SCIENTIFIC AND TECHNICAL REPORT

Program 2: Increase the Competitiveness of the Romanian Economy through Research, Development and Innovation
Subprogramme 2.1. Competitiveness through the Research, Development and Innovation
Project type: Experimental - demonstration project – PED

Project Title: New "green" technology for advanced water treatment based on functionalized polysulfones/ionic liquids membranes
Contract no: 310PED/2020
Project code: PN-III-P2-2.1-PED-2019-3013
Project acronym: GreenTechMembr
Coordinator: "Petru Poni" Institute of Macromolecular Chemistry, Iasi
Partner: Politehnica University Timisoara
Project leader: dr. Anca Filimon

Stage 3 (2022) – Validation and demonstration of the obtained membranes functionality in the treatment unit through the technological process of microfiltration

Reporting period: january – july 2022

I. Stage summary

The general objective of the GreenTechMembr project is to develop a new technology for water treatment (TRL4), by integrating an experimental demonstrator for its use in a technological microfiltration process (TRL3), starting from a conceptual model of TRL2 level. In this sense, in accordance with the established implementation plan, **in 2022** the research regarding the evaluation of the performance of the obtained membranes integrated in the technological installation (MTU) proposed for water treatment continued. In order to achieve this objective, **Stage 3** was based on the following activities:

Activity 3.1 *- Demonstration of the membranes functionality in the treatment unit by microfiltration for water treatment*
Activity 3.2 *- Morphological and structural characterization of membranes after their use in MTU*
Activity 3.3 *- Dissemination of the results*

Activities 3.1 and 3.2 of experimental development type (started in the previous stage (**Stage 2/2021**, together with the consortium partner), through the conducted studies highlighted the substantial impact that ionic liquids have on the surface morphology of the obtained membranes and demonstrated their functionality and performance in the water treatment unit by microfiltration.

The membranes performance in the filtration process was evaluated by establishing their efficiency in the treatment of various aqueous solutions (synthesis waters containing inorganic pollutants - various metal ions: Cd^{2+}, anions: NO_3^-, etc. and organic pollutants or pharmaceutical products (diclofenac) and/or wastewater from different sources). Also, the evaluation of the probability of membrane clogging (deposition, adsorption or adhesion of different types of molecules/microorganisms on the membrane and/or capture in its pores) and implicitly, the membrane's lifetime was followed.

For this purpose, the efficiency of the quaternized polysulfone membranes (PSFQ) functionalized with ionic liquids was evaluated in the process of treating water with nitrogen content through the microfiltration process. Thus, the obtained membranes (PIM - by mixing the polysulfonic solutions (PSFQ) with ionic liquids Cyphos IL-101 and Aliquat 336 in different ratios (3wt% and 15wt%, respectively) and SLM - by deposition/immersion of PSFQ membranes already obtained in the selected ionic liquids - **Stage 1/2020**) were used in the water treatment process with a content of 60 mg/L and 100 mg/L NO_3^-, respectively. The obtained results indicate that both the functional group of the used ionic liquids and the structure of the membranes, through their porosity, contribute to the removal of NO_3^- ions from water. In addition, both in the case of PIM membranes and in the case of SLM membranes, the ammonium-based ionic liquid (Aliquat 336) has a greater influence on the microfiltration efficiency developed by the membranes than the phosphonium-based ionic liquid (Cyphos IL-101). Moreover, from the studies carried out through these activities, it was demonstrated that in the case of the membranes obtained by inclusion (PIM) and using methyl trialkyl ammonium chloride (Aliquat 336) as ionic liquid, a single treatment cycle is sufficient to obtain the desired efficiency, the recirculation of the permeate not being necessary. For this reason, this type of membrane has been successfully used in the treatment of deep waters. It was found that the metal ions that are present in the deep water do not negatively influence the microfiltration process, in addition, a slight decrease in their concentration was also observed. By using a two-membrane module in the microfiltration, the efficiency of the process increased by approximately 20%. Through the conducted research, it was highlighted that the studied membrane has an affinity for anions.

The membrane efficiency is characterized by its lifetime. Thus, the obtained membranes were also used in several treatment-washing cycles both in the case of treating water with Cd^{2+} content, and in the case of treating water with diclofenac (DCF) content. The efficiency and performances developed by the obtained membranes integrated in the MTU treatment unit were monitored (after the adsorption/extraction of Cd^{2+} and/or DCF from aqueous solutions) by microscopy/spectroscopy methods (AFM, SEM, FTIR). After the adsorption/retention/impregnation of the organic/inorganic pollutants, the morphology of the membrane surfaces is not changed, only the accumulation of the pollutant in the membrane pores can be observed from the microscopic analyses, and through the FTIR analysis, both the presence of the ionic liquid and the accumulation of the pollutant (**the activity 3.2**) were highlighted. Once again, the substantial impact that ionic liquids have on the membranes surface morphology was highlighted. This does not change after the use of membranes in water treatment processes by filtration, and their efficiency remains constant even after 4 filtration/washing cycles.

Consequently, following the experiments performed according to **activities 3.1 and 3.2**, it was found that the presence of the ionic liquids significantly improves the efficiency of the studied membranes and increases with the increase of the ionic liquid content in the membrane structure. On the other hand, PIM membranes show a higher efficiency compared to SLM membranes. In addition, the polysulfone membranes functionalized with ammonium-based ionic liquids (PSFQ/Aliquat 336) developed a higher filtration performance than polysulfone membranes functionalized with phosphonium-based ionic liquids (PSFQ/Cyphos IL-101), as it was also demonstrated from the studies performed in **activity 3.1**.

The results obtained according to **activity 2.3 (Stage 2/2021)**, regarding the potential of the developed materials to act as antimicrobial agents against different types of bacteria (*Staphylococcus aureus, Escherichia coli*) and fungi (*Candida albicans*), allowed, in **activity 3.2** of experimental development type, the evaluation of the efficiency of the membranes used for water sterilization. The antibacterial efficiency of the polysulfone membranes functionalized with ionic liquids (PIM-PSFQ/Aliquat 336) against faecal indicator bacteria from water (total coliforms and faecal streptococci), using the multitube test method

described in STAS 3001/1991-Water/Bacteriological analysis, was evaluated following the identification of the bacterial species of Coci type retained on the surface of the composite membrane. The choice of the membrane (PIM-PSFQ/Aliquat 336) was made taking into account the previous results (**activity 2.3/Stage 2/2021**) according to which *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans* exhibit the greatest sensitivity to this type of membrane. Thus, through the proposed methodology, the membranes that presented improved characteristics and performance for the proposed purpose were analyzed, evaluated and selected.

All consortium members participated in **activity 3.3** of support type. **4 ISI scientific papers** (**2 published and 2 sent for publication**) were developed, **5 papers presented** at national/international conferences, **2 book chapters** (Ed. Wiley - accepted for publication) and **1 patent application**. Also, **a bachelor thesis** was developed/coordinated. In order to promote the project and disseminate its results, **a presentation** (supported by CO coordinator (ICMPP) and P1 partner (UPT)) at an event in the field of the project's theme, **was awarded** (results also visible on the website of **the GreenTechMembr project** https://icmpp.ro/greentechmembr/).

ISI scientific papers:

1. Green blends based on ionic liquids with improved performance for membrane technology: Perspectives for environmental applications, A. Filimon, A.M. Dobos, O. Dumbrava, F. Doroftei, L. Lupa, Int. J. Mol. Sci. 2022, 23(14), 7961; https://doi.org/10.3390/ijms23147961.
2. Materials based on quaternized polysulfones with potential applications in biomedical field: Structure–properties relationship, A. Bargan, M.D. Onofrei, I. Stoica, F. Doroftei, S. Dunca, A. Filimon, Int. J. Mol. Sci. 2022, 23(9), 4721; https://doi.org/10.3390/ijms23094721.
3. New efficient quaternized polysulfonic/ionic liquids based membranes for cadmium containing water treatment through microfiltration, A. Filimon, L. Lupa, L. Cocheci, I. Stoica, M.D. Onofrei, P. Negrea, J. Membr. Sci. (under review).
4. Treatment of water with nitrates content through microfiltration using new efficient quaternized polysulfonic/ionic liquids-based membranes, L. Lupa, A. Filimon, L. Cocheci, O. Dumbrava, Water Res. (under review).

Book chapter:

1. Ionic Liquid-Based Composites Materials for Membranes Applications, L. Lupa, A.M. Dobos, A. Bargan, A. Filimon, in: Handbook of Water Pollution, Wiley-Scrivener Publisher (accepted 2022).
2. Nitrates and Nitrites: Sources, Method of Analysis and Treatment, L. Lupa, , L. Cocheci, A. Filimon, in: Handbook of Water Pollution, Wiley-Scrivener Publisher (accepted 2022).

National/international scientific events:

1. Development of new composite membranes based on functionalized polysulfone and ionic liquids for cadmium separation from aqueous solution, L. Lupa, I. Stoica, L. Cocheci, P. Negrea, A. Filimon, 12th International Conference on Materials Science and Engineering – BraMat 2022, Brasov, Romania, March 9-12, 2022 (**oral communication**).
2. Impact of polysulfone functionalization with n,n-dimethylbutylamine on conformational characteristics, O. Dumbrava, A. Filimon, L. Marin, 12th International Conference on Materials Science and Engineering – BraMat 2022, Brasov, Romania, March 9-12, 2022 (**oral communication**).
3. Sol-gel transition in polysulfonic systems containing triethylphosphonium groups, A.M. Dobos, A. Popa, A. Filimon, 12th International Conference on Materials Science and Engineering – BraMat 2022, Brasov, Romania, March 9-12, 2022 (**oral communication**).
4. Dynamic properties of the (hydroxypropyl)methyl cellulose/poly(vinylpyrrolidone) water systems. Influence on the formation of fibrous materials, M.D. Onofrei, D. Serbezeanu, A. Anisiei, A. Filimon, International Conference on Rheology, Understanding the Viscoelastic Behavior of Materials – Progress and Challenges, May 26, 2022, Iasi, Romania (**poster**).
5. System for functionalized membranes testing for water treatment, L. Lupa, P. Negrea, L. Cocheci, A. Filimon, The 26th International Exhibition of Inventions "INVENTICA 2022", Romania, June 22-24, 2022, Iasi, Romania (**poster**).

Patent application:

Process of obtaining polysulfonic membranes functionalized with ionic liquids applicable in technological processes of water treatment by microfiltration
(*Procedeu de obținere a unor membrane polisulfonice funcționalizate cu lichide ionice aplicabile în procese tehnologice de tratare a apelor prin microfiltrare*)
A. Filimon, A.M. Dobos, A. Bargan, L. Lupa
National patent demand, no. 3958/25.07.2022

Awards:

L. Lupa, P. Negrea, L. Cocheci, A. Filimon A. Filimon, System for functionalized membranes
testing for water treatment; The 26th International Exhibition of Inventions "INVENTICA 2022", Iasi, Romania, June 22-24, 2022 (**Honorary diploma, Gold Medal**).

Other results:

Bachelor thesis: Treatment of water with nitrates content by microfiltration (*Tratarea apelor cu conținut de azotați prin microfiltrare)*, Tirean Teodora, Coordonator: L. Lupa, A. Filimon.

Within the project, the implementation team fulfilled its tasks, all activities and indicators proposed for this stage were achieved.

Project leader,

dr. Anca Filimon