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Habilitation thesis

Nanomateriale pentru dezvoltarea proceselor și tehnologiilor cu membrane

Nanomaterials for the development of membrane processes and technologies

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Introduction

In the era of nanomaterials, nanotechnologies and artificial intelligence, obtaining high-purity products is imperative.

Classical processes, technologies, techniques and procedures are no longer operative except in obtaining raw materials. Among the classical technologies that are still suitable for the exploitation of raw materials are sedimentation, filtration, centrifugation, solvent extraction, distillation, rectification...

The advent of membranes and the processes in which they are used has made it possible to increase the purity of products. These processes have an excellent quality/cost ratio.

At the same time, membrane processes are unconventional and environmentally friendly. Processes that use membranes as separation systems solve stringent problems regarding the separation, concentration or purification of liquid and gaseous effluents and are applied in various fields: chemical and petrochemical industry, pharmaceutical industry, microelectronics, agri-food industry, wastewater treatment, drinking water, energy, gas purification/separation, biological engineering, biotechnology, triage, bioseparations and, last but not least, medicine and biomedicine.

The advancement of membrane processes, technologies and methods was made possible by the improvement and development of experimental techniques for membrane preparation and characterization.

The arguments for the development of membrane technology were supported by two primary applications: obtaining drinking water through reverse osmosis of seawater and the use of the artificial kidney in applied medicine.

Two other characteristics of membrane technologies were particularly important. Most membrane processes are environmentally friendly and make a decisive contribution to the greening of material production.

High selectivity and sensitivity control through various operational parameters (pH, ionic strength, redox potential, reactant concentration, volatility, electrical or magnetic properties) has led to a proliferation of applications.

The habilitation thesis presents the professional and academic activity and highlights the own research directions, which fall within the current and constant effort of researchers to obtain high-performance membrane nanomaterials and clean purification, concentration and separation technologies.

Scientific achievements

This part of the habilitation thesis presents significant results in five research directions in which relevant results were obtained, and which constitute the core of future research:

- ***- Synthesis, characterization and applications of magnetic nanoparticles for membrane separation processes***
- ***- Use of osmium nanoparticles in reaction and membrane separation processes***
- ***- Recovery of toxic elements from aqueous solutions (e.g. Thorium)***
- ***- Recuperative separation of organic or inorganic compounds through innovative membrane processes***
- ***- Determination of operational limits in liquid membrane processes***

- ***Synthesis, characterization and applications of magnetic nanoparticles for membrane separation processes***

Magnetic nanoparticles are obtained today by various technically and economically accessible processes. This chapter presents the preparation by an electrochemical process and the characterization of magnetic nanoparticles based on iron and silver oxides. Their application is made in separation processes in an oscillating magnetic field.

The separation of target substances (o-nitrophenol and m-nitrophenol) in an oscillating magnetic field showed that the overall extraction performances (extraction efficiency (EE) and flux (J)) increased in the order: $EE_{NP3} > EE_{NP1} > EE_{NP2}$, respectively: $J_{NP3} > J_{NP1} > J_{NP2}$. The separation efficiency using magnetic silver-iron oxide nanoparticles is correlated with the saturation magnetization and silver content. Thus, it is possible to suggest a dependence of the total flux of nitrophenol through the membrane on diffusion, convection and silver-assisted transport. Or, expressed in other words, the total flux cumulates the effect of solvent magnetization and silver content.

The presented example of the use of magnetic nanoparticles, in particular composite ones, in separation processes shows that the range of their applications can be expanded.

The results of membrane separation processes can be amplified, both in terms of flux and selectivity, by using magnetic nanoparticles that allow, in addition to diffusive transport, convective transport generated by oscillating magnetic fields.

It can be stated that other properties of composite magnetic nanoparticles such as: selectivity, sensitivity and complexation capacity can contribute decisively to the development of new separation processes, including membrane ones.

The use of osmium nanoparticles in reaction and membrane separation processes

The preparation of osmium nanoparticles by reducing the tetroxide with 1-undecenoic acid and their use in membrane separation and reaction processes represents a priority of our team in the specialized literature.

The first subchapter presents the results obtained from the reduction of 5-nitrobenzimidazole by transformation into 5-aminobenzimidazole, in the reaction system with the osmium-polymer membrane (Os-P) with molecular hydrogen, in an aqueous membrane system, with the source phase of pH 6 and the receiver phase of pH 1.

The osmium-polymer membranes (OS-P) were obtained using cellulose acetate (CA) and polysulfone (PSF) membranes obtained by phase inversion and commercial polypropylene (PP) tubular fibers as supports, and the osmium in the form of nanoparticles was generated by the reduction reaction of osmium tetroxide in t-butyl alcohol with molecular hydrogen.

The obtained membranes osmium-cellulose acetate (OS-CA), osmium-polysulfone (Os-PSf) and osmium-polypropylene tubular fibers (Os-PP) were characterized morphologically and structurally: SEM, high resolution SEM (HR-SEM), EDAX thermal analysis (TGA, DSC).

The process performances were tested in the reduction of 5-nitrobenzimidazole solution 0.5g/L to 5-aminobenzimidazole with molecular hydrogen varying the nature and surface area of the membrane, the molecular hydrogen flow rate and the operating time.

The results obtained show that:

- - the conversion of 5-nitrobenzimidazole to 5-aminobenzimidazole in the osmium-polymer membrane (Os-P) reaction system depends on the nature of the polymer,
- - the conversion of 5-nitrobenzimidazole to 5-aminobenzimidazole in the osmium-polymer membrane (Os-P) reaction system is slightly independent of the hydrogen flow rate in the system.
- - the efficiency of 5-aminobenzimidazole separation depends on the operating time, being correlated with the conversion of 5-nitrobenzimidazole to 5-aminobenzimidazole, in the osmium-polymer membrane (Os-P) reaction system.

Both the separation efficiency of 5-aminobenzimidazole (EE) and 5-nitrobenzimidazole to 5-aminobenzimidazole (η) vary in the same order: EE Os-PP > EE Os-CA > EE Os-PSf and, respectively, η Os-PP > η Os-CA > η Os-PSf.

Aspects of the possible mechanism of the transformation of 5-nitrobenzimidazole to 5-aminobenzimidazole with hydrogen gas in the osmium-polymer membrane (Os-P) reaction system are presented and its elucidation is proposed by using deuterium (2H or D) instead of hydrogen or heavy water (D2O) as the reaction medium.

The second subchapter presents the preparation and characterization of a liquid membrane based on osmium nanoparticles obtained directly in n-decanol (nDol), which is the basic solvent of the liquid membrane.

The dispersion of osmium nanoparticles in n-decanol is achieved by the method of reducing osmium tetroxide with 1–undecenoic acid (UDA). The resulting membrane was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDAX), thermal analysis (TG, DSC), Fourier transform infrared spectroscopy (FTIR) and dynamic light scattering (DLS).

The study determined the conversion of p-nitrophenol (pNP) to p-aminophenol (pAN) by varying the concentration of nanoparticles in the membrane nanodispersion, as well as the flow rate of the source phase through the membrane and the separation efficiency of p-aminophenol (pAN) formed as a function of the membrane flow rate through the receptor phase of variable pH.

The results obtained show that membranes based on the dispersion of osmium nanoparticles in n-decanol can be used with an efficiency of over 90% for the reduction of p-nitrophenol and the separation of p-aminophenol.

The examples of the use of osmium nanoparticles will allow the expansion of research on heterogeneous catalysis in both reduction and selective oxidation processes.

Recovery of toxic elements from aqueous solutions (ex: Thorium)

This chapter addresses nanofiltration as a process for removing or recovering thorium from dilute synthetic aqueous solutions.

The composite membrane proposed for study is made of sulfonated polyether ether ketone (sPEEK) in which amino benzo15C5 ether (ABCE) is embedded.

The performances of the nanofiltration process are compared between an sPEEK membrane and a composite membrane (ABCE-sPEEK), prepared by the same procedure.

The membranes were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy EDAX, thermal analysis (TG and DSC) and from the perspective of thorium removal performance.

At all test parameters, pH and thorium ion concentration, working pressure, and agitation regime, the composite membrane (ABCE-sPEEK) has superior performances compared to the sPEEK membrane.

The thorium retention for the composite membrane (ABCE-sPEEK) reaches a maximum of 98% compared to the sPEEK membrane which does not exceed 90%.

The fluxes determined under the optimal conditions resulting from the study (pressure, stirring regime, concentration and pH of the thorium solution) are maximum 16 $Lm^{-2}h^{-1}$ for the composite membrane (ABCE-sPEEK) and 15 $Lm^{-2}h^{-1}$ for the sPEEK membrane.

The described application regarding the nanofiltration of thorium particles highlights the importance of improving the selectivity of membranes by attaching complexed compounds.

Recuperative separation of organic or inorganic compounds through innovative membrane processes

The development of new systems to improve the performance of liquid membranes by increasing the mass transfer surface area is an essential aspect of promoting industrial applications.

Starting from the results previously obtained in the separation and transport of chemical species in a permeation module with dispersion of aqueous phases, in the form of droplets, this chapter presented the effect of interposing freely rotating spheres between the droplets and the membrane phase. These spheres determine the contact of the aqueous phases in the form of a film with the membrane phase of organic solvent. The study was carried out in a membrane system in which the source phase of variable pH is made up of phenolic derivatives of technical-economic and environmental interest (4-nitrophenol (NP), 2,4-dichlorophenol (DCP), and 2,4 dinitrophenol (DNP)), the membrane of n-alkyl alcohols (n-octanol and n-decanol), and the receiver phase of high pH aqueous solution

The transport of 4-nitrophenol is determined both by the pH difference between the aqueous phases, the nature of the membrane solvent, and the nature of the material used to make the spheres. Thus, the transport in the module with glass spheres (Gl) is superior to that using copper spheres (Cu), but especially steel spheres (St). In all cases studied, the sphere module (Ms) has superior transport results to the droplet module (Md).

The extraction efficiency (EE) and transport of 2,4-dichlorophenol (DCP), and 2,4 dinitrophenol (DNP), studied in the glass sphere module, show that by adjusting the pH of the source phase, the two phenolic derivatives can be separated. At acidic pH of the source phase (pH=2) the two derivatives are extracted with very good results (EE>90%), and at pH 4-6 they

can be separated, DCP having double the separation efficiency compared to DNP. At pH 8 of the source phase, the extraction efficiency is halved for both phenolic compounds.

The influence of the material of the spheres on the perturbation modulus suggests possibilities for controlling the performance of the membrane process by chemically modifying the surface of the spheres, especially glass ones.

The results presented open the area of membrane separations depending on the design of the membrane phases and the permeation modulus.

Determining operational limits in liquid membrane processes

This chapter presents the operational limits of a type of hybrid membrane constituted as a bulk liquid membrane (BLM), but which operates with the dispersion of the source (SP) and receiver (RP) aqueous phases, and the membrane is a dispersion of nanoparticles in an organic solvent (NP-OSM).

The main characteristics and recommendations for operating with the proposed experimental hybrid membrane system, as an example, were: source phase volume 5000-15000mL, receiver phase volume 500mL, membrane solvent volume 300-500mL, volume ratio between source phase and receiver phase 10-20:1, volume ratio between receiver phase and membrane 1-5:1, membrane thickness 30-40mm, aqueous phase flow rate through a single droplet orifice 20mL/min, aqueous droplet diameter 4-5mm, membrane solvent n-octanol or n-decanol, magnetic nanoparticles (diameter 40+10nm), ionic or molecular chemical species (silver ions and p-nitrophenol), magnetic stirrer speed, 100rot/min, operating temperature 15-35^{o}C.

Under the conditions presented, separation efficiencies of over 90% are obtained for both ionic and molecular chemical species (silver ions and p-nitrophenol).

The concrete way of dealing with the problems raised by the operation of dispersion-based liquid membranes opens the way to studying increasingly diversified and sophisticated liquid membrane systems.

Researchers' perspectives

The results of the research conducted and presented in the synthesis in the five subchapters of this thesis are part of the efforts of researchers from the Faculty of Chemical Engineering and Biotechnology, but also from the National University of Science and

Technology POLITEHNICA Bucharest, to obtain, characterize and apply nanoparticles and nanosystems from the most diverse classes of compounds.

From the most recent publications we have had, in the last five years, the concerns we have promoted in the following directions result:

- - Synthesis of magnetic nanoparticles based on iron oxides
- - Obtaining composite silver-magnetite nanoparticles
- - Synthesis of magnetic nanoparticles with organic coatings
- - Synthesis of osmium nanoparticles
- - Obtaining composite and liquid membranes based on nanodispersions
- - Complex characterization of nanoparticles from a morpho-structural, compositional and process performance point of view
- - Applications of nanoparticles and membranes in separation, concentration and controlled release processes of chemical species of interest for the environment and biomedicine.

The successes of the research activity carried out in a close-knit team over the last five years allow for the continuation of research activity in the following areas:

- ***- Synthesis of new magnetic nanoparticles with organic and inorganic coatings***
- ***- Obtaining metallic nanoparticles for transport and catalysis***
- ***- Creation of polymer-nanoparticle and selective liquid-nanoparticle membrane systems (liquid membranes based on nanodispersions)***
- ***- Promotion of new characterization methods, especially in terms of selectivity and sensitivity in dedicated processes***
- ***- Broadening applications in process engineering, clean and green technologies***
- ***- Biological and biomedical applications***