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 2 (2021) - Properties optimization of the polysulfone membranes functionalized with ionic liquids and their application conditions in microfiltration processes using treatment unit (MTU) with the integrated experimental demonstrator (SLM, PIM)

Reporting period: January - December 2020

Stage summary

The general/overall objective of the GreenTechMembr project is to develop a new water treatment technology/a new technology for the water treatment (TRL4) by integrating an experimental demonstrator for its use in a microfiltration technological process (TRL3), starting from a conceptual model of TRL2 level. In this sense, according to the established implementation plan, **in 2021** was started the research regarding the optimization of the properties of the polysulfonic membranes functionalized with ionic liquids (PSFQ / IL), which will be integrated and used as separation media in a membrane water treatment unit (MTU). To achieve this goal, **Stage 2** was based on the following activities:

Activity 2.1 *- Designing and obtaining of PIMs fibrous membranes*

Activity 2.2 *- Optimization of the surface parameters depending on the composition of the membranes in order to apply them in MTU*

Activity 2.3 *- Testing the membranes as a biocide and establishing the mechanism of inhibition against different types of bacteria*

Activity 2.4 *- Optimization of the operating parameters of the treatment unit (MTU) depending on the composition of the obtained membranes (experimental demonstrator (SLMs, PIMs))*

Activity 2.5 *- Commissioning of the proposed technological installation for water treatment*

Activity 2.6 *- Morphological and structural characterization of the membranes after use in MTU*

Activity 2.7 *- Dissemination of the results*

Within the **activity 2.1 of experimental development type**, fibrous materials were obtained by electrospinning solutions consisting in chemically modified polysulfone with quaternary ammonium groups (PSFQ) and various ionic liquids (trihexyl tetradecyl phosphonium chloride (Cyphos IL-101) and methyl trialkyl ammonium chloride (Aliquat 336)). In order to successfully obtain the fibrous materials that modelate the membranes properties, the rheological study has allowed the control and optimization of the solution parameters in correlation with the operating parameters of the device and the environmental parameters (temperature, humidity). Therefore, the concentration of 25 g/dL was selected to obtain fibers with submicron size.

The development of new surfaces with a range of improved structures and features was the purpose of the researches conducted in **activity 2.2 of experimental development**. In order to achieve high-performance membranes with applicability in water treatment, the control and establishment of hydrophobic/hydrophilic balance, surface morphology and permeability effect are necessary properties that provide important informations about the membrane materials obtained. For this purpose, the surface properties were evaluated by measuring the contact angle. The morphology, dictated by roughness, local surface properties and the existence of porous formations, was investigated by atomic force microscopy. On the other hand, as an initial attempt to evaluate the performance of the membranes obtained in practical applications, in technological processes of water treatment, was determined the water absorption capacity for polysulfonic membranes functionalized with ionic liquids, in dynamic regime, from sorption isotherms, using DVS technique (Dynamic Vapor Absorption). Thus, through the proposed methodology were analyzed, evaluated and selected the membranes that presented improved characteristics and performance for the proposed purpose.

Activity 2.3 of experimental development type, has allowed, through the obtained results regarding the antimicrobial activity, to establish the potential of the obtained materials to act as antimicrobial agents against different types of Gram-positive, Gram-negative bacteria (*Staphylococcus aureus, Escherichia coli*) and fungi (*Candida albicans*) for water sterilization. The sensitivity of the three microorganisms to the analyzed systems (PSFQ, PSFQ/Aliquat 336 and PSFQ/Cyphos IL-101) was observed by appearance of the inhibition zones.

In **activities 2.4 and 2.5 of experimental development type**, the operating parameters of the MTU treatment unit were optimized using membranes obtained from the systems consisted of PSFQ and various ionic liquids in water treatment with Cd^{2+} content and the performance of the integrated PIM, SLM component in water treatment containing diclofenac (DCF) was determined. In this context, it was found that a long contact time between the membrane and the water to be treated is required. Thus, in order to achieve this, and to obtain a high degree of elimination of the pollutants from the water, it is recommended to recirculate the permeate in several treatment cycles. In addition, the presence of ionic liquid leads to a significant improvement in the filtration performance of the studied membranes, their efficiency increasing with the increasing of the ionic liquid content in the membrane structure. Polysulfonic membranes functionalized with ammonium-based ionic liquids (PSFQ/Aliquat 336) exhibited a higher performance than the polysulfonic membranes functionalized with phosphonium based ionic liquids (PSFQ/Cyphos IL-101), as demonstrated by the studies performed in **activities 2.2 and 2.3**.

The studies performed in **activity 2.6**, studies that will be continued in the next stage (**Stage 3/2022**), highlighted the major impact that ionic liquids it have on the surface morphology. This does not change after the use of membranes in the processes of water treatment by filtration, and their efficiency remains constant for 4 cycles of filtration/washing.

All the members of the consortium participated in the **2.7 support type activity**. There were **2 ISI scientific papers (1 accepted/published and 1 submitted for publication**), **7 papers presented** at national/international conferences, **1 book chapter** (submitted for publication - Wiley Ed.) and **1 patent application**. Also, **2 papers** were elaborated/coordinated**: bachelor's thesis and dissertation**. To promote the project and disseminate its results **2 presentations** were held (by the CO coordinator

(ICMPP) and partner P1 (UPT)) at events related to the project theme **that were awarded** (visible results on the **GreenTechMembr project** website https://icmpp.ro/greentechmembr/).

ISI scientific papers:

1. Processing of quaternized polysulfones solutions as tool in design of electrospun nanofibers: Microstructural characteristics and antimicrobial activity, A. Filimon, N.Olaru, F. Doroftei, A. Coroaba, S. Dunca, Journal of Molecular Liquids, 330, 115664 (2021)
2. New insights on solvent implications in the design of materials based on cellulose derivatives using experimental and theoretical approaches, A. Filimon, M.D. Onofrei, Materials, 14, 6627 (2021)
3. Green blends based on ionic liquids with improved performance for membrane technology: Perspectives for environmental applications, A. Filimon, L. Lupa, A.M. Dobos, O. Dumbrava, Colloids and Surfaces A: Physicochemical and Engineering Aspects (trimisa spre publicare, 2021).

Book chapter:

1. Processing of biocomposites materials for membranes applications in water treatment, A.M. Dobos, A. Bargan, L. Lupa, A. Filimon, in: Handbook of Bioplastics and Biocomposites Engineering Applications, Wiley-Scrivener Publisher (trimis spre publicare 2021).

National/international scientific events:

1. Tratarea avansata a apei bazata pe membrane de polisulfone functionalizate/lichide ionice, T. Novacut, S.N. Tolea, L. Lupa, A. Filimon; Apa - Esenta vietii, Apa pretuita in centrul vietii imbunatatite, AquaSensTim
   2021, Timisoara, Romania, 22 martie 2021 (**oral communication**)
2. Utilizarea membranelor pe bază de lichide ionice în procesul de îndepărtare a ionilor de Cd^{2+} din soluții apoase, T. Novacut, L. Lupa, A. Filimon; Simpozionul Științific Studențesc Al Facultății De Chimie Industrială Și Ingineria Mediului, Timisoara, 15 iunie 2021 (**poster**)
3. Tratarea apelor cu conținut de diclofenac prin separare membranară, A. Gosa, L. Lupa, A. Filimon; Simpozionul Științific Studențesc Al Facultății De Chimie Industrială Și Ingineria Mediului, Timisoara, 15 iunie 2021 (**oral communication**)
4. New "green" technology for advanced water treatment based on functionalized polysulfones/ionic liquids membranes (GreenTechMembr), A. Filimon, L. Lupa; The 25th International Exhibition of Inventions "INVENTICA 2021", Iași, Romania, 23-25 iunie 2021 (**poster**)
5. Applying of modified materials with ionic liquids in advanced water treatment technologies, L. Lupa, L. Cocheci, R. Lazau, A. Filimon, P. Negrea; International Meet & Expo on Materials Science and Nanomaterials (MATERIALSMEET2021), Valencia, Spain, 11-13 octombrie 2021 (**oral communication**)
6. Ionic liquids-based polysulfone membranes for cadmium removal from aqueous solutions, L. Lupa, S.N. Tolea, O. Dumbrava, A. Filimon; 11th International Conference on Environmental Engineering and Management, Environmental Engineering for a Clean and Healthy Planet, Muttenz, Switzerland, 8-10 septembrie 2021 (**oral communication**)
7. Performance of quaternized polysulfone membranes in environmental applications dictated by the ionic liquid nature, A. Filimon, O. Dumbrava, A.M. Dobos, M.D. Onofrei; International Scientific Events: Materials, Methods & Technologies, Burgas, Bulgaria, 19-22 august 2021 (**oral communication**)

Project prezentation:

1. A. Filimon, Lavinia Lupa; New “green” technology for advanced water treatment based on functionalized polysulfones/ionic liquids membranes (GreenTechMembr); The 25th International Exhibition of Inventions “INVENTICA 2021”, Iași, Romania, 23-25 iunie 2021
2. T. Novacut, S.N. Tolea, L. Lupa, A. Filimon; Tratarea avansata a apei bazata pe membrane de polisulfone functionalizate/lichide ionice, Apa - Esenta vietii, AquaSensTim – 2021, Timisoara, Romania, 22 martie 2021

National patents demand:

1. Sistem de testare a membranelor functionalizate la tratarea apelor
   L. Lupa, P. Negrea, L. Cocheci, A. Filimon
   Cerere de brevet de inventie, nr. 24576/26.11.2021

Awards:

1. A. Filimon, L. Lupa; New “green” technology for advanced water treatment based on Functionalized polysulfones/ionic liquids membranes (GreenTechMembr); The 25th International Exhibition of Inventions “INVENTICA 2021”, Iași, Romania, 23-25 iunie 2021 (**Diploma of excellence, Silver medal**)

2. T. Novacut, S.N. Tolea, L. Lupa, A. Filimon; Tratarea avansata a apei bazata pe membrane de polisulfone functionalizate/lichide ionice; Apa - Esenta vietii, AquaSensTim – 2021, Timisoara, Romania, 22 martie 2021 (**Mention**)

Other results:

1. **Bachelor’s thesis:** *Utilizarea membranelor pe bază de lichide ionice în procesul de îndepărtare a ionilor de* Cd^{2+} *din soluții apoase,* Tania Novacu
   Coordonator: L. Lupa, A. Filimon

2. **Dissertation:** *Tratarea apelor cu conținut de diclofenac prin separare membranară*, student masterand Gosa Adela
   Coordonator: L. Lupa, A. Filimon