Appendix No 5

REMOVAL OF RADIONUCLIDES AND HEAVY METALS FROM LIQUID WASTE BY METHODS BASED ON MEMBRANE PROCESSES

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Centre for Radiochemistry and Nuclear Chemistry

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS SUBMITTED FOR THE HABILITATION PROCEDURE

Warsaw, September 2023

1. Name and surname:

Agnieszka Lucyna Miśkiewicz

2. **Academic diplomas and degrees:**

- PhD in chemistry (10.09.2013)

Doctoral dissertation: "New liquid and solid phase radioactive tracers for applications in the study of membrane processes"

Supervisor: prof. dr hab. inż. Grażyna Zakrzewska-Kołtuniewicz

Institute of Nuclear Chemistry and Technology, Warsaw

- MSc in chemistry (14.07.2004)

Master's thesis: "Synthesis and structural studies of diboronic acids" - thesis defended with honours

Supervisor: prof. dr hab. Andrzej Sporzynski

Faculty of Chemistry, Warsaw University of Technology

3. Information on employment in research institutes or faculties/departments or school of arts:

- 01.05.2015 - present — Deputy Head of Centre for Radiochemistry and Nuclear Chemistry, Institute of Nuclear Chemistry and Technology, Warsaw
- 01.03.2014 - present — adiunct, Institute of Nuclear Chemistry and Technology, Warsaw
- 01.11.2006 - 01.03.2014 — assistant, Institute of Nuclear Chemistry and Technology, Warsaw
- 01.01.2005 - 01.11.2006 — chemist, Institute of Nuclear Chemistry and Technology, Warsaw
- 01.10.2003 - 31.03.2004 — assistant, Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology

4. Description of the achievements, set out in art. 219 para 1 point 2 of the Act of 20 July 2018 Law on Higher Education and Science (Journal of Laws of 2020, item 85, as amended:

a) Title of scientific achievement:

Removal of radionuclides and heavy metals from liquid waste by methods based on membrane processes

b) List of scientific publications constituting the basis for scientific achievement:

- [**H01**]: L. Fuks, **A. Miśkiewicz*,** G. Zakrzewska-Kołtuniewicz, Sorption-Assisted Ultrafiltration Hybrid Method for Treatment of the Radioactive Aqueous Solutions. *Chemistry*, **2022**, 4, 1076–1091.DOI: 10.3390/chemistry4030073
- [**H02**]: L. Fuks*, **A. Miśkiewicz***, I. Herdzik-Koniecko, G. Zakrzewska-Koltuniewicz. Fly Ash as a Potential Adsorbent for Removing Radionuclides from Aqueous Solutions in an Adsorption-Membrane Assisted Process Compared to Batch Adsorption. *Membranes* **2023**, 13, 572, DOI: 10.3390/membranes13060572
- [**H03**]: **A. Miśkiewicz***, G. Zakrzewska-Kołtuniewicz, Application of biosorbents in hybrid ultrafiltration/sorption processes to remove radionuclides from low-level radioactive waste. *Desalination and Water Treatment*, **2021**, 242, 47–55, DOI: 10.5004/dwt.2021.27870
- [**H04**]: **A. Miśkiewicz***, W. Starosta, R. Walczak and G. Zakrzewska-Kołtuniewicz, MOF-Based Sorbents Used for the Removal of Hg^{2+} from Aqueous Solutions via a Sorption-Assisted Microfiltration. *Membranes*, **2022,** 12, 1280, DOI: 10.3390/membranes12121280
- [**H05**]: A. Abramowska, D. K. Gajda, K. Kiegiel, **A. Miśkiewicz**, P. Drzewicz, G. Zakrzewska-Kołtuniewicz, Purification of flowback fluids after hydraulic fracturing of Polish gas shales by hybrid methods. *Separation Science and Technology*, **2018**, 53 (8), 1207–1217, DOI: 10.1080/01496395.2017.1344710
- [**H06**]: **A. Miśkiewicz***, A. Nowak, J. Pałka, G. Zakrzewska-Kołtuniewicz, Liquid Low-Level Radioactive Waste Treatment Using an Electrodialysis Process. *Membranes*, **2021** 11, 324 p. 1-12, doi.org/10.3390/membranes11050324
- [**H07**]: **A. Miśkiewicz*,** G. Zakrzewska-Kołtuniewicz, E. Dłuska, P. F. Walo, Application of membrane contactor with helical flow for processing uranium ores. *Hydrometallurgy*, **2016**, 163, 108–114, DOI: 10.1016/j.hydromet.2016.03.017
- [**H08**]: **A. Miśkiewicz***, G. Zakrzewska-Kołtuniewicz, The application of the radiotracer method for the investigation of the cake layer formation on the membrane surface in the cross-flow flat-sheet membrane module. *Desalination and Water Treatment*, **2018,** 128, 228–235, DOI: 10.5004/dwt.2018.22866
- [**H09**]: **A. Miśkiewicz*,** G. Zakrzewska-Kołtuniewicz, S. Pasieczna-Patkowska, Photoacoustic spectroscopy as a potential method for studying fouling of flat-sheet

ultrafiltration membranes. *Journal of Membrane Science*, **2019**, 583, 59-69, DOI: 10.1016/j.memsci.2019.04.048

- [**H10**]: **A. Miśkiewicz**[*], G. Zakrzewska-Kołtuniewicz Application of the radiotracer method to study the fouling of tubular microfiltration membranes. *Desalination*, **2022**, 534,115795, DOI: 10.1016/j.desal.2022.115795

c) *Description of scientific achievement*

A detailed discussion of the scientific achievement, the purpose and scope of the research, along with a summary of the scientific publications included in the achievement, can be found in Appendix 5A.

5. Presentation of significant scientific or artistic activity carried out at more than one university, scientific or cultural institution, especially at foreign institutions:

Scientific cooperation before obtaining a doctoral degree:

- From September 1, 2007 to December 20, 2007, I did an internship at the University of New Lisbon, as part of the EU Marie Curie Transfer of Knowledge project. Under the leadership of prof. J.G. Crespo and prof. S. Velizarova, I conducted research on the removal of organic compounds from aqueous solutions using the electrooxidation process combined with membrane processes. The result of this research was the following article: A. Miśkiewicz, S. Velizarov, „Effect of molecular mass on boron-doped diamond anodic mineralization of water-soluble organic polymers" Separation and Purification Technology, 2011, 83, 166-172.
- In the period 01/04/2004 - 30/06/2004 I had an internship at the Faculty of Physical Chemistry, University of Rostock under the Socrates-Erasmus program. During the internship, under the supervision of prof. S. Verivkina, I conducted experimental work on the determination of vapor pressure and enthalpy of vaporization of organic compounds.

Scientific cooperation after obtaining a doctoral degree:

- Maria Skłodowska-Curie University, Department of Chemical Technology – dr hab. Sylwia Pasieczna-Patkowska – working together on testing membrane fouling, resulting in a joint publication in J. Membr. Sci. (2019) [**H09**];

- Warsaw University of Technology, Faculty of Chemical and Process Engineering – dr hab. Ewa Dłuska, PhD Eng. Agnieszka Markowska-Radomska – working together on fouling reduction and the use of a membrane contactor, resulting in several joint publications, including: [**H07**];
- Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Department of Geoengineering and Environmental Engineering - dr hab. Leszek Lankof - work related to the radioactive waste disposal, including the migration of radionuclides in the vicinity of repositories. A joint article was published in the journal Nukleonika (2015);
- Polish Geological Institute National Research Institute – Dr. Zbigniew Frankowski - joint work related to the radioactive waste disposal;
- Silesian University of Technology, Faculty of Energy and Environmental Engineering, dr hab. Łukasz Bartela - joint work on a project related to the decarbonization of coal-fired energy through the use of nuclear reactors (DEsire project);
- Collegium Civitas, Institute of Sociology - dr Katarzyna Iwińska - joint work on study the public participation in decision-making processes related to nuclear energy and study the social effects of the development of nuclear power plants in Poland, participation in the following projects: IPPA, PLATENSO and IAEA CRP No 18541;
- University of Lodz, Faculty of Economics and Sociology – dr hab. Mariusz Plich - joint work on the study of the socio-economic effects of NPP development in Poland, participation in the IAEA CRP No. 18541 project;
- Warsaw School of Economics, Collegium of Economic Analysis - dr Michał Antoszewski - joint work on the study of the socio-economic effects of NPP development in Poland, participation in the IAEA CRP No. 18541 project.

6. Presentation of teaching and organizational achievements as well as achievements in popularization of science or art

Teaching achievements:

Master's theses - substantive supervisor from the INCT:

• "The use of an acentric membrane helicoidal module for the separation of model radioactive wastewater", Kamil Kłos, Faculty of Chemical and Process Engineering, Warsaw University of Technology, 2014;

• "Analysis of the use of an acentric membrane helicoid contactor for filtration of suspension after uranium ore leaching", Paweł Walo, Faculty of Chemical and Process Engineering, Warsaw University of Technology, 2013;

Engineering diploma theses - substantive supervisor on the part of INCT:

• "The application of the electrodialysis process to the treatment of liquid radioactive waste", Jędrzej Pałka, Faculty of Chemical and Process Engineering, Warsaw University of Technology, 2020;

• "Analysis of membrane fouling used in the filtration process of liquid radioactive waste", Katarzyna Biliniak, Faculty of Chemical and Process Engineering, Warsaw University of Technology, 2019;

• "The use of the radiotracer method in the study of membrane processes" Jakub Iwanicki, Faculty of Chemical and Process Engineering, Warsaw University of Technology, 2019;

• "The use of membrane desalination processes as a method of decontamination during normal operation of power plants and in emergency situations", Agnieszka Nowak, Faculty of Chemistry, Warsaw University of Technology, 2018; The work received the 3rd prize of the Polish Nucleonic Society in 2018 in the competition for the best engineering thesis in the field of nucleonics.

• "Research on the phenomenon of fouling of membranes used to treat liquid radioactive waste", Monika Żuchowska, Faculty of Chemical and Process Engineering, Warsaw University of Technology, 2018;

The above-mentioned master's and diploma theses were carried out as part of research projects conducted at the Center for Radiochemistry and Nuclear Chemistry, IChTJ, and their subject and scope were defined with my participation.

Moreover, during my studies, in the period 01.10.2003 - 31.03.2004, I was employed in the Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology as an assistant-trainee. My duties included conducting laboratory exercises in physical chemistry for students, helping in the operation of didactic laboratories and in the organization of exams and colloquiums.

<u>Organizational achievements:</u>

• Member of the organizing committee of the international conference "International Conference on Development and Applications of Nuclear Technologies, NUTECH-2014", Warsaw, September 21-24, 2014;

and the conference "Science and technology towards the challenge of building a nuclear power plant, Mądralin-2013", Warsaw, February 13-15, 2013;

• Member of the team organizing the Public Hearing "Do we need a new radioactive waste repository?", under the EU framework project "Implementing Public Participation Approaches in Radioactive Waste Disposal (IPPA)", Radisson Blu Hotel, Warsaw, May 8, 2013;

• Member of the team organizing a series of workshops and trainings for stakeholders of the radioactive waste repository in Poland, as part of the EU IPPA project (2014-2017):

- November 24, 2011 at the Ministry of Economy in Warsaw - workshops on the application of the RISCOM model in various EU countries and the system for assessing the impact of a radioactive waste repository on the environment in Poland with reference to the Aarhus and Espoo Conventions.
- April 24-25, 2013 in the Zielna Center in Warsaw - workshops devoted to communication in conflict situations, and the art of presentation and debate.
- November 4-5, 2013, Warsaw, workshop entitled "Integrating public participation into decision-making processes for sustainable governance of nuclear waste in Poland"
- June 18-19, 2012, training entitled: "Integrating public participation into decision making processes for sustainable governance of nuclear energy and waste in Poland."

• Member of the team organizing a series of workshops within other EU framework projects implemented at the Center for Radiochemistry and Nuclear Chemistry ICHTJ

- "New MS Linking for an Advanced Cohesion in Euratom (NEWLANCER)"
- "Enhancing education, training and communication processes for informed behaviors and decision-making related to ionizing radiation risks (EAGLE)"

- "Building a platform for enhanced social research related to nuclear energy in Central and Eastern Europe (PLATENSO)"

Activities disseminating science:

Before obtaining my doctoral degree, since 2005 I actively participated in the dissemination of science by taking part in events such as: Science Picnic, Night of Museums and the Science Festival. In the period October 2010 - April 2011 I was the coordinator of IChTJ activities related to the popularization of science and the promotion of the Institute, organizing shows at the Faculty of Chemistry of the Adam Mickiewicz University in Poznań entitled "The life and work of Maria Skłodowska - Curie Women in Science") and the Science Picnic.

7. Apart from information set out in 1-6 above, the applicant may include other information about his/her professional career, which he/she deems important.

- 1st prize in the competition of the Polish Nucleonic Society in the competition for the best doctoral theses in the field of atomic science defended in 2012/2013, October 2013;
- Bronze Cross of Merit - decoration of the President of the Republic of Poland for activities for science by order of May 20, 2015;
- II degree Team Award of the Director of ICHTJ for a series of five original and valuable scientific publications on the issues of the fuel cycle and the search for alternative sources of fissile materials, December 2018;

Agnieszka Miśkiewicz
....
(Applicant's signature)

Appendix 5A. Discussion of scientific achievement

Removal of radionuclides and heavy metals from liquid waste by methods based on membrane processes

1. The purpose of the research

The purpose of my research, which formed the basis of the presented scientific achievement, was to remove radionuclides and heavy metals from liquid wastes that pose a threat to humans and the environment by using methods based on membrane processes. As part of my research, I tested and evaluated both pressure-based membrane techniques (ultrafiltration, (UF) and microfiltration, (MF) (H01-H04), reverse osmosis, (RO) (H05)) and current-based techniques (electrodialysis, ED) (H06). In order to achieve high efficiency of radionuclide separation from solutions of model liquid radioactive waste and real waste, hybrid processes were used, in which a membrane process (MF or UF) was combined with an adsorption process using low-cost, readily available sorbents obtained from waste materials, such as. waste (sludge) from the fertilizer industry, (clay-salt slime, CSS) (H01), or fly ash (H02), and biosorbents such as alginic acid and its derivatives (H03). Another material supporting sorption in the hybrid process analyzed during the study was metal-organic framework (MOF) matrices. MOF-type substances have been used to remove Hg2+ ions from aqueous solutions by the MF/sorption process [H04]. Hybrid processes, sorption-assisted filtration, for each of the systems analyzed, were preceded by studies to evaluate the sorbent used and determine the optimal sorption conditions.

Another type of hazardous waste for which a preliminary concept for treatment and concentration using membrane processes was developed was hydraulic fracturing fluids from gas shale (H05). These wastewaters are characterized by high salinity and content of heavy metals, including rare earth metals, radioactive elements and various types of organic compounds. For this type of wastewater, the development of a multi-stage process using various physicochemical methods was required. Membrane processes were an important part of the entire technological scheme for the treatment of post-fracking fluids in the developed concept for the pretreatment of fluids after hydraulic fracturing.

Membrane processes using a tubular module with a metallic membrane, have also been used as an alternative method for leaching uranium from uranium ores [H07]. In the study conducted, a microfiltration membrane was used as a membrane contactor to separate the liquid phase, containing uranium ions, from the solid phase, which is the ore residue after leaching, For this hybrid-leaching/microfiltration process, the membrane module was used both as a phase contactor in the leaching process and also as an apparatus for processing the liquid waste remaining after leaching uranium ore.

Membrane processes, however, in addition to their unquestionable advantages, have limitations that to some extent hinder their use on an industrial scale. The main limitation to the widespread use of membrane techniques on an industrial scale, is the occurrence of fouling, or membrane blockage, which causes a decrease in process performance over time and implies the need for periodic membrane cleaning. Getting to know the mechanisms of fouling and the factors that influence this phenomenon is important for achieving a more complete control of the performance of membrane modules and extending their operating time, as a result of reducing the frequency and duration of periodic cleaning. Thus, in order to gain a better understanding of the phenomena that lead to membrane blockage, which would further reduce their impact and maximize the efficiency of membrane modules used in liquid waste treatment processes, I have attempted to study fouling occurring with the membranes I use. The work on the study of fouling is the subject of 3 papers of the series that make up the scientific achievement [H08], [H09], [H10]. To explore this phenomenon, I proposed the use of radio-marker techniques, whose potential for use in the study of membrane processes I confirmed during the preparation of my doctoral dissertation.

Thus, the work comprising my scientific achievement presents a broad analysis of the feasibility of using membrane processes to remove radionuclides and heavy metals from liquid wastes. The proposed membrane processes were optimized by me in terms of the efficiency of separation of hazardous components of these wastes, both at the stage of the process supporting microfiltration and ultrafiltration (sorption stage), and during the establishment of the conditions of the entire hybrid process. In addition, in order to minimize the occurrence of membrane blockage and its adverse effects, which allows for the intensification of the membrane processes used, I analyzed the parameters affecting this phenomenon and attempted to describe it, depending on the test system used.

2. Introduction

The development of materials engineering has made the availability of membranes and the variety of materials from which they are made, contributing to the expansion of application areas [1, 2]. Membrane processes are used both in environmental protection and in many industrial fields. Among the main applications of membrane techniques are desalination of seawater and brackish water (mainly by reverse osmosis, RO), softening and treatment of drinking water, concentration of mine water and landfill leachate, concentration of whey, juices or clarification of wine (UF, MF).

The main advantages of membrane processes include:

- mild process conditions,
- variety of membrane materials allowing a wide range of applications,
- ease of scale-up,
- the possibility of combining them with other methods into a process that runs in a single apparatus (so-called hybrid systems).

These aforementioned advantages of membrane processes and the possibility of using increasingly modern membrane materials, caused that these processes have been selected for use in the treatment of liquid radioactive waste and other hazardous industrial wastewater.

Many nuclear power generation activities generate radioactive waste, and such waste is also generated by the medical or industrial use of radioactive isotopes. The classification of radioactive waste according to various criteria, including the criterion related to the source of its generation, is shown in the diagram below (Figure 1).

Fig. 1: Classification of radioactive waste.

Both liquid radioactive waste and other industrial effluents must be properly treated and then stored in such a way that they do not pose a threat to humans and the environment. The scheme for handling radioactive waste is shown in the figure (Fig. 2).

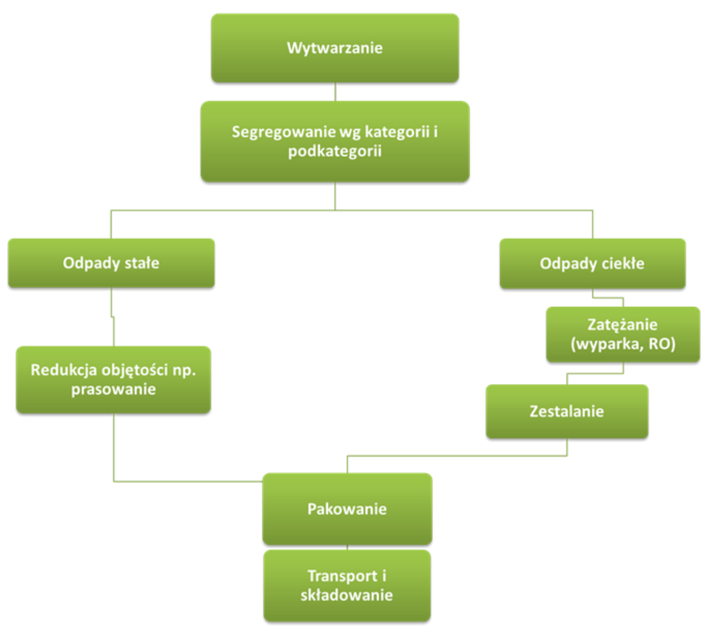

Fig. 2: Diagram of radioactive waste management.

Low-level liquid radioactive waste (LLW) is a large part of liquid radioactive waste, and although the radionuclide content is not high in it, it is an important problem due to its large volume. The first step in the treatment of radioactive wastewater is the separation of sludge and organic contaminants. As a result of pre-treatment, waste sent to further processing stages contains: radionuclides, inactive salts, detergents and organic compounds that have not been removed.

Further processing consists of effluent concentration and recovery of some water. This stage is important for minimizing the volume of waste for disposal. The choice of the appropriate method of concentrating liquid waste depends mainly on the characteristics and class of waste, its volume, the assumed degree of decontamination and the cost of the chosen process. In the case of liquid radioactive waste, it is also necessary to solidify the concentrated wastewater, since only solid waste can be disposed of in radioactive waste repositories.

In order to minimize the amount of waste sent to the landfill, it is necessary to separate the radionuclides, or concentrate them in the smallest possible volume. The next step in the handling of liquid radioactive waste is to solidify it into a permanent form. It should be mentioned here that some waste components (e.g., organic compounds) adversely affect the solidification process, as their presence in the solidified waste can cause radionuclides to leach from the matrices more easily [3]. Separation of radioactive components from other waste components is therefore also necessary to ensure the durability of radionuclide binding in the matrix, which is the so-called first engineering barrier. This is of paramount importance to ensure the safe storage of waste by isolating it from the environment.

At present, the following methods are used to separate radioactive components in the treatment of liquid radioactive waste [4, 5]:

- precipitation,
- evaporation,
- ion exchange,
- extraction,
- membrane techniques,
- biological processes,
- electrochemical processes

However, the high dilution of liquid radioactive waste makes the use of certain methods for the separation of radionuclides (precipitation, evaporation, extraction) unprofitable from an economic and ecological point of view. Membrane techniques can be used to purify and concentrate liquid waste with both very low and very high concentrations of the separated components. Applications of membrane processes such as micro-, ultra- and nanofiltration, reverse osmosis, dialysis and electrodialysis in nuclear technologies are well known [6-8]. Some of these methods not only concentrate radionuclides in a small volume, but can also be used to separate them for recycling. The physicochemical basis of pressure processes such as ultrafiltration and microfiltration, which, next to reverse osmosis, are the most frequently used membrane methods in industry, unfortunately result in low selectivity in the separation of metal ions (including radionuclides and heavy metals). In order to improve their separation properties, most membrane processes can be carried out in multiple stages or can be used in combination with other methods (hybrid systems).

3. New sorbents for radionuclides and heavy metals in hybrid systems: sorption combined with membrane process

3.1. Hybrid methods based on membrane techniques

Hybrid methods are encountered when two or more processes are combined, often carried out in a single apparatus. Hybrid systems are more flexible than single processes, and can be more easily optimized to achieve the desired effect. Because of these advantages, membrane-based hybrid processes can be used in the treatment of liquid radioactive waste as well as other industrial wastewater.

The solution of combining a membrane process (MF, UF) with the complexation of ions present in these streams is of great interest in the treatment of various types of wastewater and contaminated water streams [9]. For this purpose, for example, soluble macromolecular compounds are used, thus obtaining an enlargement of the molecular weight of the separated complexes, which hinders their passage through the pores of the membrane causing separation. An example of the application of Complexation-Assisted UltraFiltration (CAUF) is, for example, the removal of boric acid from water or the reduction of the volume of radioactive wastewater from decommissioning and decontamination of nuclear installations [10, 11]. An interesting alternative to the CAUF method is the use of solid particles or adsorbents suspended in an aqueous solution, the so-called Sorption-Assisted UltraFiltration (SAUF) method.

Hybrid processes combining ultrafiltration and microfiltration with complexation by macromolecular substances or with sorption have been used by the INCT Membrane Processes Laboratory team for many years [12-17]. A schematic of the hybrid process of MF or UF combined with sorption is shown in the figure (Fig. 3).

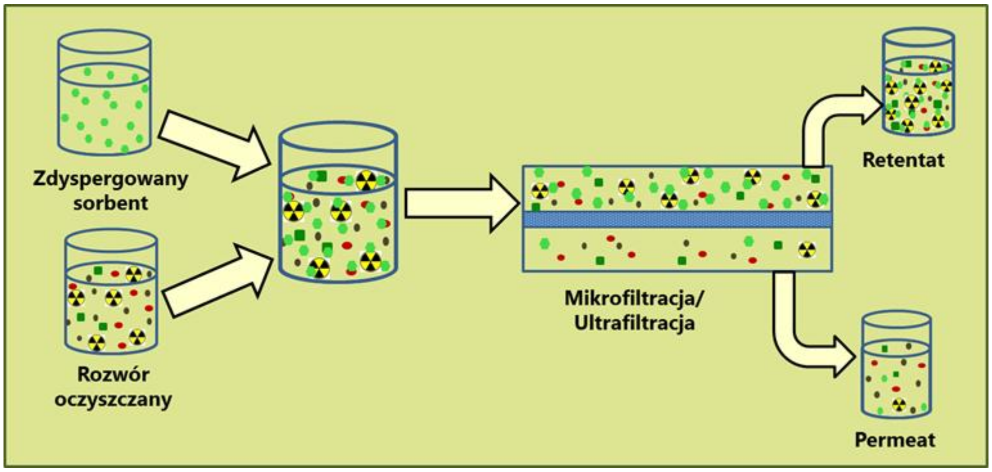

Fig. 3: Schematic diagram of the hybrid process of MF or UF combined with sorption.

Studies carried out in our Laboratory have shown the possibility of increasing the Decontamination Factor (DF) of liquid radioactive waste through the membrane process by using macromolecular ligands that bind radioactive ions. By selecting a suitable ligand, it was possible to achieve an increase in the decontamination factor by up to several hundred times. It was found that when using soluble polymers, one should take into account not only their chemical form, but also their degree of cross-linking and particle size. The choice of polymer concentration and process conditions (e.g., solution pH) are equally important [12, 13].

The experience gained has allowed the development of these methods toward optimization, both through the use of new, more efficient radionuclide-binding materials [14, 15] and through proper control of process conditions [16, 17].

The selection of a radionuclide or metal ion-binding substance that is suitable for a given type of liquid waste and is guaranteed to increase retention in a hybrid process is a key point in such a process. A good binding material (chelator, sorbent) should be characterized by:

- sufficiently high molecular weight (chelator) or adequate particle size distribution (sorbent) in relation to the pore size of the membrane used,
- ability to selectively bind to ions and molecules,
- stability of the bond: metal-binding substance,
- non-toxicity,
- low price and easy availability.

In addition, it is important to determine the optimal conditions for the complexation or sorption reaction to proceed with maximum efficiency (pH, reaction time, reactant ratio).

3.2. Removal of radionuclides and heavy metals from liquid waste by using hybrid methods: sorption combined with a membrane process.

3.2.1. Use of inorganic waste materials

As part of my research on the removal of radionuclides and heavy metals from liquid wastes through hybrid methods, I have analyzed the possibility of using waste materials such as clay salt slime (CSS) and fly ash (FA) from potash fertilizer production in combination with micro- and ultrafiltration [**H01**, **H02**]. CSS sorbent has been previously tested in sorption processes carried out under static conditions [18, 19]. Analyses of the composition of this waste material showed that its main components are illite (42.2-51.1% by weight) and dolomite (19.6-24.8% by weight). Due to its favorable structure (aluminosilicates) and because of its availability (cheap and available in big quantities), this material was investigated by me as an intervening alternative to other radionuclide-binding agents that can be used in hybrid processes [**H01**]. Experiments to determine the feasibility of using this sorbent in a hybrid process in combination with a membrane process, I conducted, (similar to the studies with fly ash), in an Amicon filter cell (type 8400, Millipore) with a capacity of 350 mL, placed on a magnetic stirrer. (Figure 4). Pressure, providing the flow of the purified solution, was provided by the nitrogen stream from the cylinder.

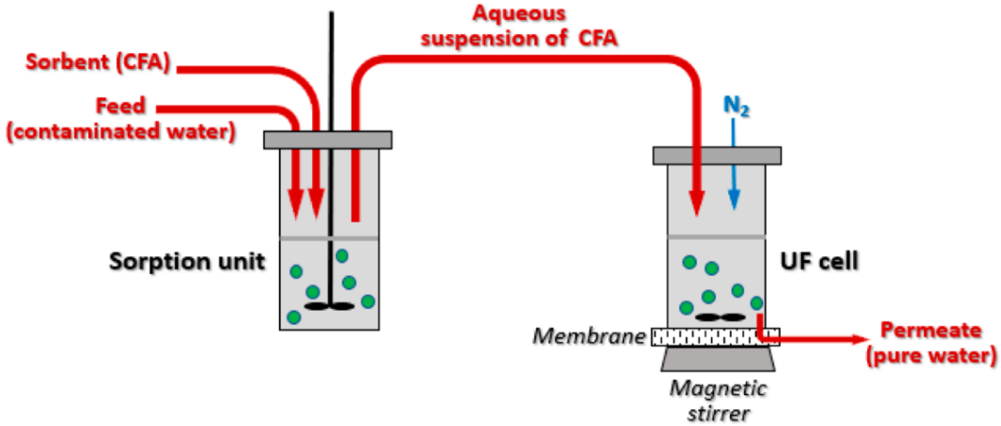

Fig. 4: Schematic of the system for conducting the sorption-assisted UF process [**H02**].

In order to obtain satisfactory results of radionuclide separation, it was necessary to optimize the proposed method, from the selection of a suitable membrane (the material of which it is made and the size of the pores) through the selection of sorption parameters (pH, ratio of reactants, reaction time) and the conditions of the membrane process (pressure determining the permeate flow rate). The membrane that met the requirements for obtaining adequate process efficiency (permeate flux size) and separation efficiency, in the case of this sorbent, was a membrane made of polyethersulfone (PES) with a Molecular Weight Cut-Off (MWCO) point of 10 kDa.

The result of the research was the development of an effective method for separating radionuclides present in liquid radioactive waste model solutions. Using the proposed method of combining ultrafiltration with sorption using CSS sorbent, all radionuclides Cs, Co and Am present in solution were removed from aqueous solution with close to 100% efficiency (>99%). An additional advantage of the tested hybrid method is the possibility to carry out two processes (radionuclide sorption and phase separation) in one apparatus, which reduces the cost of the entire operation.

The second material I used as a cheap and readily available sorbent was fly ash [**H02**]. I also conducted experiments with fly ash using an Amicon filter chamber. A series of trial experiments showed that a membrane made of polyethersulfone (PES) with an average pore size of 0.22 μm was most beneficial. The result of the experiments carried out in this way was a high radionuclide removal efficiency (100%) for ^{137}Cs, ^{241}Am and ^{60}Co solution.

The efficiency of radionuclide removal from liquid waste using a hybrid process (microfiltration/sorption) was compared with that of the stationary adsorption method, carried out in a stirred reactor. The result of this comparison indicates that both methods are equally effective, but it should be noted that the hybrid process requires much less sorbent (4 times less) to achieve the same radionuclide separation effect.

Main achievement:

Demonstration of the feasibility of using industrial waste materials as an adsorbent for radionuclides and using them in a hybrid MF/sorption or UF/sorption process.

3.2.2. Use of biosorbents

Other materials that can be used as a sorbent to remove radionuclides from aqueous solutions and liquid radioactive wastes in the hybrid ultrafiltration/sorption process I tested include alginic acid and sodium alginate [**H03**]. These compounds, which belong to the group of biopolymers, are widely studied for their use in wastewater treatment, including metal ion removal, as they are a cheap, renewable and abundant biological raw material [20, 21]. The sorption capacity of biosorbents depends on the chemical composition of their cell wall and the presence of macromolecules with different functional groups that interact with metal ions. Studies show that alginate-based biosorbents can effectively remove metals found in industrial wastewater, and in dispersed form can support the ultrafiltration process [22]. The chemical structure and, in particular, the presence of carboxyl groups and oxygen atoms having free electron pairs (Fig. 5) allows the formation of bonds with metal ions, including radionuclides, present in liquid waste.

Fig. 5: β-D-mannuric and α-L- guluronic acids, forming the structure of alginic acid.

The processes of metal ion binding by biosorbents can be generally divided into non-specific and specific. Specific binding of metal cations occurs through interactions with appropriate functional groups. The types of these groups and their number depend on the type of biosorbent. In the case of biosorbents based on alginic acid and its derivatives, the most important role in the binding of metal ions is attributed to carboxyl groups [23]; however, hydroxyl groups can also be involved in the binding of metal ions (Fig. 6).

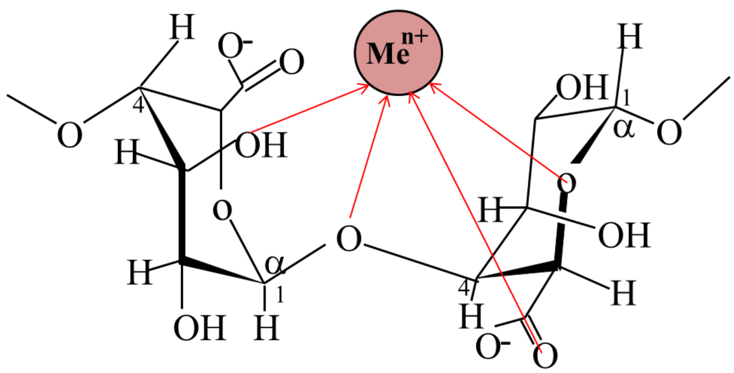

Fig. 6: Proposed mechanism of metal ion binding by sodium alginate.

The efficiency of metal ion removal by biosorbents depends largely on the reaction conditions, i.e. the pH of the solution, the contact time of the reactants and the mass ratio of the reactants. I conducted such a study by evaluating the removal efficiency of cations present in liquid radioactive waste, such as Co^{2+}, Sr^{2+} and Cs^{+} using alginic acid and sodium alginate [**H03**]. As a result of this research, I determined the optimal conditions for sorption of the aforementioned cations on the studied biosorbents. In addition, I proposed a description of the sorption process with a kinetic model, considering a pseudo-first-order model and a pseudo-double-order model of the sorption reaction of selected cations on the studied biosorbents.

Calculations showed that the sorption process of all studied cations, namely Co^{2+}, Sr^{2+} and Cs^{+} can be described by the pseudo-second-order model, while the sorption capacity of both biosorbents at equilibrium (q_e) was similar. The highest qe values (90-97 mg/g) were obtained for Co^{2+} and Sr^{2+}, while for Cs^{+} the adsorption capacity of both biosorbents was about 72 mg/g. Significantly higher values of reaction rate constants (k_2) were also obtained for Co^{2+} and Sr^{2+} ions than those obtained for Cs^{+} ions.

With the optimal sorption conditions established, the UF/sorption process experiment was then carried out in a continuously operating system (Fig. 7). The membrane system was equipped with a tubular ceramic membrane (length - 0.25 m, outer diameter - 0.01 m) with a molecular weight cutoff of MWCO=10 kDa.

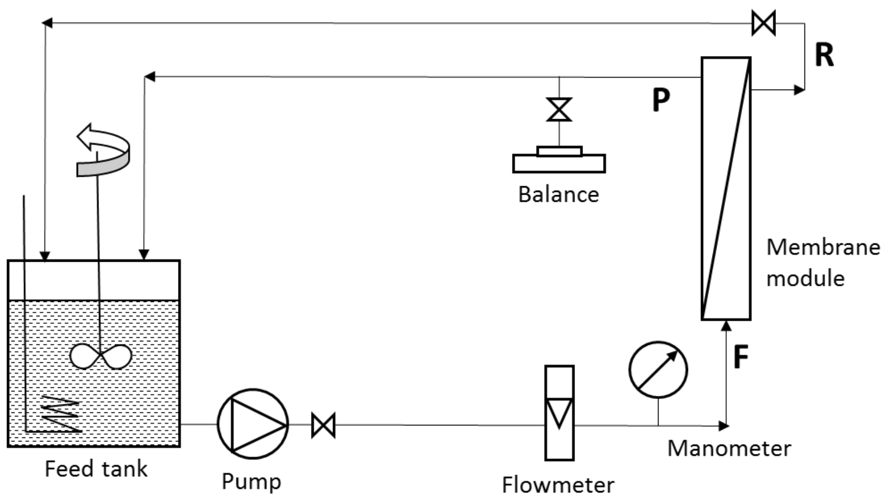

Fig. 7: Schematic of the test facility used for the sorption-assisted UF process using alginic acid and sodium alginate [**H03**].

The research was conducted using aqueous solutions containing the radionuclides ^{60}Co and ^{85}Sr, and sodium alginate as a sorbent. The proposed hybrid UF/sorption process allowed for efficient removal of radionuclides, and thus a high decontamination factor (DF) of the purified solution.

Achievement:

(a) description by mathematical model of the sorption kinetics of Co^{2+}, Sr^{2+} and Cs^{+} ions on alginic acid and sodium alginate;

(b) decontamination of model solutions of liquid radioactive waste by a hybrid UF/sorption process

3.2.3. Use of MOF-type substances

In addition to waste materials, or other low-cost materials of natural origin, work is underway on modern materials that could efficiently and selectively remove metal ions from liquid waste. One such material that has been attracting ever-increasing interest in recent times is metal-organic-framework (MOF). The reason why there is so much interest in these materials is due to their unique properties, the multitude of possible structures and the relatively simple method of synthesizing them.

MOF structures are built from small metallic or oxy-metallic groups connected to each other by coordination bonds through organic ligands with at least two functional groups, mainly carboxyl groups. The possibility of independent shaping of the form of the organic and inorganic parts makes it possible to obtain a theoretically unlimited number of structures differing in porosity parameters: pore geometry, size of specific surface area of pores and physicochemical properties.

Due to the promising properties of MOF-type substances, they were investigated by me for their applicability in the MF/sorption hybrid process for the removal of Hg^{2+} ions from aqueous solutions [**H04**]. As part of the research, a method was developed to synthesize two MOF-type sorbents UiO-66modified with thioglycolic acid and a composite of UiO-66 with cellulose. The chemical structure of UiO-66 is described by the formula: $Zr6O_4(OH)_4(BDC)_6$, where BDC stands for the anion of doubly ionized terephthalic acid. The octahedral walls of the cluster in the structure of this compound are surrounded alternately by four oxygen anions and four hydroxyl groups. The role of the linker in the primary structure is played by the anion of the commonly available terephthalic acid (Fig. 8).

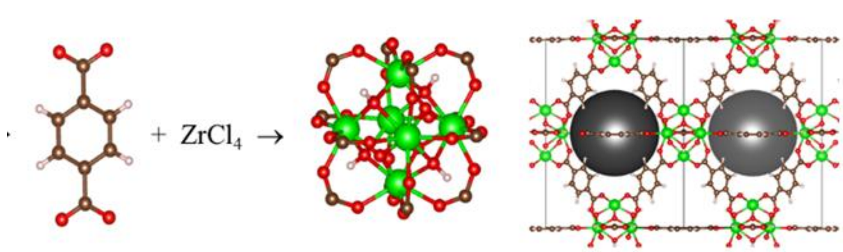

Fig. 8: Image of structural building units and crystal structure of UiO-66 MOF, showing octahedral pores [**H04**].

After confirming that the expected sorbent was obtained, for which the following techniques were used: high-resolution scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF), the two synthesized sorbents were used to remove mercury ions by sorption-assisted microfiltration. The influence of hydrodynamic conditions prevailing in the membrane module on the stability of the sorbent during the experiment proved to be a key parameter determining the ability to successfully remove Hg^{2+} ions from aqueous solutions.

Summarizing the research on hybrid processes based on membrane techniques, it should be emphasized that they are an excellent alternative to other methods of removing radionuclides and heavy metals from liquid wastes. The use of low-cost, readily available materials as binding agents for metal ions and radionuclides in hybrid processes makes the whole process even more attractive, also from the point of view of its economics, as well as environmental protection.

4. Other new applications of membrane processes for treating radioactive solutions

Often, liquid radioactive waste in its composition contains a number of other substances that make it difficult or even impossible to obtain a suitable form of waste that can be transferred for disposal. Nevertheless, the use of membrane processes in the purification of radioactive solutions, is not limited only to the removal of radionuclides or metal ions. Membrane methods can also be used to purify radioactive solutions of more complex composition. These include, for example, liquid organic wastes, or after-treatment fluids from hydraulic fracturing in shale gas extraction.

4.1. After-treatment fluids from hydraulic fracturing of gas-bearing shale.

Post-treatment fluids after hydraulic fracturing of gas-bearing shale are an example of solutions that, in addition to radionuclides, contain a number of other substances. Shale gas extraction generates huge amounts of these toxic fluids, creating a serious problem for the environment. The extraction fluids are characterized by high salinity and contain heavy metals, including rare earth metals, radioactive elements and organic compounds [24]. These fluids must therefore be purified before further use or discharge into the environment. A scheme for treating fluids after hydraulic fracturing proposed the use of membrane techniques [H05]. The fluid subjected to purification was characterized by a high concentration of solutes, in particular a very high concentration of chlorides. Analysis of samples by alpha spectrometry and gamma spectroscopy showed that radioisotopes of uranium (^{238}U and ^{234}U) and ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{212}Pb, ^{208}Tl and ^{40}K were present in the tailings fluid. A multi-step process was developed to treat these wastes, consisting of mechanical removal of suspended solids, removal of organic compounds, heavy metal separation and water recovery. Membrane methods: nanofiltration (NF) and reverse osmosis (RO) were used for the final step of post-treatment fluid purification. The reverse osmosis (RO) process was particularly effective and was proposed as the final purification step. As a result of this process, not only macromolecular substances were removed, but also most of the ions present in the fluid [**H05**].

4.2. Radioactive solutions containing organic compounds

The composition of low-level liquid waste from the use of radioisotopes in scientific research, medicine and industry is often complex. In Poland, this type of waste is sent to the Radioactive Waste Disposal Facility (ZUOP) in Świerk, where it is treated using conventional methods such as evaporation or chemical precipitation. However, this type of waste, in addition to high concentrations of inorganic salts, usually contains organic compounds from, for example, decontamination of laboratories or equipment. The presence of organic substances adversely affects the later stages of radioactive waste processing and the safety of its final storage. Therefore, it is advisable to separate such compounds before the next stages of handling. As part of our work on the removal of organic compounds from aqueous solutions, we use processes such as ozonation, Fenton reaction and electro-oxidation, among others, in the Separation Methods Laboratory [25, 26]. Another interesting solution to the problem of the content of organic compounds in liquid waste can be the use of one of the membrane techniques - electrodialysis (ED) [**H06**]. Electrodialysis is the process of selective release of ions and charged molecules through an ion-exchange membrane, under the influence of an applied voltage. The electrodialysis module consists of alternating cation- and anion-exchange membranes separated by spacers, and the membrane stack is placed between two electrodes (Fig. 9). The advantages of electrodialysis include: greater tolerance of the membranes to changes in solution pH and high chloride content, the ability to operate at temperatures as high as 50°C, elimination of the use of additional reactants, reduction of product losses and minimization of the volume of environmentally harmful waste.

Electrodialysis was used by me to concentrate radionuclides from model liquid waste solutions and to separate organic compounds contained in these solutions [**H06**]. The conditions of the electrodialysis process, i.e. the current intensity and voltage, the ratio of diluate (purified stream) and concentrate (concentrated stream) flow velocities, were tested to determine the optimal parameters for efficient separation of radionuclides and organic compounds. The results of the tests showed that electrodialysis is a favorable method for the disposal of liquid radioactive waste, as it enables both a high degree of solution desalination and radionuclide removal.

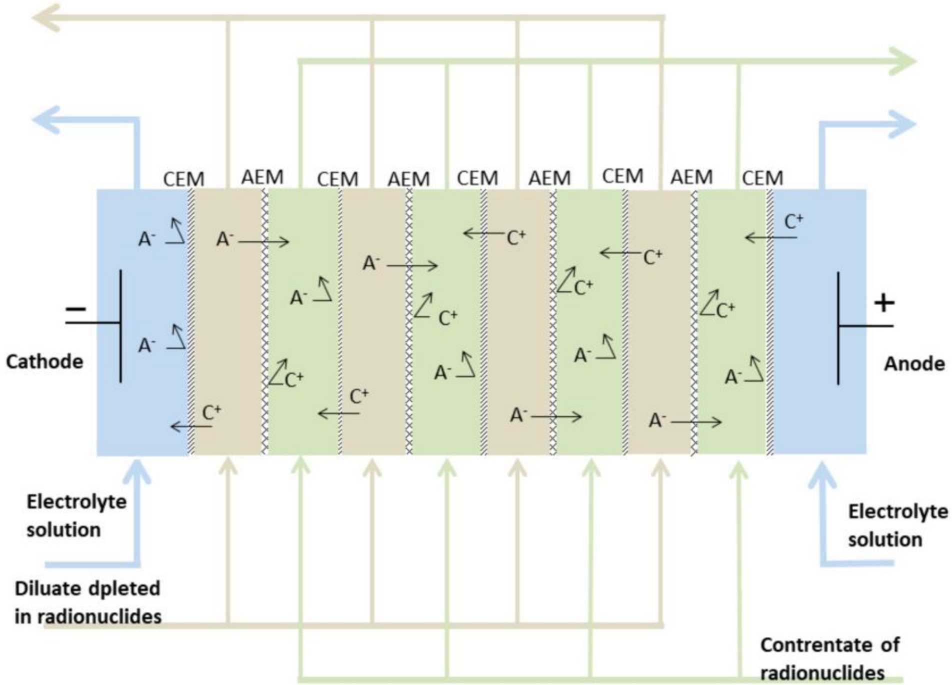

Figure 9: Schematic diagram of the ion-exchange membrane configuration in the membrane module used in the electrodialysis process [**H06**].

In addition, in the event that the organics that make up the additional fouling of the solution are non-ionic compounds (e.g., Triton-X used in radiochemical decontamination), then using ED it is possible to simply separate them from the radionuclides, concentrated along with other inorganic components of the wastewater (e.g., salts) in the concentrate stream. In this way, the problem of solidifying liquid waste contaminated with organic compounds can be solved. In addition, it is possible to recover the organic components for reuse if, for example, for economic or other reasons, it makes sense to do so. If the organic compounds present in radioactive solutions are ionic compounds, then the ED process can also be used to separate them, but proper control of the process conditions or the use of monoanionoselective membranes is necessary [27, 28].

4.3. Uranium ore leaching

In addition to their separation function, membrane modules can also serve as contactors for various chemical processes and reactions [29-31]. Membrane contactors are systems that use porous membranes to transfer mass between phases, but the membrane does not act as a selective barrier It is instead used as a non-selective septum with a developed surface area; placed between two phases, it increases their contact area, and its function is to keep the two phases separate and in contact simultaneously.

As part of my ongoing work on the broader use of processes and membrane modules, I conducted research on the use of one of the membrane modules we use, as a membrane contactor. A helicoidal flow membrane module equipped with a tubular metallic membrane was used for this purpose [32]. This module served as a contactor in an alternative method for leaching uranium from uranium ore [**H07**]. In the conducted experiments, I investigated the influence of such process parameters as the feed flow rate and the rotation frequency of the inner cylinder located in the membrane module on the leaching efficiency. Analyses of the obtained results showed that the use of a membrane contactor makes it possible to achieve high leaching efficiency of uranium and its associated metals (La, Th, V) from crushed uranium ore. By conducting the process in a membrane apparatus at room temperature, a similar degree of leaching was obtained to that which can be obtained by leaching uranium in a stationary stirred reactor, which requires a temperature of 80°C [33].

An additional advantage of using a membrane contactor in this process was that two processes (leaching and phase separation) were carried out in a single apparatus. Here, the microfiltration membrane was also used to separate the liquid phase, containing uranium ions, from the solid phase, which is the ore residue after leaching in the membrane contactor.

Achievement:

(a) Use of the membrane module both as a contactor in the uranium leaching process and also for the treatment of liquid waste remaining after uranium ore leaching (hybrid process - leaching/microfiltration).

(b) Obtaining European Patent No. 2604713

5. Reduction of adverse phenomena occurring in membrane filtration equipment used in nuclear technologies; minimization of membrane fouling.

Membrane processes are among the effective and economical separation methods, however, adverse phenomena accompanying the filtration process that occur in the membrane layer lead to a decrease in process efficiency over time and often membrane fouling and are the cause of limitations in the widespread use of membrane techniques.

Membrane blockage phenomena can be partially reduced by:

- pretreatment solution preparation;
- membrane cleaning and washing;
- modifying the surface properties of the membrane by introducing a low-density solvent stream,
- appropriate shaping of hydrodynamic conditions in membrane modules, including:
    - increasing turbulence in areas adjacent to the membrane surface by intense mixing of the liquid over the membrane surface or high linear velocities of the liquid;
    - using turbulence promoters, such as moving parts, rotating filter baffles;
    - conducting filtration in a cross-flow regime, so-called "cross-flow."

All measures carried out to reduce membrane blockage are extremely important, as they contribute to prolonging the service life of the membrane and increase the efficiency of the membrane process, and thus reduce the cost of using the process.

In order to develop methods that enable proper operation, full utilization of membrane apparatuses and the assumed intensity of the physical and chemical processes that take place in them, it is necessary to fully understand and diagnose the phenomena that limit them (membrane fouling).

5.1. Study of membrane fouling using radioactive tracers and photoacoustic methods

Despite many ongoing works and a number of references on membrane blocking (fouling), the basic mechanisms governing this phenomenon are still not fully understood [34-35]. In my doctoral dissertation entitled: "New radioactive tracers of the liquid and solid phases for applications in the study of membrane processes," I attempted to apply the radio-marker method to the study of membrane processes and phenomena occurring in membrane filtration apparatus. I developed this research in my further work.

Tracer techniques are a non-invasive method of learning about the dynamics of media flow in apparatuses, so they are an alternative to other ways of learning about the phenomena occurring inside these devices. The use of radioactive tracers allows the use of very small amounts of tracer due to the very high sensitivity of detection of ionizing radiation. Measurements using radionuclides as tracers are non-contact measurements, since radiation detection can take place remotely through layers of other materials.

The results of the research carried out within the framework of the doctoral dissertation showed that a lot of valuable information about the fouling phenomenon can be obtained using the radio-tag method [36-39]. Therefore, the method of studying membrane fouling using radio markers was the basic method I decided to use to analyze this phenomenon in membrane modules (tubular and flat), which I used to remove radionuclides and metal ions from liquid waste. The ongoing work was a continuation and development of the methods developed in my doctoral thesis.

The first work focused on the study of fouling occurring in a cross-flow flat module during filtration of bentonite suspension, as a material used in sorption-assisted filtration processes [**H08**]. The stage of selecting a radioactive tracer and preparing the labeled phase is extremely important for obtaining meaningful and reliable experimental results. The radiolabel should meet several basic requirements, which include, first of all, a sufficiently short half-life; a sufficiently high specific activity of the radioisotope used; and the type and energy of radiation emitted by the isotope, which can be recorded during the experiment.

For the labeling of the solid phase - bentonite - ^{140}La was chosen because of its relatively short half-life ($t_{1/2}$= 40.3 h), the high energy of the emitted gamma radiation (E_1 = 0.8 MeV, E_2 = 1.6 MeV), easy detection, as well as the appropriate durability of binding to bentonite. The optimal conditions for adsorption of lanthanum on bentonite determined experimentally in preliminary studies were as follows: pH in the range of 5 - 7; the time required to reach equilibrium was 5 min. The labeled suspension was the feed solution to the membrane module, shown schematically in Figure 10. I carried out filtration in a closed system, i.e. the permeate and retentate streams were returned to the pig iron tank. Meanwhile, the formation of a precipitate layer on the membrane surface was recorded by measuring the specific activity of the precipitate thanks to a scintillation probe placed under the membrane module and connected to a radiometer.

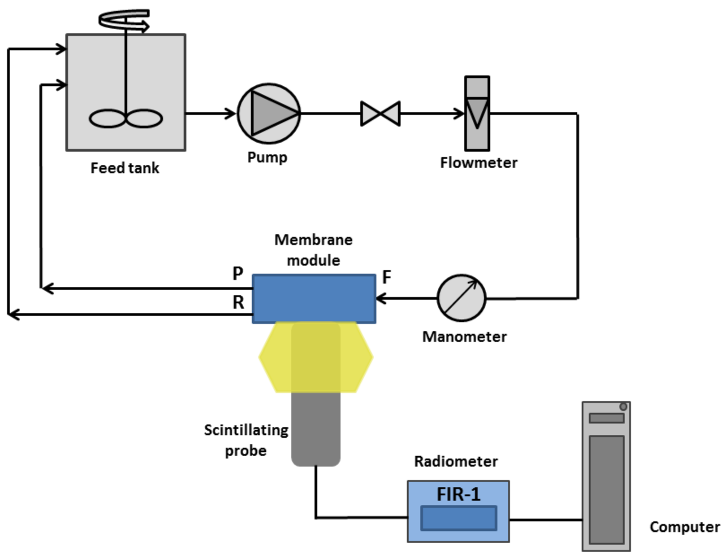

Fig. 10: Schematic of the test installation with a flat module [**H08**].

The results of the experiments showed the possibility of the proposed method to determine, in situ, both the kinetics of sludge formation on the membrane, the determination of its thickness and permeability, depending on the conditions of the process. Example results are shown in Figure 11.

a) **b)**

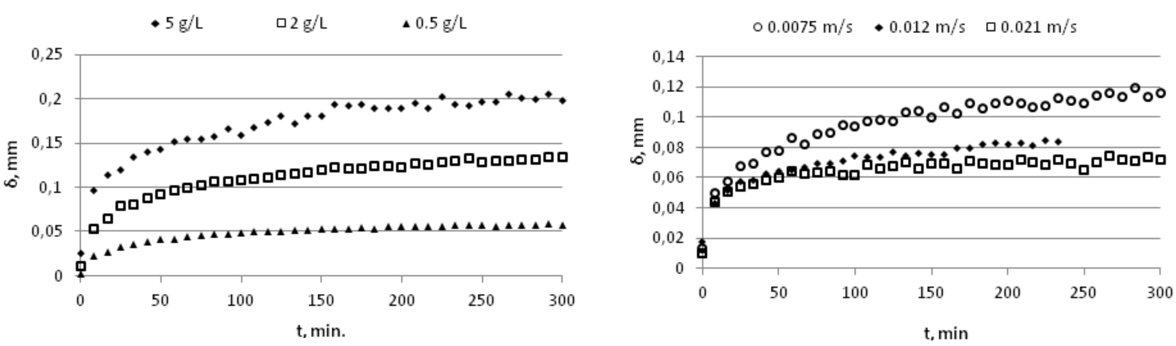

Fig. 11: Change in the thickness of the bentonite deposit on the flat membrane as a function of: a) bentonite concentration, (Δp = 0.15 MPa, u = 0.0075 m/s); b) liquid flow velocity over the membrane (Δp = 0.3 MPa, c = 2 g/L).

Thanks to the use of the radio-marker method, information on the progress of membrane blockage was obtained in situ, during the experiments. Such a tool allows rapid operator response and adjustment of process conditions to minimize the adverse effects of fouling. Therefore, this novel method can be successfully applied to control the course of membrane processes. In addition, it can be considered as an alternative or complement to other known techniques for studying membrane fouling.

Achievement:

Quantifying the blocking phenomenon of a flat membrane by determining the thickness of the deposit formed on the membrane surface.

Photoacoustic spectroscopy (FT-IR/PAS) [**H09**] was another technique I used, in addition to the radioimmunoassay method, to study the fouling of flat membranes. Using the FT-IF/PAS (Fig. 12), technique, optically opaque, infrared scattering, irregularly shaped samples with different morphologies can be studied [40]. Like tracer techniques, it is non-destructive, does not require lengthy preparation of the material to be analyzed, and can be used in the analysis of layered materials.

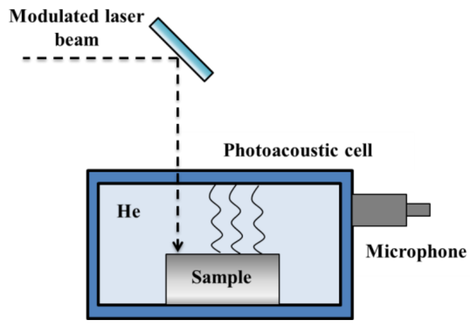

Fig. 12: Principle of photoacoustic spectroscopy.

Analyses of the surface of flat membranes made of PES carried out using photoacoustic spectroscopy (FT-IR/PAS) have demonstrated the effectiveness of this method for studying the fouling kinetics of such membranes **[H09]**. This method is sensitive enough that even small changes in the thickness of the membrane's accumulated film can be recorded with it. The model liquids in the study were solutions of water-soluble poly(acrylic acid) (PAA) of different molecular weights and a suspension of red clay. PAA and red clay were chosen as model substances frequently used in our Laboratory in hybrid ultra- or microfiltration processes assisted by complexation or sorption, and whose presence in filtered fluids contributes to membrane blockage and a decrease in process product flux. The conducted research concerned the possibility of in situ tracking of the degree of membrane fouling during filtration of these two types of media, as well as the study of the effect of the size of the molecular weight of the separated particles on the intensity of membrane blocking. The results of the experiments showed that the course of the fouling phenomenon, which differs for the two types of filtered media and depends on the molecular weight of PAA, can be easily recorded by photoacoustic spectroscopy. The results obtained were confirmed by two other methods: radioimmunoassay technique (Fig. 13) and scanning electron microscopy (SEM).

In addition, it has been shown that the FT-IR/PAS method can be used during the selection of membrane cleaning methods, as well as to analyze the effectiveness of these methods.

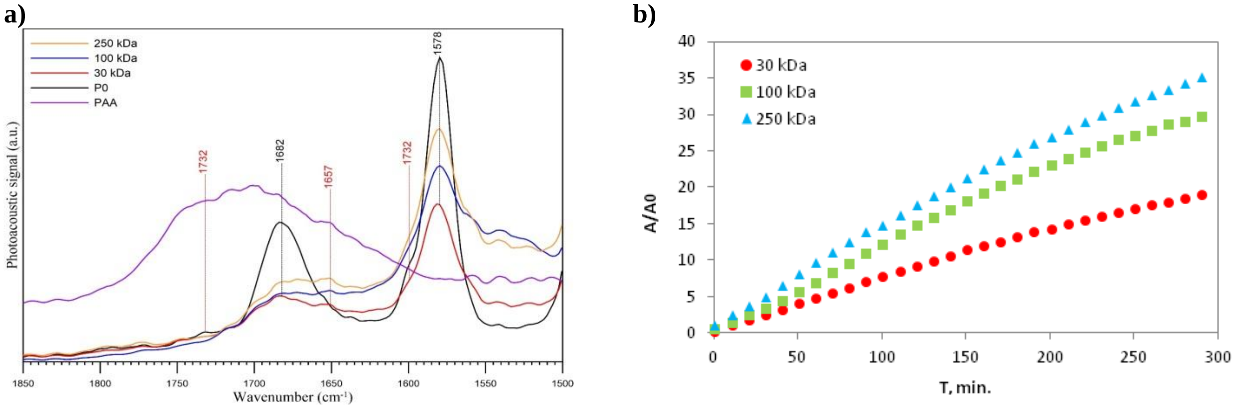

Fig. 13: Analysis of the effect of PAA particle size on the fouling of a flat membrane made of PES, MWCO=10 kDa; (a) results obtained using photoacoustic spectroscopy; (b) result obtained using the radio-marker method [**H09**].

The criterion for the application of this technique is the ability to extract a suitable band on the absorption spectrum coming from the substance deposited on the membrane, which will not overlap with the bands coming from the membrane material. It is for this reason that the FT-IR/PAS technique proved to be unusable for the analysis of membranes made of regenerated cellulose used for filtration of polyacrylic acid - there were no bands on the absorption spectrum originating from PAA that did not overlap with bands originating from RC.

Achievement:

(a) Development of a method to study membrane fouling based on photoacoustic spectroscopy,

b) Confirmation of the obtained results using other methods (radiotracer and SEM).

While fouling, which occurs in the case of flat membranes, such as those made of polymers, can be studied relatively easily using various methods (optical, photoacoustic), it is somewhat more difficult in the case of tubular membranes. Metallic or ceramic membranes pose a particular challenge, as sampling such materials for analysis, when using invasive methods, is difficult. Membranes made of these materials are often stashed for the purification of liquid radioactive waste or other industrial wastewater, due to their durability and resistance to ionizing radiation and aggressive substances. During purification of these solutions using tubular membrane modules, macromolecular substances used to complex metal ions or radionuclides present in the solutions cause blocking of the membrane surface and pores, and the distribution of the membrane elongation layer can be non-uniform. The rate of membrane blocking and the distribution of the deposit layer will depend on the hydrodynamic conditions in the module and the type of filter medium. These parameters, affecting the fouling of tubular membranes, were investigated by us using a radio-labeling method [**H10**] with a model compound, often used in hybrid processes as a metal ion and radionuclide binding agent - polyacrylic acid. The isotope ^{140}La was proposed for labeling this compound. This isotope was obtained by irradiating a $La(NO_3)_3$ sample in a neutron flux of 5×10^{13} $s^{-1}m^{-2}$ at the Maria Reactor (Spruce). As a result of earlier experiments, the reaction conditions of ^{140}La with PAA (pH, contact time, reactant ratio) were determined, and by performing leaching tests of the radionuclide, it was shown that the binding of the radionuclide ^{140}La by polyacrylic acid was stable. The diagram below shows how La^{3+} is bound by polyacrylic acid molecules (Figure 14). One PAA chain provides multiple carboxyl groups, which are among the most suitable ligands for lanthanum cations [41].

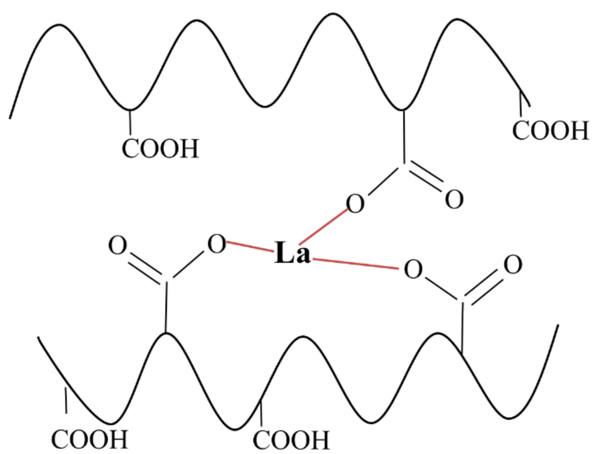

Fig. 14: Scheme of La ion binding by polyacrylic acid.

Polyacrylic acid labeled with ^{140}La (^{140}La-PAA), selected on the basis of the experiments described above, was used to determine the fouling of a ceramic tubular membrane, which is a component of one of the membrane installations used in the Laboratory to study the removal of radionuclides from aqueous solutions or model liquid radioactive waste (Fig. 15).

In order to accurately determine the amount of PAA accumulated at specific points on the membrane during filtration of the PAA solution, 4 scintillation probes (7-10) were placed along the membrane module (1). With this arrangement, it was possible to track "in-situ" fouling of the membrane in individual parts of the membrane.

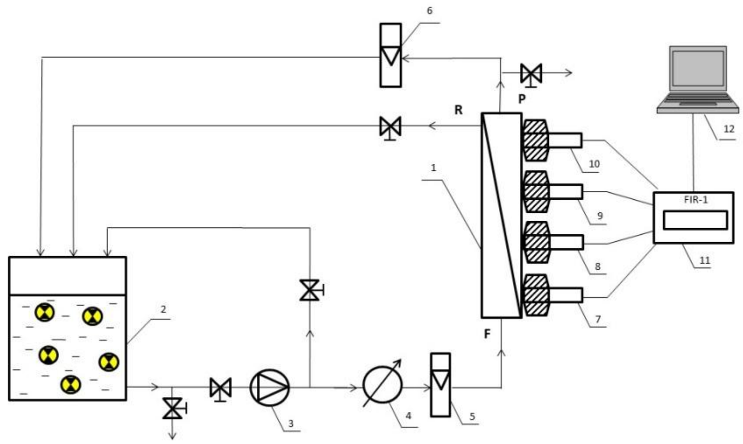

Fig. 15: Membrane system with ceramic tube module. 1 - membrane module, 2 - feed tank, 3 - pump, 4 - pressure gauge 5, 6 - flow meters, 7-10 - scintillation probes, 11 - radiometer, 12- computer. [H10].

In addition, we showed that depending on the size of the complexing agent molecules (30, 100 and 250 kDa), there are different kinetics of the fouling phenomenon and a different distribution of molecules along the membrane module. To describe the kinetics of fouling, I used two kinetic models: pseudo-first-order and pseudo-double-order, with calculations showing that the latter better describes the blocking of the membrane under study. This model can be expressed in the form of the equation:

$$\frac{dA_t}{dt} = k_2(A_e - A_t)^2$$

where:
A_t - specific activity at time t,
A_e - specific activity at equilibrium,
k_2 the pseudo-drug reaction rate constant of PAA deposition on the membrane (1/min).

Polyacrylic acid with the lowest MW (i.e., 30 kDa) blocked the membrane the fastest, causing the greatest decrease in permeate flux, as indicated by the decrease in the reaction rate constant - k_2 (Fig. 16). However, the amount of precipitate formed on the membrane (illustrated by the magnitude of the measured specific activity of the precipitate layer, A_e) is the smallest in this case.

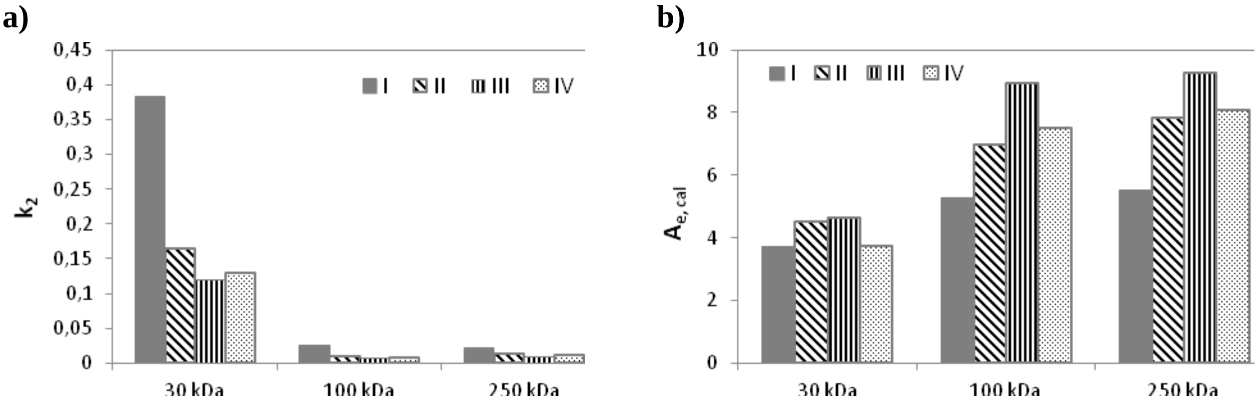

Fig. 16: Comparison of kinetic parameters (a) reaction rate constant and (b) A at equilibrium, obtained in different membrane sectors (I - IV) for PAA with different MW [**H10**].

This indicates the existence of different mechanisms of membrane blockage, which depend on the size of the particles contained in the filtered medium.

The results of the studies described in this work have allowed a more complete understanding of the unfavorable phenomenon of tubular membrane fouling and appropriate control of the process to increase its efficiency.

Achievement:

Development of a method for testing the fouling of tubular membranes using radio tracers.

5.2. Reduction of fouling through the use of dynamic filtration

Studies on the phenomenon of fouling, carried out by various methods, described in Section 5.1, have made it possible to gain a better understanding of this unfavorable phenomenon and, at the same time, have indicated the possibility of reducing it. Minimization of fouling is possible, among other things, thanks to appropriate shaping of hydrodynamic conditions in membrane modules, for example, by using dynamic filtration. In my research on the removal of metal ions and radionuclides, which is part of the described scientific achievement [**H04**], [**H07**], as well as in earlier works [16, 17, 32], I used a membrane module that met the conditions of a dynamic filtration apparatus. It is a tubular module in which a rotor is placed, the rotation of which generates Couette-Taylor flow, the so-called helicoidal flow.

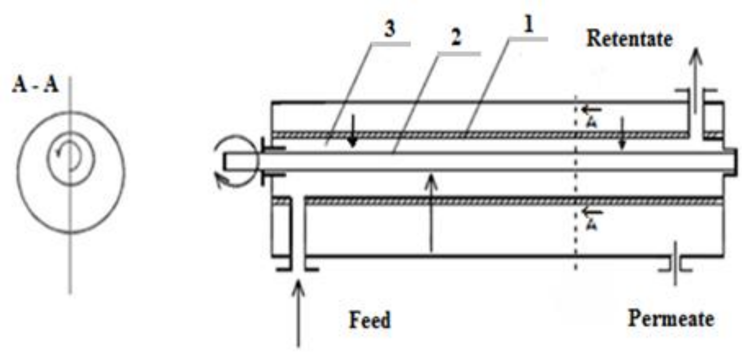

Fig. 17: Schematic of the helicoidal flow module. 1-membrane, 2-rotor, 3-space with Couette-Taylor flow.

The use of this solution, for example, in the process of leaching uranium from ores [**H07**], has revealed many of its advantages, including a reduction in the thickness of the layer of precipitate formed on the membrane during filtration, and thus a smaller decrease in permeate flux over time, thus increasing the efficiency of the membrane process (Fig. 18a).

a) b)

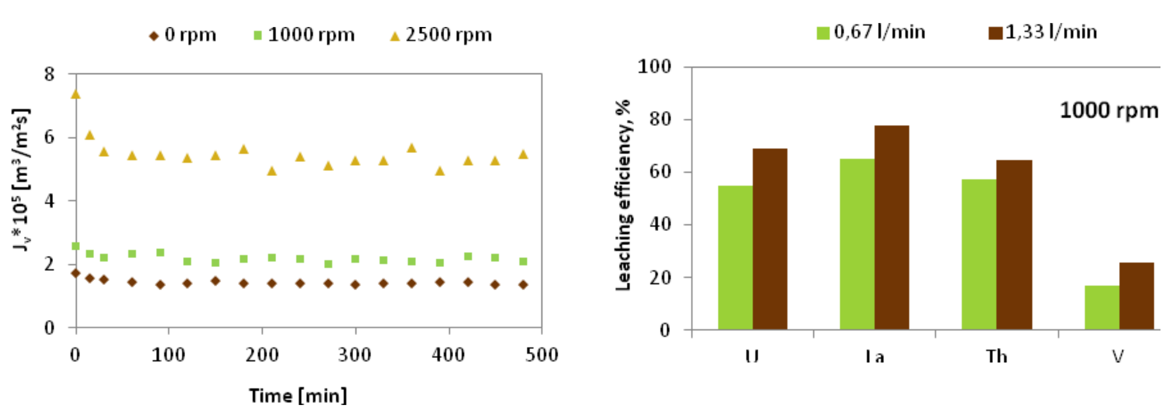

Fig. 18. Comparison of: a) permeate flux versus rotor rotation frequency (Ω); Q_S=0.67 l/min, b) elemental leaching capacity versus feed solution flow rate (Q_S) [**H07**].

In addition, in a helicoidal flow module, it is possible to achieve efficient mixing of the reactants and, consequently, high mass transfer coefficients, as indicated by the satisfactory values of the uranium leaching rate (Fig. 18b) obtained in such a process without the need for elevated temperatures. Similar uranium leaching values can be obtained by conducting the process in a stirred reactor, however, in this case it is necessary to raise the temperature to 80°C.

Achievement:

Reduction of fouling in a tubular membrane module through dynamic filtration.

6. Summary

The work that makes up my scientific achievement is a wide-ranging analysis of the feasibility of using membrane processes to remove radionuclides and heavy metals from liquid wastes. The proposed membrane processes were optimized by me in terms of efficiency of separation of hazardous components of these wastes. In addition, in order to minimize the occurrence of membrane blockage and its adverse effects, which would enable the intensification of the processes used, I analyzed the parameters affecting this phenomenon and attempted to describe and reduce it, depending on the test system used.

The main achievements in the use of new sorbents for the removal of radionuclides and heavy metals from liquid wastes by using membrane hybrid techniques include:

- demonstration of the feasibility of using industrial waste materials as an adsorbent for radionuclides and using them in a hybrid MF/sorption or UF/sorption process;
- optimization of a hybrid MF/sorption process using fly ash (FA) allowing efficient removal of radionuclides from aqueous solutions and reducing the amount of sorbent relative to the amount of sorbent that needs to be used in a sorption process conducted under stationary conditions;
- description with a mathematical model of the kinetics of sorption of Co^{2+}, Sr^{2+} and Cs^{+} ions on alginic acid and sodium alginate;

- decontamination of model liquid waste solutions by a hybrid UF/sorption process using sodium alginate.

Seeking other opportunities to apply membrane techniques to the purification of radioactive solutions, I conducted a number of studies, the most important achievements of which were:

- development of a method for pretreatment of fluids after hydraulic fracturing, in which membrane techniques were an important part of the overall process;
- development of a method for effective removal of radionuclides and other inorganic compounds from radioactive solutions by electrodialysis;
- determination of conditions for separation of organic compounds present in radioactive solutions, e.g., in subcontamination fluids, using ED;
- use of a membrane module in the uranium leaching process simultaneously as a contactor and also for the treatment of liquid waste remaining after uranium ore leaching (hybrid process - leaching/MF).

In order to intensify the membrane processes used to remove radionuclides and heavy metals from liquid waste, I attempted to investigate the unfavorable phenomenon of membrane blocking. When analyzing fouling, I used the radiotracer technique, as well as photoacoustic spectroscopy (FT-IR/PAS) and scanning electron microscopy (SEM). Achievements in this part of the work include:

- quantifying the phenomenon of flat membrane fouling by determining the thickness of the deposit formed on the membrane surface;
- development of a method for studying membrane fouling based on photoacoustic spectroscopy and also confirmation of the results obtained using other methods (radioimmunoassay and SEM);
- development of a method for testing the fouling of tubular membranes using radio-markers;
- more complete understanding of the phenomenon of fouling of tubular membranes, enabling appropriate control of the filtration process to increase its efficiency;
- reducing fouling in tubular membrane module by using dynamic filtration.

The results of the work that is the subject of my scientific achievement entitle me to conclude that the removal of radionuclides and heavy metals from liquid wastes through the use of methods based on membrane processes is a favorable solution and can be an alternative to other methods used for this purpose. Hybrid processes based on membrane techniques and using low-cost, readily available materials as binding agents for metal ions and radionuclides improve the economics of the overall process and reduce the environmental impact.

I have also shown that the unfavorable phenomenon of a decline in membrane process performance due to membrane fouling can, after proper diagnosis of its causes and identification of mechanisms, be reduced. I believe that the scientific achievement I have described can be a step towards eliminating the obstacles standing in the way of even wider application of membrane techniques in various industries and environmental protection.

7. References:

[1] M. Bodzek, Możliwości wykorzystania nanotechnologii i nanomateriałów w procesach uzdatniania wody i oczyszczania ścieków. Cz. II, Membrany i procesy membranowe, Technologia Wody, 2020, Nr 6 (74) 8-19

[2] A.G. Fane, R. Wang, M.X. Hu, Synthetic Membranes for Water Purification: Status and Future, Angew. Chem. Int. Ed. 2015, 54, 3368 – 3386, DOI: 10.1002/anie.201409783

[3] M. A. Glaus, A. Laube, L. R. Van Loon, A generic procedure for the assessment of the effect of concrete admixtures on the sorption of radionuclides on cement: Concept and selected results. MRS Online Proceedings Library Archive (2003) 807.

[4] R. O. Abdel Rahman, H. A. Ibrahium, Yung-Tse Hung, Liquid Radioactive Wastes Treatment: A Review, Water 2011, 3, 551-565; DOI:10.3390/w3020551 [5] INTERNATIONAL ATOMIC ENERGY AGENCY Handling and Processing of Radioactive Waste from Nuclear Applications, 2001, TECHNICAL REPORTS SERIES No. 402, IAEA, VIENNA

[6] G. Zakrzewska-Trznadel, Advances in membrane technologies for the treatment of liquid radioactive waste, Desalination, 2013, 321, 119–130. DOI: 10.1016/j.desal.2013.02.022.

[7] A.K. Pabby, Membrane techniques for treatment in nuclear waste processing: global experience, Membr. Technol., 2008, 11, 9-13

[8] D. Chen, X. Zhao, F. Li, X. Zhang, Rejection of nuclides and silicon from boron-containing radioactive waste water using reverse osmosis, Sep.Purific.Technol., 2016, 163, 92-99, DOI: 10.1016/j.seppur.2016.02.027

[9] M. D. Garba, M. Usman, M. A. Jafar Mazumder, A. Al‑Ahmed, Inamuddin, Complexing agents for metal removal using ultrafltration membranes: a review, Environ. Chem. Lett., 2019, 17, 1195–1208, DOI: 10.1007/s10311-019-00861-5

[10] B.M. Smyth, P.Todd, N. Bowman, Hyperbranched chelating polymers for the polymer-assisted ultrafiltration of boric acid. Separ. Sci. Technol., 1999, 34, 1925-1945.

[11]. B.F. Smyth, R.R. Gibson, G.D. Janinen, T.W. Robinson, N.C. Schroeder, N. Stalnaker, Preconcentration of low levels of americium and plutonium from waste waters by synthetic water-soluble metal-binding polymers with ultrafiltration. J. Radioanal. Nuci. Chem., 1998, 234, 225-229.

[12] G. Zakrzewska-Trznadel, M. Harasimowicz, Removal of radionuclides by membrane permeation combined with complexation, Desalination 2002, 144, 207–212, https://doi.org/10.1016/S0011-9164(02)00313-2

[13] G. Zakrzewska-Kołtuniewicz, A. Miśkiewicz „Processing of radioactive solutions from the fuel cycle by means of membrane methods" in:. „PET-MOF-CLEANWATER Project", Warsaw, Poland, 2020 IChTJ, Warsaw, 2020 (red.: W. Starosta, B. Sartowska).

[14] N. Uzal, A. Jaworska, A. Miśkiewicz, G. Zakrzewska-Trznadel, C. Cojocaru, „Optimization of Co2+ ions removal from water solutions via polymer enhanced ultrafiltration with application of PVA and sulfonated PVA as complexing agents" J. Colloid Interf. Sci. 2011, 362, 615–624

[15] A. Miśkiewicz, G. Zakrzewska-Kołtuniewicz, W. Starosta, Chapter 4 "MOF assisted membrane process for removal of radionuclides and other hazardous elements from aqueous solutions" in UJ Monograph: „Waste PET-MOF-Cleanwater: Waste PET-Derived Metal-Organic Framework (MOFs) as Cost-effective Adsorbents for Removal of Hazardous Elements from Polluted Water, Editors: J. Ren, P. Nosizo Nomngongo, Tien-Chien Jen, 11/10/2022, DOI: 10.36615/9781776419463-04

[16] C. Cojocaru, G. Zakrzewska-Trznadel, A. Miśkiewicz, "Removal of cobalt ions from aqueous solutions by polymer assisted ultrafiltration using experimental design approach Part 2: Optimization of hydrodynamic conditions for a crossflow ultrafiltration module with rotating part", J. Haz. Mat., 2009, 169, 610–620

[17] C. Cojocaru, G. Zakrzewska-Trznadel, M. Harasimowicz, A. Jaworska, A. Miśkiewicz, Optimization of polymer enhanced membrane filtration in helical apparatus, VII Scientific Conference of Environment Engineering 4-7 June 2008, Ustroń, „Membrane and Membrane Processes in Environmental protection", Monografie Komitetu Inżynierii Środowiska, PAN, 2008, vol. 49 ISBN 83-8929, s. 359-363.

[18] L. Fuks, I. Herdzik-Koniecko, L. Maskalchuk, T .Leontieva, Clay-salt slimes of the JSC "Belaruskali" as potential engineering barriers in the radioactive waste repositories: Sorption of Cs(I), Sr(II), Eu(III) and Am(III). Int. J. Environ. Sci. Technol. 2018, 15, 2047–2058

[19] L. Fuks, L. Maskalchuk, I. Herdzik-Koniecko, T. Leontieva, Clay-salt slimes of the "Belaruskali" - novel sorbents for management of liquid radioactive wastes and decontamination of environmental water streams, J. Radioanal. Nucl. Chem., 2019, 320 87-100

[20] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res., 2003, 37, 4311-4330, DOI: 10.1016/S0043-1354(03)00293-8

[21] Ji L., Xie S., Feng J., Li Y., Chen L.: Heavy metal uptake capacities by the common freshwater green alga Cladophora fracta. J. Appl. Phys., 24, 979-983 (2012).45.

[22] A. Maureira, B.L. Rivas, Metal ions recovery with alginic acid coupled to ultrafiltration membrane. Eur. Polym. J., 2009, 45, 573-581

[23] W. Plazinski, Binding of heavy metals by algal biosorbents. Theoretical models of kinetics, equilibria and thermodynamics, Adv. Colloid Interf. Sci., 2013, 197–198, 58–67, DOI: 10.1016/j.cis.2013.04.002.

[24] A. Mykowska, J. Hupka, Natural radioactivity of solid and liquid phases from shale oils and gas prospecting in Pomeriana, Pol. J. Environ. Stud., 2014, 23(6), 2137.

[25] A. Miśkiewicz; K. Kiegiel; I. Herdzik-Koniecko; L. Fuks; G. Zakrzewska- Koltuniewicz, Treatment of Liquid Radioactive Waste Containing Organic Substances, International Conference on Radioactive Waste Management Solutions for a Sustainable Future, IAEA, Wiedeń, Austria, 1–5 Listopada 2021

[26] A. Miśkiewicz, S. Velizarov, „Effect of molecular mass on boron-doped diamond anodic mineralization of water-soluble organic polymers" Sep. Purif. Technol. 2011, 83, 166-172,

[27] Y., Zhang, L. Pinoy, B. Meesschaert, B. Van Der Bruggen, Separation of small organic ions from salts by ion-exchange membrane in electrodialysis. Am. Inst. Chem. Eng. J. 2010, 57, 2070–2078.

[28] K. Majewska-Nowak, Wykorzystanie metod elektromembranowych do odsalania roztworów zawierających substancje organiczne, Ochrona Środowiska, 2014, Vol. 36(4), 33-43

[29] E. Drioli, E. Crurcio, G. Di Profio, State of the art and recent progresses in membrane contactors. Chem. Eng. Res. Des., 2005, 83(3), 223-233, DOI: 10.1205/cherd.04203

[30] A. Mansourizadeh, I. Rezaei, W. J. Lau, M. Q. Seah, A. F. Ismail, A review on recent progress in environmental applications of membrane contactor technology, J. Environ. Chem. Eng., 2022, 10(3), 107631, DOI: 10.1016/j.jece.2022.107631

[31] A. Markowska-Radomska, E. Dłuska, G. Zakrzewska-Kołtuniewicz, A. Miśkiewicz: Odzysk metali ziem rzadkich z roztworów po ługowaniu magnesów trwałych w procesie zintegrowanym z wykorzystaniem emulsyjnych membran ciekłych. Inż. Ap. Chem., 2017, 56, 4, 128-129

[32] G. Zakrzewska-Trznadel, M. Harasimowicz, A. Miśkiewicz, A. Jaworska, E. Dłuska, S. Wroński "Reducing fouling and boundary-layer by application of helical flow in ultrafiltration module employed for radioactive wastes processing, Desalination, 2009, 240, 108-116,

[33] K. Kiegiel, G. Zakrzewska-Kołtuniewicz, D.Gajda, A Miśkiewicz, A. Abramowska, P. Biełuszka, B. Danko, E. Chajduk, S. Wołkowicz, Dictyonema black shale and Triassic sandstones as potential sources of uranium. Nukleonika, 2015, 60(3), 515-522, doi: 10.1515/nuka-2015-0096;

[34] H. S. Abid, D. J. Johnson, R. Hashaikeh, N. Hilal, A review of efforts to reduce membrane fouling by control of feed spacer characteristics, Deasalination, 2017, 420, 384-402, DOI: 10.1016/j.desal.2017.07.019

[35] M. Parau, T. F. Johnson, J. Pullen, D. G. Bracewell, Analysis of fouling and breakthrough of process related impurities during depth filtration using confocal microscopy, Biotechnol. Prog., 2022, 38, 3233, DOI: 10.1002/btpr.3233

[36] A. Miśkiewicz, G. Zakrzewska-Trznadel, A. Jaworska, A. Dobrowolski, Zastosowanie technik izotopowych do badania procesów membranowych, Monografie Komitetu Inżynierii Środowiska, PAN, 2010, vol.66, ISBN 978-83-89293-91-6, s.49-59;

[37] A. Miśkiewicz, G. Zakrzewska-Trznadel, A. Jaworska-Sobczak, Zastosowanie metody znaczników promieniotwórczych do badań procesów membranowych i aparatów do filtracji membranowej, Monografie Komitetu Inżynierii Środowiska, PAN, 2012, vol. 96, ISBN 978-83-89293-23-7, s.199-210;

[38] A. Miśkiewicz, G. Zakrzewska-Trznadel, A. Dobrowolski, A. Jaworska-Sobczak, Using tracer methods and experimental design approach for examination of hydrodynamic conditions in membrane separation modules, Appl. Rad. Isotop., 2012, 70, 837-847
[39] A. Miskiewicz, G. Zakrzewska-Trznadel Investigation of hydrodynamic behavior of membranes using radiotracer techniques, EPJ Web of Conferences, 2013, 50, 01005
[40] J. Kurczewska, J. Ryczkowski, S. Pasieczna-Patkowska, G. Schroeder, Photoacoustic infrared spectroscopic studies of silica gels with organically functionalized surface, Spectrosc. Lett. 2016, 49(8), 529–534, DOI: 10.1080/00387010.2016.
[41] X. Qi, Z. Wang, S. Ma, L. Wu, S. Yang, J. Xu, Complexation behavior of poly(acrylic acid) and lanthanide ions, Polymer, 2014, 55(5), 1183-1189, DOI: 10.1016/j.polymer.2014.01.051

8. Description of the publication series

The described scientific achievement entitled. "Removal of radionuclides and heavy metals from liquid wastes by using methods based on membrane processes" is based on a series of 10 scientific publications of which I am a co-author ([**H01]-[H10]**), which were published in international peer-reviewed journals (total IF, according to the year of publication, is 34.793), and which are on the ministerial list of scientific journals in 2023 (total number of points of the Ministry of Science and Higher Education is 910). All publications were written after I received my PhD. In 9 papers of the series, I am a correspondence author and in 7 of them, I am also the first author. These are:

- **[H01]** L. Fuks, **A. Miśkiewicz*,** G. Zakrzewska-Kołtuniewicz, Sorption-Assisted Ultrafiltration Hybrid Method for Treatment of the Radioactive Aqueous Solutions, *Chemistry*, **2022**, 4, 1076–1091.DOI: 10.3390/chemistry4030073

IF (in 2022):-	**IF (in 2023): 2.1**
MNiSW points: -	**Citations: 3/1**

In this work, the possibility of using a low-cost waste material, i.e. waste (sludge) from the fertilizer industry, (clay-salt slime, CSS), as an adsorbent, in the treatment of liquid radioactive fallout by a hybrid method - ultrafiltration/sorption, is presented. In order to obtain optimal

results of radionuclide removal, I proposed, on the basis of experiments, the use of appropriate process conditions and membrane type, which were then tested.
My contribution to this article was the developing the research concept, planning the sorption-assisted filtration experiments, analyzing and interpreting the obtained results, and participating in the preparation and submission of the manuscript. I also prepared responses to the reviewers' comments.

- **[H02]** L. Fuks*, **A. Miśkiewicz***, I. Herdzik-Koniecko, G. Zakrzewska-Kołtuniewicz. Fly Ash as a Potential Adsorbent for Removing Radionuclides from Aqueous Solutions in an Adsorption-Membrane Assisted Process Compared to Batch Adsorption. *Membranes* **2023**, 13, 572, DOI: 10.3390/membranes13060572

IF: 4.106	**IF (in 2023): 4,106**
MNiSW poins: 100	**Citations: -new publication**

This publication presents the possibility of using a waste material, such as fly ash, in a sorption-assisted microfiltration process for the treatment of liquid radioactive waste. In this paper, we compared the removal efficiency of radionuclides present in liquid waste, obtained using a hybrid MF-adsorption process and a stationary adsorption method, carried out in a stirred reactor. The results of the research presented in this work showed that by using the hybrid method, it is possible to achieve comparable radionuclide removal efficiency to that achieved by using the conventional method, while reducing the sorbent mass used.

My contribution to this article was the planning the assisted filtration experiments, analyzing and interpreting the results obtained, and participating in the preparation and submission of the manuscript. I also prepared responses to the reviewers' comments.

- **[H03] A. Miśkiewicz***, G. Zakrzewska-Kołtuniewicz, Application of biosorbents in hybrid ultrafiltration/sorption processes to remove radionuclides from low-level radioactive waste, *Desalination and Water Treatment*, **2021**, 242, 47–55, DOI: 10.5004/dwt.2021.27870

IF (in 2021):1.254	**IF (in 2023):1.273**
MNiSW points: 100	**Citations: 2/-**

In this work, I attempted to evaluate the feasibility of using the biosorbents alginic acid and sodium alginate to remove selected radionuclides from aqueous solutions and liquid radioactive waste using a hybrid ultrafiltration/sorption process. I carried out a series of studies, as a result of which I determined the optimal adsorption conditions for model cations found in liquid radioactive waste such as Co^{2+}, Sr^{2+} and Cs^{+} on the above-mentioned biosorbents. I also proposed to describe the sorption process with a kinetic model, with calculations showing that the pseudo-drug model describes well the sorption process of selected cations on selected biosorbents. With established sorption conditions (pH, reactant ratio, reaction time), I carried out the UF/sorption process with solutions containing the radionuclides ^{60}Co and ^{85}Sr, obtaining high decontamination factors (DF).
My contribution to this article was the developing the research concept, planning and performing the assisted filtration experiments, analyzing and interpreting the obtained results, and preparing and sending the manuscript. I also prepared responses to the reviewers' comments.

- **[H04] A. Miśkiewicz***, W. Starosta, R. Walczak and G. Zakrzewska-Kołtuniewicz, MOF-Based Sorbents Used for the Removal of Hg^{2+} from Aqueous Solutions via a Sorption-Assisted Microfiltration, *Membranes*, **2022,** 12, 1280, DOI: 10.3390/membranes12121280

IF (in 2022): 4.106	**IF (in 2023):4.2**
MNiSW points: 100	**Citations: -**

In this work, we have shown that the hybrid method, based on the membrane process applied to the treatment of liquid waste, can also use modern materials of the MOF (Metal Organic Framework) type. In the first stage of the work, methods were developed for the synthesis of two types of metal-organic sorbents, a thioglycolic acid-modified UiO-66 type and a composite of UiO-66 with cellulose. After confirming that the expected sorbent was obtained, for which techniques such as high-resolution scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) were used, tests were carried out using the obtained sorbent to remove mercury ions from aqueous solutions by sorption-assisted microfiltration (SAMF). The influence of hydrodynamic conditions, prevailing in the membrane module, on the stability of the sorbent during the experiment proved to be a key parameter determining the possibility of effective removal of Hg^{2+} ions from aqueous solutions.

My contribution to this article was the preparing the research concept, planning the sorption-assisted filtration experiments, analyzing and interpreting the obtained results, preparing and sending the manuscript. I also prepared responses to the reviewers' comments.

- **[H05]** A. Abramowska, D. K. Gajda, K. Kiegiel, **A. Miśkiewicz**, P. Drzewicz, G. Zakrzewska-Kołtuniewicz, Purification of flowback fluids after hydraulic fracturing of Polish gas shales by hybrid methods, *Separation Science and Technology*, **2018**, 53 (8), 1207–1217, DOI: 10.1080/01496395.2017.1344710

IF (in 2018): 1.37	**IF (in 2023):2.799**
MNiSW points: 25	**Citations: 7/7**

In this work, we have shown that membrane methods are also effective in the treatment of industrial liquid wastes of complex composition, which can include post-treatment fluids after hydraulic fracturing of gas-bearing shales. The reverse osmosis (RO) process, which was used in the final stage of fluid purification, proved particularly effective. As a result of this process, not only the macromolecular substances were removed, but also most of the ions present in the fluid.

My contribution to this article was the planning and carrying out experiments using membrane processes, analyzing and interpreting the results obtained, describing a section of the study on the application of membrane processes in the purification of fluids after hydraulic fracturing of shale, and contributing to the preparation of responses to reviewers' comments.

- **[H06] A. Miśkiewicz**[*], A. Nowak, J. Pałka, G. Zakrzewska-Kołtuniewicz, Liquid Low-Level Radioactive Waste Treatment Using an Electrodialysis Process, *Membranes*, **2021** 11, 324 p. 1-12, doi.org/10.3390/membranes11050324

IF (in 2021): 4.106	**IF (in 2023):4.2**
MNiSW points: 100	**Citations: 7/5**

This paper presents the possibility of using one of the electromembrane techniques - electrodialysis (ED) for the concentration of radionuclides from model liquid waste solutions and for the separation of organic compounds. Testing the purification process conditions proposed by me (current intensity and voltage, ratio of diluate and concentrate flow rates) led to the determination of the optimal electrodialysis parameters. The use of these parameters led to the effective separation of radionuclides and the tested model organic compounds.

My contribution to this article was the developing the research concept, planning experiments using the electrodialysis process, performing research as part of the engineering works carried out under my supervision by students: the Faculty of Chemical and Process Engineering of the Warsaw University of Technology (Jedrzej Pałka) and the Faculty of Chemistry of the Warsaw University of Technology (Agnieszka Nowak), analyzing and interpretation of the obtained results as well as the preparation and submission of the manuscript. I also prepared responses to the reviewers' comments.

- **[H07] A. Miśkiewicz*,** G. Zakrzewska-Kołtuniewicz, E. Dłuska, P. F. Walo, Application of membrane contactor with helical flow for processing uranium ores, *Hydrometallurgy*, **2016**, 163, 108–114, DOI: 10.1016/j.hydromet.2016.03.017

IF (in 2016): 1.933	**IF (in 2023):4.217**
MNiSW points: 45	**Citations: 3/3**

This publication presents the possibility of uranium ore leaching in a membrane contactor. The selection of appropriate process conditions made it possible to obtain the degree of uranium leaching in the process carried out at room temperature in a membrane apparatus, comparable to that which can be obtained in a stirred stationary reactor at 80°C, which makes the hybrid process less energy-intensive. An additional advantage of using a membrane contactor was conducting two processes (leaching and phase separation) in one apparatus.

My contribution to this article was the developing the research concept, planning experiments with the use of a membrane contactor in the uranium ore leaching process, performing research as part of the master's thesis of a student of the Faculty of Chemical and Process Engineering of the Warsaw University of Technology (Pawel Walo) under my supervision, analyzing and interpreting the results obtained and preparation and submission of the manuscript. I also prepared responses to the reviewers' comments.

- **[H08] A. Miśkiewicz***, G. Zakrzewska-Kołtuniewicz, The application of the radiotracer method for the investigation of the cake layer formation on the membrane surface in the cross-flow flat-sheet membrane module, *Desalination and Water Treatment*, **2018,** 128, 228–235, DOI: 10.5004/dwt.2018.22866

IF (in 2018): 1.234	IF (in 2023):1.273
MNiSW points: 100	**Citations: 2/-**

In this article, we describe the results of research on the blocking of flat membranes during the filtration of bentonite suspension, as a material used in sorption-assisted filtration. The tests were carried out using a radiotracer selected appropriately for the labeled phase. The experiments showed the possibility of using the proposed method to determine in situ, both the kinetics of sediment formation on the membrane, and the permeability of the sediment layer and its resistance.

My contribution to the work consisted in developing the research concept, planning experiments using the radiotracer method of selected membrane modules, analyzing and elaborating the results, and preparing and sending the manuscript. I also prepared responses to the reviewers' comments.

- **[H09] A. Miśkiewicz*,** G. Zakrzewska-Kołtuniewicz, S. Pasieczna-Patkowska, Photoacoustic spectroscopy as a potential method for studying fouling of flat-sheet ultrafiltration membranes, *Journal of Membrane Science*, **2019**, 583, 59-69, DOI: 10.1016/j.memsci.2019.04.048

IF (in 2019): 7.183	IF (in 2023):9.5
MNiSW points: 140	**Citations: 5/5**

This article is also a description of the fouling study of membranes used to treat liquid waste. In this work, I proposed the use of another method of fouling research - photoacoustic spectroscopy

(PAS) and comparison of the obtained results with the results of research conducted with the use of radiolabels and electron spectroscopy (SEM).
My contribution to the work consisted in developing the research concept, planning experiments using the radiotracer and photoacoustic methods of selected membrane modules, analyzing and elaborating the results, and preparing and sending the manuscript. I also prepared responses to the reviewers' comments.

- **[H10] A. Miśkiewicz**[*], G. Zakrzewska-Kołtuniewicz Application of the radiotracer method to study the fouling of tubular microfiltration membranes, *Desalination*, **2022**, 534,115795, DOI: 10.1016/j.desal.2022.115795

IF (in 2022): 9.501	**IF (in 2023):9.9**
MNiSW points: 200	**LiczbCitations: -**

In this work, we showed that the phenomenon of fouling, causing a decrease in the filtration efficiency of tubular ceramic membranes often used for the treatment of liquid radioactive waste, can also be studied using radiotracers. As model substances causing blocking of the membrane, we used polyacrylic acid with different molecular weight, used in hybrid UF/complexation or MF/complexation processes, and we showed that depending on the size of the complexant molecules, there is a different fouling kinetics and a different distribution of molecules along the membrane module. The results of the research described in this paper allowed for a more complete understanding of the unfavorable phenomenon of fouling and the appropriate control of the process in order to increase its effectiveness.
My contribution to the work consisted in developing the research concept, planning radiotracer experiments for selected membrane processes, analyzing and elaborating the obtained results, as well as preparing and sending the manuscript. I also prepared responses to the reviewers' comments.

In addition to the above-mentioned 10 works included in the achievement, the author's 14 additional publications should be mentioned, which constitute a supplement (auxiliary material). The list below applies only to the author's publications that were quoted in this study when describing her scientific achievement. These are:

1. **A. Miśkiewicz**, G. Zakrzewska-Kołtuniewicz, W. Starosta, Chapter 4 ”MOF assisted membrane process for removal of radionuclides and other hazardous elements from aqueous solutions” in UJ Monograph „Waste PET-MOF-Cleanwater: Waste PET-Derived Metal-Organic Framework (MOFs) as Cost-effective Adsorbents for Removal of Hazardous Elements from Polluted Water, (Eds: J. Ren, P. Nosizo Nomngongo, Tien-Chien Jen), **2022,** DOI: https://doi.org/10.36615/9781776419463-04
2. G. Zakrzewska-Kołtuniewicz, **A. Miśkiewicz** „Processing of radioactive solutions from the fuel cycle by means of membrane methods” in:. „PET-MOF-CLEANWATER Project” (red.: W. Starosta, B. Sartowska), **2020**, IChTJ, Warsaw, Poland,
3. **A. Miśkiewicz,** G. Zakrzewska-Trznadel, A. Jaworska-Sobczak, „Zastosowanie metody znaczników promieniotwórczych do badań procesów membranowych i aparatów do filtracji membranowej, Monografie Komitetu Inżynierii Środowiska, PAN, **2012,** vol. 96, 199-210, ISBN 978-83-89293-23-7,
4. **A. Miśkiewicz**, G. Zakrzewska-Trznadel, A. Jaworska, A. Dobrowolski, „Zastosowanie technik izotopowych do badania procesów membranowych”, Monografie Komitetu Inżynierii Środowiska, PAN, **2010**, vol.66, 49-59, ISBN 978-83-89293-91-6,
5. C. Cojocaru, G. Zakrzewska-Trznadel, M. Harasimowicz, A. Jaworska, **A. Miśkiewicz,** Optimization of polymer enhanced membrane filtration in helical apparatus, VII Scientific Conference of Environment Engineering 4-7 June 2008, Ustroń, Monografie Komitetu Inżynierii Środowiska, PAN, **2008**, vol. 49, ISBN 83-8929, s. 359-363.
6. K. Kiegiel, G. Zakrzewska-Kołtuniewicz, D.Gajda, **A Miśkiewicz**, A. Abramowska, P. Biełuszka, B. Danko, E. Chajduk, S. Wołkowicz, “Dictyonema black shale and Triassic sandstones as potential sources of uranium”, *Nukleonika*, **2015**, 60(3), 515-522, doi: 10.1515/nuka-2015-0096;
7. **A. Miskiewicz,** G. Zakrzewska-Trznadel Investigation of hydrodynamic behavior of membranes using radiotracer techniques, *EPJ Web of Conf.,* **2013**, 50, 01005
8. **A. Miśkiewicz**, G. Zakrzewska-Trznadel, A. Dobrowolski, A. Jaworska-Sobczak “Using tracer methods and experimental design approach for examination of hydrodynamic conditions in membrane separation modules, *Appl. Rad. Isotop.*, **2012,** 70, 837-847,

9. N. Uzal, A. Jaworska, **A. Miśkiewicz**, G. Zakrzewska-Trznadel, C. Cojocaru, Optimization of Co^{2+} ions removal from water solutions via polymer enhanced ultrafiltration with application of PVA and sulfonated PVA as complexing agents, *J. Col. Interf. Sci.,* **2011,** 362, 615–624,
10. **A. Miśkiewicz**, S. Velizarov, Effect of molecular mass on boron-doped diamond anodic mineralization of water-soluble organic polymers, *Sep. Purif. Technol*., **2011**, 83, 166-172,
11. C. Cojocaru, G. Zakrzewska-Trznadel, **A. Miśkiewicz**, Removal of cobalt ions from aqueous solutions by polymer assisted ultrafiltration using experimental design approach Part 2: Optimization of hydrodynamic conditions for a crossflow ultrafiltration module with rotating part, *J. Haz. Mat.*, **2009,** 169, 610–620,
12. G. Zakrzewska-Trznadel, M. Harasimowicz, **A. Miśkiewicz**, A. Jaworska, E. Dłuska, S. Wroński, Reducing fouling and boundary-layer by application of helical flow in ultrafiltration module employed for radioactive wastes processing, *Desalination*, **2009**, 240, 108-116,
13. A. Markowska-Radomska, E. Dłuska, G. Zakrzewska-Kołtuniewicz, **A. Miśkiewicz**: Odzysk metali ziem rzadkich z roztworów po ługowaniu magnesów trwałych w procesie zintegrowanym z wykorzystaniem emulsyjnych membran ciekłych. *Inż. Ap. Chem.*, **2017,** 56, 4, 128-129
14. K. Kiegiel, G. Zakrzewska-Kołtuniewicz, D.Gajda, **A Miśkiewicz,** A. Abramowska, P. Biełuszka, B. Danko, E. Chajduk, S. Wołkowicz, Dictyonema black shale and Triassic sandstones as potential sources of uranium. *Nukleonika*, **2015,** 60(3), 515-522, doi: 10.1515/nuka-2015-0096;