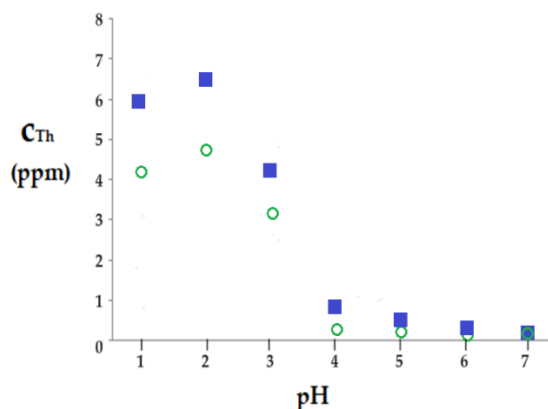


Figure 14. Variation of thorium concentration in permeate during nanofiltration of thorium dioxide nanodispersion as a function of pH: blue thorium dioxide obtained from the electrolysis process of the welding electrode, and green thorium dioxide obtained by precipitation from solution

Chapter 5. THORIUM RECOVERY FROM DILUTED AQUEOUS SOLUTIONS BY NANOFILTRATION WITH POLYMER-CROWN ETHER COMPOSITE MEMBRANES

Chapter 5 includes the results presented in the publication reported only by the doctoral student:

Nechifor, A. C., Albu, P. C., Motelica, L., **Man, G. T.**, Grosu, A. R., Tanczos, S.-K., Grosu, V.-A., Marinescu, V. E., & Nechifor, G. * (2024). Thorium Recovery with Crown Ether–Polymer Composite Membranes. *Applied Sciences*, 14(21), 9937. <https://doi.org/10.3390/app14219937>

Chapter 5 also includes a part of the publication reported only by the doctoral student:

Man, G. T., Albu, P. C., Nechifor, A. C., Grosu, A. R., Tanczos, S.-K., Grosu, V.-A., Ioan, M.-R., & Nechifor, G. * (2023). Thorium Removal, Recovery and Recycling: A Membrane Challenge for Urban Mining. *Membranes*, 13(9), 765. <https://doi.org/10.3390/membranes13090765>

The specific objectives addressed in this chapter are:

- Preparation of planar membranes of sulfonated polyether-ether-ketone (sPEEK)
- Preparation of planar composite membranes based on sulfonated polyether-ether-ketone (sPEEK) and 4-amino-benzo-15-crown-5 ether (ABCE).

- Morphological, compositional, structural and process performance characterization of the prepared membranes

- Recovery (retention or rejection) of thorium by nanofiltration using the obtained membranes

5.1. Introduction

Regardless of the nature of the systems from which thorium originates, natural waters that come into contact with rare earth ores or composite metal industrial wastes, it must be recovered, removed, separated, rejected or retained [51].

5.2. Results and discussions

The morphological, compositional and structural characterization of the prepared membranes was carried out by scanning electron microscopy (SEM), energy dispersive X-ray (EDAX) and thermal analysis (TG and DSC), and the performances in the thorium rejection process from acidic aqueous solutions were carried out by determining the permeate fluxes (J) and thorium retention (R%).

5.2.1. Characterization of the prepared membranes

5.2.1.1. Morphological characterization

The cross-sectional morphology of the two membranes: the sPEEK membrane (Figure 15) and the ABCE-sPEEK composite membrane was examined in section and on the selective upper surface using scanning electron microscopy (Figure 16).

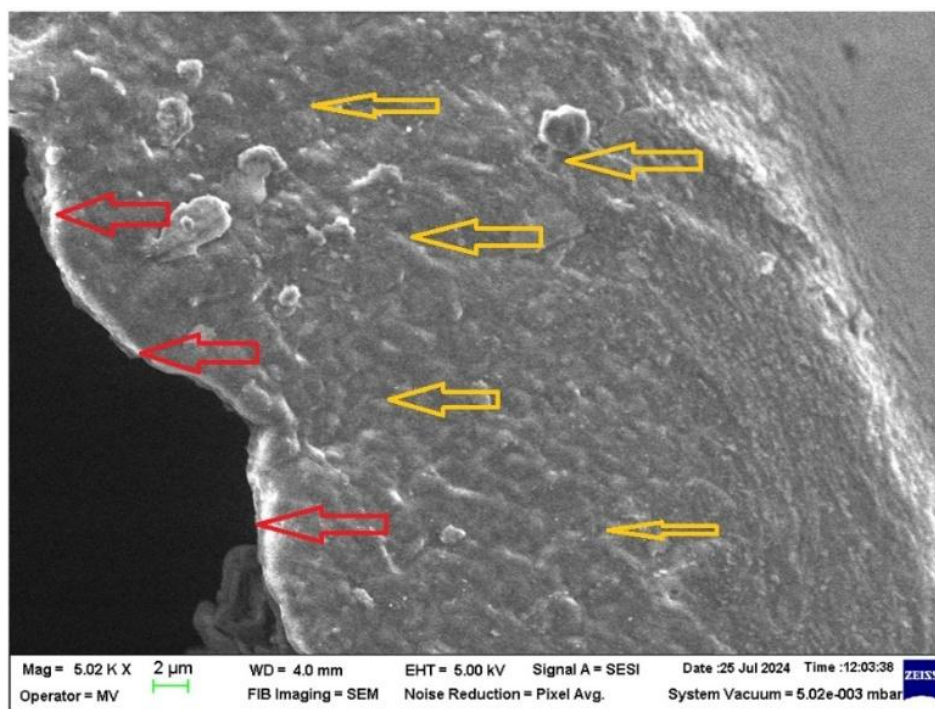


Figure 15. Scanning electron microscopy images of the sPEEK membrane section

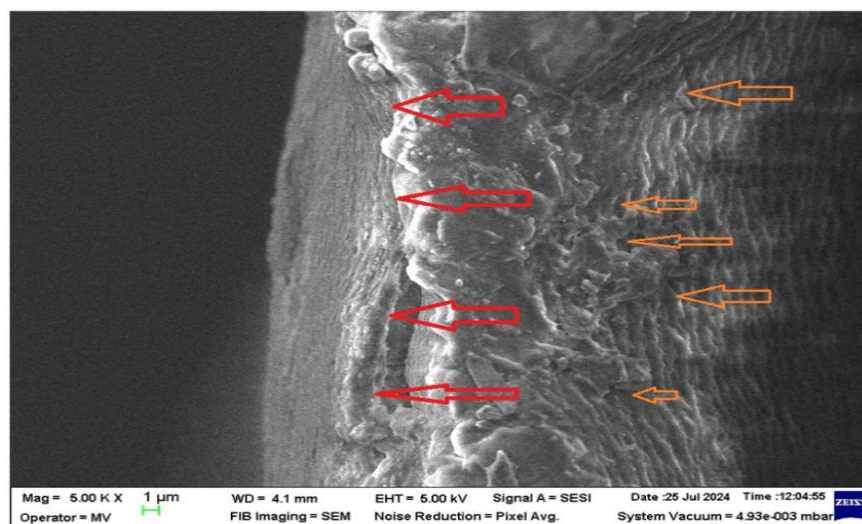


Figure 16. Scanning electron microscopy images of the ABCE-sPEEK composite membrane: section;

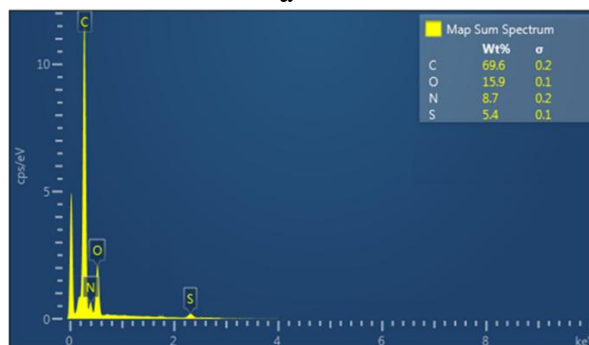
5.2.1.2. Compositional analysis

Compositional analysis (EDAX) was performed on the membrane surface (Figures 17 a and b).

The EDAX spectrum of the sPEEK membrane (Figure 17) highlights the presence of 80.5% carbon, 12.5% oxygen and 6.8% sulfur



a



b

Figure 17. Energy dispersive X-ray spectroscopy: a-sPEEK membrane; b-ABCE-sPEEK composite membrane

The appearance of thorium dioxide is also related to the pH of the solution [268, 269], but in this work we consider the separation of thorium from acidic solutions, pH from 0 to 4, when the predominant chemical species is Th^{4+} (Figure 18).

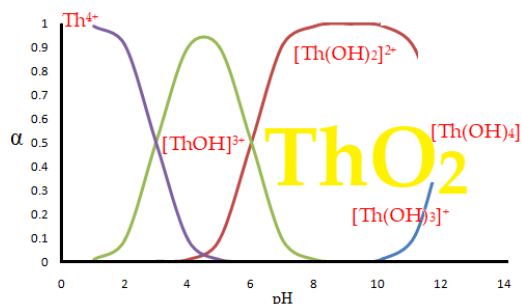


Figure 18. Hypothetical stability diagram of thorium hydroxo-complexes in aqueous medium reprinted from [249].

5.2.1.3. Determination of hydrodynamic performances of prepared membranes

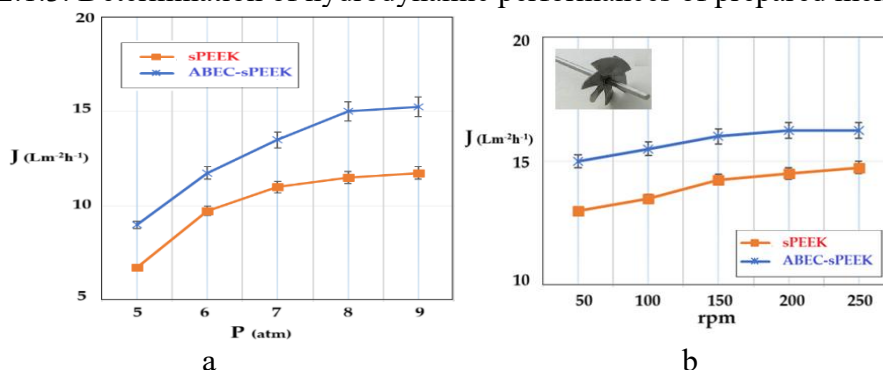


Figure 19. Dependence of permeate flow (J) on: a-working pressure (P), b-stirring rate (rpm)

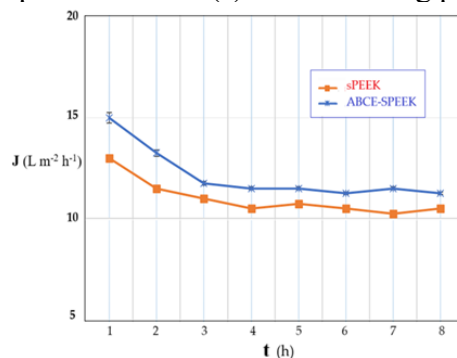


Figure 20 Flux dependence (J) as a function of operating time: sPEEK membrane (orange) and ABCE-sPEEK composite membrane (blue)

The performance of the ABCE-sPEEK composite membrane is in all operating situations superior to the performance of the reference sPEEK membrane.

PART C. General conclusions, originality and research perspectives

C. 1. General conclusions

The doctoral thesis: Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metal matrices using composite nanofiltration membranes represents the original, theoretical and experimental exemplification of the use of composite membranes in various and important separations of chemical species.

Chapter 1 - SYNTHESIS OF SPECIALTY LITERATURE, shows the following:

1. Membranes and membrane processes developed after the implementation of two technologies: obtaining drinking water from seawater and hemodialysis (artificial kidney).

2. The membrane is constituted as a window of a complex system of chemical species, which opens under an electro-chemical potential difference (driving force).

Chapter 2- POLYMER/AG AND NITRON NANOCOMPOSITE MEMBRANES FOR THE REJECTION (REMOVAL) OF NITROGEN AION FROM AQUEOUS SOLUTIONS,

Starting from cellulose acetate or polysulfone polymers, by incorporating either Ag0 nanoparticles or the Ag0:nitron nanoparticle complex into these materials, eight new nanocomposite membranes suitable for use in nanofiltration processes for the rejection (removal) of nitrates from aqueous solutions were obtained.

From a thorough analysis of the specialized literature on nitrate removal by commercial nanofiltration membranes, we showed that cellulose-based nanocomposite membranes, M2-M4, are comparable or even more efficient, in terms of rejection (retention or removal) and transmembrane fluxes, than the commercial membranes previously used in nitrate removal by nanofiltration.

The better performance of nanocomposite membranes M2-M4 in the rejection (removal) of nitrate ions from aqueous solutions can be explained by a combined mechanism of chemisorption on nitron centers with adsorption on Ag0 nanoparticles or on the polymeric material. The incorporation of both silver nanoparticles and the nitron reagent into the membranes led to the improvement of their nanofiltration performance and made them suitable for the rejection (removal) of nitrates from water. The M3 membrane, obtained by functionalizing cellulose acetate with Ag0/nitron, demonstrated a high nitrate rejection (94.4%) and a better permeability value (89.98 L/m²·h) than commercial nanofiltration membranes, and further research will be conducted to evaluate the performance of these membranes.

Chapter 3 - RECUPERATIVE SEPARATION OF THORIUM AND TUNGSTEN THROUGH MEMBRANE ELECTROLYSIS AND NANOFILTRATION

Among the waste electrical and electronic devices and equipment (EEED), those containing thorium are extremely hazardous.

Chapter 3 of the doctoral thesis reflects the resolution of the specific objectives through a method of recuperative separation of thorium from waste high-temperature welding electrodes W-Th:

For the mineralization of the electrodes, electrolysis was chosen in a strongly acidic (pH 1) or strongly basic (pH 13) environment at an anodic potential of 2.0 V.

After electrolysis, thorium separation is done by nanofiltration through a Chi/PPHFM composite membrane for the acidic solution and nanofiltration through a sEPDM/PPHFM composite membrane for the basic solution.

From the acidic solution, the thorium ion is recovered in the permeate, and from the basic solution, the thorium dioxide is recovered in the concentrate. Simultaneously with the thorium recovery, tungsten is also recovered from the membrane processes as tungstic acid and, respectively, as tungstate ion.

The separation efficiency (EE) of thorium is over 95% at an operating pressure of 5 atm.

The results of the study were interpreted and justified by POURBAIX diagrams.

Chapter 4 - RECUPERATIVE SEPARATION OF THORIUM, TUNGSTEN AND ALUMINUM WITH COMPOSITE MEMBRANES BY MEMBRANE ELECTROLYSIS AND NANOFILTRATION

The specific objectives of this chapter have been answered and the following are presented:

The recovery and recycling of metals that generate toxic ions in the environment is of particular importance, especially when these are tungsten, aluminum and, especially, thorium.

The separation and recovery of tungsten, thorium and aluminum from high-temperature welding electrodes in a hybrid membrane electrolysis and nanofiltration installation has been presented.

The membranes used are sulfonated polyether ether ketone (sPEEK) for the separation of the anodic and cathodic spaces in the electrolysis cell and chitosan deposited on polypropylene capillary membranes (C-PHF-M) in the nanofiltration module.

By electrolysis at 20.0V and variable pH, speciations of the three studied elements could be separated. Favorable conditions for both electrolysis and nanofiltration were obtained at pH from 6 to 9, when soluble tungstate ion was formed, and aluminum hydroxide and thorium dioxide as solids. By a first nanofiltration, tungsten ion is obtained in the permeate and thorium dioxide and aluminum hydroxide in the concentrate. By adding a pH 13 solution over the two precipitates, aluminum is solubilized as soluble sodium aluminate, which will be found after the second nanofiltration in the permeate, thorium dioxide remaining intact (error of ± 0.1 ppm) on the C-PHF-M membrane.

Variants of the operating procedure of the hybrid electrolysis and nanofiltration plant were suggested by superimposing the Pourbaix diagrams of tungsten, thorium and aluminum.

Increasing the working potential above 20.0V does not bring about any change in chemical speciation other than the accentuated appearance of molecular oxygen release in the anodic space.

Chapter 5 – THORIUM RECOVERY FROM DILUTED AQUEOUS SOLUTIONS BY NANOFILTRATION WITH POLYMER-CROWN ETHER COMPOSITE MEMBRANES

In this part of the doctoral thesis (Chapter 5) the mentioned objectives regarding the recovery (rejection) of thorium from aqueous solutions of concentration similar to the background level in the regions where rare earths are exploited (10^{-4} - 10^{-7} mol/L) or composite metal industrial wastes (10^{-3} - 10^{-6} mol/L) are addressed.

The thorium recovery technique was nanofiltration through integral or composite polymeric membranes.

An integral polymeric membrane made of sPEEK and a composite membrane incorporating sPEEK and a crown ether (ABCE) whose cavity has a radius similar to the ionic radius of thorium were prepared.

Both membranes were obtained by immersion-precipitation from polymeric solutions in sulfuric acid.

The complex morphological, structural and process characterization, with techniques similar to those presented in the previous chapters, shows that the composite membrane has superior performance, compared to the integral polymer membrane, under the same operating conditions.

The thorium recovery (rejection) for exceeds the value of 90%, for both membranes, which makes them usable at the industrial pilot level.

Other complexing compounds can also be tested to enhance the performance of the nanofiltration process, which can be a goal of further research.

To explain the results obtained, an adsorption-complexation separation mechanism was proposed.

DOCTORAL THESIS - Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes - HAS MET THE GENERAL OBJECTIVE AND ALL SPECIFIC OBJECTIVES BEING VALIDATED BY SIX PUBLISHED ISI ARTICLES, OF WHICH THREE ARE HIGH IMPACT (Q1 and Q2 categories).

The results of the thesis were presented at three international conferences and symposia.

C2. Originality of research results

As part of the research carried out during the doctoral internship for the development of the doctoral thesis - Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes, the following original results were obtained:

Preparation of composite membranes:

- o Polymer (PP) – polymer (sPEEK) composite membrane for nanofiltration
- o Polymer (PP) – polymer (Chitosan) composite membrane for nanofiltration
- o Polymer composite membrane (Psf and CA) – silver nanoparticles
- o Polymer composite membrane (Psf and CA) – silver nanoparticles – complexing agent (nitron)
- o Ionized polymer planar membrane (sPEEK)
- o Polymer composite membrane (sPEEK) – complexing agent (crown ether - ABCE)
- o Ionized polymer electrolysis membrane (sEPDM)

- Nanofiltration with composite membranes for:

- o Treatment of water containing nitrate ions with polymer composite membranes (Psf and CA) – silver nanoparticles
- o Treatment of water containing nitrate ions with polymer composite membranes (Psf and CA) – silver nanoparticles – complexing agent (nitron)

- o Recuperative separation of thorium ions from waste (welding electrodes of high temperatures) using the membranes prepared

C3. Research Perspectives

The research conducted during the doctoral internship for the development of the doctoral thesis, Contributions to experimental studies on the rejection of nitrate anion in traces from water and the recovery of thorium from metallic matrices using composite nanofiltration membranes, opens the following research directions:

1. *Preparation of new polymer-polymer composite membranes for nanofiltration*
2. *Obtaining composite membranes containing metal nanoparticles*
3. *Synthesis of composite membranes based on metal nanoparticles and complexing agents (classical or crown ethers)*
4. *Expanding the range of composite membrane characterization methods*
5. *Nanofiltration involving new composite membranes*
6. *Recuperative separation by nanofiltration of solutions containing anions, metal cations, organic ions or macromolecular ions*

List of works published by Eng. Geani-Teodor MAN included in the doctoral thesis

1. Razvan, A., **Man, G. T.**, Dumitru, F. *, Pandeale, M., Trusca, R., Motelica, L., ... & Nechifor, G. * (2024). Nanocomposite membranes prepared from cellulose acetate or polysulfone with Ag0 nanoparticles and nitron reagent for nitrate ion removal. *Desalination and Water Treatment*, 318, 100400. <https://doi.org/10.1016/j.dwt.2024.100400> **FIC=0,8; Citări 6**
2. **Man, G. T.**, Albu, P. C., Popescu, D. I., Marinescu, V.E. & Nechifor, A. C. (2024). Thorium Recovery from the Tungsten Welding Electrodes by Electrolysis and Nanofiltration. *U.P.B. Sci. Bull., Series B*, 86(2), pp.81-92, **FIC=0,3;**
3. **Man, G. T.**, Albu, P. C., Nechifor, A. C., Grosu, A. R., Tanczos, S.-K., Grosu, V.-A., Ioan, M.-R., & Nechifor, G. * (2023). Thorium Removal, Recovery and Recycling: A Membrane Challenge for Urban Mining. *Membranes*, 13(9), 765. <https://doi.org/10.3390/membranes13090765> **FIC=3,6; Citări 17**
4. **Man, G. T.**, Albu, P. C., Nechifor, A. C., Grosu, A. R., Popescu, D. I., Grosu, V.-A., Marinescu, V. E., & Nechifor, G. * (2024). Simultaneously Recovery of Thorium and Tungsten through Hybrid Electrolysis–Nanofiltration Processes. *Toxics*, 12(2), 103. <https://doi.org/10.3390/toxics12020103> **FIC=4,1; Citări 5**
5. Nechifor, A. C., Albu, P. C., Motelica, L., **Man, G. T.**, Grosu, A. R., Tanczos, S.-K., Grosu, V.-A., Marinescu, V. E., & Nechifor, G. * (2024). Thorium Recovery with Crown Ether–Polymer Composite Membranes. *Applied Sciences*, 14(21), 9937. <https://doi.org/10.3390/app14219937> **FIC=2,5**
6. **Man, G. T.**, Iordache, A. M., Popescu, D. I., Zgavarogea, I. R., & Şuţan, N. A. (2026). Thorium Valorization at the Interface of Technology, Risk, and Sustainability. *Toxics*, 14(3), 193. <https://doi.org/10.3390/toxics14030193>. **FIC=4,1**

List of works published by Eng. Geani-Teodor MAN not included in the doctoral thesis

1. **Man, G. T.**, Iordache, A. M., Zgavarogea, R., & Nechita, C. (2024). Recycling Lithium-Ion Batteries—Technologies, Environmental, Human Health, and Economic Issues—Mini-Systematic Literature Review. *Membranes*, 14(12), 277. <https://doi.org/10.3390/membranes14120277> **FIC=3,6; Citări 11**
2. Albu, P. C., Pîrțac, A., Motelica, L., Nechifor, A. C., **Man, G. T.**, Grosu, A. R., ... & Nechifor, G. (2024). Reduction in Olfactory Discomfort in Inhabited Premises from Areas with Mofettas through Cellulosic Derivative–Polypropylene Hollow Fiber Composite Membranes. *Materials*, 17(17), 4437. <https://doi.org/10.3390/ma17174437> **FIC=3,2**
3. Pașcu, D., Nechifor, A. C., Grosu, V.-A., Oprea, O. C., Tanczos, S.-K., **Man, G. T.**, Dumitru, F., Grosu, A. R., & Nechifor, G. (2023). Hydrogen Sulphide Sequestration with Metallic Ions in Acidic Media Based on Chitosan/sEPDM/Polypropylene Composites Hollow Fiber Membranes System. *Membranes*, 13(3), 350. <https://doi.org/10.3390/membranes13030350>. **FIC=3,6; Citări 2**
4. Goran, A., Abdalraheem AL-ANI, H. N., Grosu, A. R., **Man, G. T.**, Grosu, V. A., & Nechifor, A. C. (2023). Lead-cadmium ions recuperative separation by chitosan-sepdm-polypropylene hollow fiber composite membranes. *Studia Universitatis Babes-Bolyai, Chemia*, 68(2), p. 193 **FIC=0,3**

Eng. Geani-Teodor MAN participation in conferences and symposia

- 1) Processes in Isotopes and Molecules – PIM 2023- International Conference 19-22 September 2023 -Cluj Napoca- Poster presentation-Valorization of Agro-Industrial Residues through the Production of bioproducts with added value in the circular bioeconomy system - **G.T. Man**, C.T. Ciucure, O.R. Botoran, R.E. Ionete, E.I. Geana;
 - 2) 24TH INTERNATIONAL CONFERENCE “NEW CRYOGENIC AND ISOTOPE TECHNOLOGIES FOR ENERGY AND ENVIRONMENT” OCTOBER 18-20, 2023 BĂILE GOVORA, ROMÂNIA –(international conference), Poster presentation - Thorium removing from electric and electronic waste - **Geani Teodor Man**, Aurelia Cristina Nechifor, Alexandra Raluca Grosu, Diana Ionela Popescu (Stegarus) , Vlad-Alexandru Grosu , Gheorghe Nechifor;
 - 3) The 23rd Romanian International Conference on Chemistry and Chemical Engineering (RICCCE), 4-7 september 2024 Mamaia (Constanta)-Oral presentation-Technology Aspects of Thorium Recuperative Separation- **Geani Teodor Man**, Gheorghe Nechifor;
 - 4) 16th International Exergy, Energy and Environment Symposium (IEES-16)
- 16thINTERNATIONAL CONFERENCE ON HYDROGEN PRODUCTION - Craiova, 14-18 December-2025 - Poster presentation- Thorium: Extraction Techniques, Utilization Potential, Environmental Dynamics, and Health risks- Ramona Zgavarogea, **Geani Teodor Man**, Diana Ionela Popescu (Stegarus), Nadia Paun, Nicoleta Anca Sutan.

Selective references

1. *M. Mulder*, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Londra, (1996), pp. 286, ISBN;
2. Goran, A., Abdalraheem AL-ANI, H. N., Grosu, A. R., **Man, G. T.**, Grosu, V. A., & Nechifor, A. C. (2023). Lead-cadmium ions recuperative separation by chitosan-sepdm-polypropylene hollow fiber composite membranes. *Studia Universitatis Babes-Bolyai, Chemia*, 68(2), p. 193
3. E. Drioli and M. Nakagaki (eds.) Plenum Press, New York, 1986, p. 202, ISBN 0-306-42270-0.
4. Razvan, A., **Man, G. T.**, Dumitru, F. *, Pandeale, M., Trusca, R., Motelica, L., ... & Nechifor, G. * (2024). Nanocomposite membranes prepared from cellulose acetate or polysulfone with Ag0 nanoparticles and nitron reagent for nitrate ion removal. *Desalination and Water Treatment*, 318, 100400. <https://doi.org/10.1016/j.dwt.2024.100400>
5. Council Directive of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC), EUR-Lex - 01991L0676-20081211 - EN, <http://data.europa.eu/eli/dir/1991/676/2008-12-11>, 2008 (accessed on 17 January 2024).

6. **Man, G. T.**, Albu, P. C., Popescu, D. I., Marinescu, V.E. & Nechifor, A. C. (2024). Thorium Recovery from the Tungsten Welding Electrodes by Electrolysis and Nanofiltration. *U.P.B. Sci. Bull., Series B*, 86(2), pp.81-92
7. 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. (2021). Recuperative Amino Acids Separation through Cellulose Derivative Membranes with Microporous Polypropylene Fiber Matrix. *Membranes*, 11, p. 429. doi: [10.3390/membranes11060429](https://doi.org/10.3390/membranes11060429)
8. Mueller, N. C., van Der Bruggen, B., Keuter, V., Luis, P., Melin, T., Pronk, W., ... & Nowack, B. (2012). Nanofiltration and nanostructured membranes—Should they be considered nanotechnology or not?. *Journal of hazardous materials*, 211, 275-280. <https://doi.org/10.1016/j.jhazmat.2011.10.096>
9. **Man, G.T.**, Albu, P.C., Nechifor, A.C., Grosu, A.R., Popescu (Stegarus), D.I., Grosu, V., Marinescu, V.E., & Nechifor, G. (2023). Simultaneously Recovery of Thorium and Tungsten by Hybrid Electrolysis–Nanofiltration Processes. *Preprints* 2023121375. <https://doi.org/10.20944/preprints202312.1375.v1>
10. Molinari, R., Gallo, S., & Argurio, P. (2004). Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration–complexation. *Water research*, 38(3), 593-600. <https://doi.org/10.1016/j.watres.2003.10.024>
11. García, A.C., Latifi, M., Amini, A., & Chaouki, J. (2020). Separation of Radioactive Elements from Rare Earth Element-Bearing Minerals. *Metals* 10, 1524. <https://doi.org/10.3390/met10111524>.
12. Nechifor, A. C., Albu, P. C., Motelica, L., **Man, G. T.**, Grosu, A. R., Tanczos, S.-K., Grosu, V.-A., Marinescu, V. E., & Nechifor, G.* (2024). Thorium Recovery with Crown Ether–Polymer Composite Membranes. *Applied Sciences*, 14(21), 9937. <https://doi.org/10.3390/app14219937>.
13. Aziman, E.S., Mohd Salehuddin, A.H.J., & Ismail, A.F. Remediation of thorium (IV) from wastewater: Current status and way forward. *Separation & Purification Reviews* 2021, 50(2), pp.177-202. <https://doi.org/10.1080/15422119.2019.1639519>
14. **Man, G.T.**, Albu, P.C., Nechifor, A.C., Grosu, A.R., Tanczos, S.-K., Grosu, V.-A., Ioan, M.-R., & Nechifor, G. (2023). Thorium Removal, Recovery and Recycling: A Membrane Challenge for Urban Mining. *Membranes* 13, 765. <https://doi.org/10.3390/membranes13090765>
15. Covaliu-Mierlă, C.I.; Păunescu, O.; Iovu, H. Recent Advances în Membranes Used for Nanofiltration to Remove Heavy Metals from Wastewater: A Review. *Membranes* 2023, 13, 643. <https://doi.org/10.3390/membranes13070643>
16. Mahmoud, A.E.D., & Mostafa, E. Nanofiltration Membranes for the Removal of Heavy
17. Wang, X., Huang, W., Gong, Y., Jiang, F., Zheng, H., Zhu, T., Long, D., & Li, Q. (2016). Electrochemical behavior of Th (IV) and its electrodeposition from ThF4-LiCl-KCl melt. *Electrochim. Acta* 196, 286–293. <https://doi.org/10.1016/j.electacta.2016.02.184>
18. **Man, G. T.**, Iordache, A. M., Popescu, D. I., Zgavarogea, I. R., & Șuțan, N. A. (2026). Thorium Valorization at the Interface of Technology, Risk, and Sustainability. *Toxics*, 14(3), 193. <https://doi.org/10.3390/toxics14030193>
19. Żyła, R., Ledakowicz, S., Boruta, T., Olak-Kucharczyk, M., Foszpańczyk, M., Mrozińska, Z., & Balcerzak, J. (2021). Removal of Tetracycline Oxidation Products in the Nanofiltration Process. *Water* 13, 555. <https://doi.org/10.3390/w13040555>
20. Suhailim, N.S., Kasim, N., Mahmoudi, E., Shamsudin, I.J., Mohammad, A.W., Mohamed Zuki, F., & Jamari, N.L.-A. (2022). Rejection Mechanism of Ionic Solute Removal by Nanofiltration Membranes: An Overview. *Nanomaterials* 12, 437. <https://doi.org/10.3390/nano12030437>
21. Ali, M.E.A. (2021). Nanofiltration Process for Enhanced Treatment of RO Brine Discharge. *Membranes* 11, 212. <https://doi.org/10.3390/membranes11030212>
22. Bóna, Á., Galambos, I., & Nemestóthy, N. (2023). Progress towards Stable and High-Performance Polyelectrolyte Multilayer Nanofiltration Membranes for Future Wastewater Treatment Applications. *Membranes* 13, 368. <https://doi.org/10.3390/membranes13040368>
23. Turek, M., Mitko, K., Skóra, P., Dydo, P., Jakóbi-Kolon, A., Warzecha, A., & Tyrała, K. (2022). Improving the Performance of a Salt Production Plant by Using Nanofiltration as a Pretreatment. *Membranes* 12, 1191. <https://doi.org/10.3390/membranes12121191>