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Composite and derivatized membranes for the extraction of gadolinium from moderator's virgin heavy water

PhD thesis summary

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Bucharest

2021

The doctoral thesis entitled "Composite and derivativeized membranes for the extraction of gadolinium from virgin heavy water" was aimed at obtaining composite and derivative membranes for extraction of gadolinium from heavy water by the moderator, to evaluate the possibility of replacing the ion exchange columns, used in CANDU-type nuclear power plants, for the purification of heavy water of the Moderator System, this being alsothe reason for choosing the research theme.

By its importance, novelty and actuality, this topic is framed with priority in the international and national concerns of researchers.

The originality and uniqueness of this thesis is supported by the fact that reports on gadolinium retention over the years are very few in the specialized literature, the subject of this thesis comprising the first reporting on derivative and composite membranes used for gadolinium retention and the first reporting on mebrans with self-indicating properties for retention and indication of gadolinium retention, alsothe first reporting about functionalized membranes with ether crown for retention gd(III) and the first reporting on composite membranes with silica nanowires for retention of Gd(III).

The doctoral thesis consists of 6 chapters that include:a study of specialized literature in the field of research topic, synthesis and cavation of autoindicatory membranes for retention of gadolinium, synthesis and characterization of membranes with crown ethers for gadolinium retention, synthesis and characterization of membranes with silica nanowires for retention of gadolinium, final conclusions, personal contributions and scientific achievements .

The research hypothesis consists in obtaining derivativeized and composite membranes for gadolinium retention, having as objectives for solving in the scientific research: synthesis and characterization cellulose acetate membranes with self-insiction properties, by changing the colour of the membranesurface, cellulose acetate membranes functionalized with crown ethers, and of silica nanowire composite membranes.

Chapter I of this doctoral thesis includes a literature study on CANDU nuclear reactors, the use and applications of gadolin in the nuclear dome and other technical fields and methods / the different gadolinium extraction techniques used both in the nuclear field, for the purification of heavy water by the moderator, and in other technical fields .

A nuclear reactor cannotoperatewithout neutrons, which support the fission reaction that produces thermal energy in CANDU-type nuclear reactors(CANada Deuterium Uranium)and gives rise to other neutrons. They are trained in chain reactions. Most of the

neutrons in a CANDU-type reactor come directly from the fission reaction. Almost half the number of neutrons din a reactor at poweris emitted as part of the degradation of fission products.

In1939, Hahn and Strassman, during the bombardment of the U-235 nucleus with neutrons, discovered that sometimes the U-235 nucleus splits into two nuclei of close medium masses, producing energy and releasing other neutrons. The process was called nuclear fission.

The part of the nuclear reactor that produces heat is called the reactorcore, which includes: the fuel, the heavy cooling water and the moderator. [1]

The manufacture of nuclear fuel lozenges for nuclear power plants (NPP) is the first step in the cycle of nuclear fuel development when it is transformed from raw material (e.g. natural or enriched uranium or other fissile material) into a high-quality product, adapted to the specific needs of a nuclear power plant. The design of fuel pestles is specific to a particular type of reactor (generally based on the nuclear steam supply system) and the specific fuel management strategy of a nuclear power plant (which takes into account the length of the transformation cycle, the capacity factor, the existing fuel in the reactor core, etc.). The market for manufacturing nuclear fuel for light water reactors (LWR) is the largest - about 82% of the world's nuclear operating plants are LWR. Among the LWR projects, there are two general categories of installations: pressurized water reactors (PWR), including the Russian VVER projects and hot water reactors (BWR), which account for 63.4% and 18.4% of the operating units, respectively. Non-LWR NPP projects include: gas-cooled reactors (GCR), pressurized heavy water reactors (PHWR), Russian graphite moderated reactors (RBMK) and liquid-metal (LMR) fast-cooling reactors. PhWRs make up the second segment of functional nuclear power plants, after LWRs, accounting for 11% of all reactors operating worldwide. [2]

CANDU reactors use UO_2 as a fuel, to the detriment of uranium metal, because UO_2 ceramic fuel pills have excellent corrosion resistance and are stable in a radioactive environment. It also uses heavy water as a neutron moderator at the expense of graphite, as it is the only way to achieve critical mass for a reactor using natural uranium.

The main feature of these reactors is that, due to the excellent moderation properties of heavy water, they can be fed with natural uranium or only with light enriched uranium (usually below 2%). The option of natural uranium, in particular, has the advantage that it does not require an enrichment plant for the manufacture of fuel. A relatively large number of heavy water reactor projects have been developed over the years in different countries, using the concept of pressure tubes. [3]

The purpose of a power plant is to generate electricity safely, reliably and economically. An obvious difference between a nuclear power plant and a fossil fuelled power plant is the heat source. Nuclear fuel produces heat by fission with the help of the Moderator System. In the fission process, fissile atoms separate after the absorption of slow neutrons. This releases fast neutrons and generates heat. Fast neutrons cannot continue to generate fission. The moderator slows down the fast neutrons without absorbing much of them so that fission chain reactions can be generated. Less than 2% of fission neutrons are absorbed by the moderator. Upon a collision with a heavy water molecule, most neutrons transfer their energy to heavy water. This slows down the neutrons and heats the heavy water. The heavy water circulating through the Primary Heat Transport System takes over the heat resulting from the fission reaction of the uranium dioxide fuel, thus converting nuclear energy into thermal energy. At the level of a boiler, this heat circulated by heavy water is ceded to light water, which vaporizes. Aburul acts a turbine that converts thermal energy into mechanical energy. An electric generator converts mechanical energy into electrical energy. [1]

Advanced-designed heavy water pressure (PHWR) reactors feature two independent rapid shut-off mechanisms to meet the current in-depth defense safety requirements. The 500 MW Indian PHWR project(s) is one such reactor designed to have two independent stopping systems that operate on different principles. The first of these is called The No. 1 (SDS-1) and consists of 28 mechanical cadmium stop bars. The second system, called The Rapid Stop System no. 2 (SDS-2), works by injecting a concentrated solution of highly absorbent material of neutrons (moderator poison) directly into the moderator. [5]

The trend, in terms of absorbent neutron materials, is the use of boron-based compounds, abundant materials, with relatively affordable costs and with which developers have extensive experience. Today, more effective boron-based compounds are still being developed, although boric anhydride precipitates and is difficult to extract from the heavy water of the Moderator System. The use of rare earths, the elements with the largest known absorption section of all stable nuclei, shows a great advance in this area. Despite this advantage, these rare earths, based mainly on the use of samarium and gadolin, have the disadvantage of emitting secondary gamma radiation with very high energy and being very dense, so their use must be studied. An optimal solution for the development of new absorbent neutron materials is the use of boron-based materials that incorporate rare earths, allowing for a compromise to develop optimal neutron absorption solutions for different energy spectrums. [6]

In the form of a liquid nitrate solution injected into the moderator, gadolini is also used as a strong poison in the Rapid Stop System no. 2 (SDS-2) of the CANDU reactors (Hart and

Olmstead, 1995); the choice of gadolinium nitrates, at the expense of boric anhydride, is mainly due to the faster chemical dissolution in the heavy water of the first of these two molecules. An accurate assessment of the capture properties of gd isotope neutrons is therefore necessary and to estimate the safety margins of SDS-2. [10]

By means of the Liquid Poison Addition System in moderationor the reactivity control is performed by automated addition of appropriate amounts of gadolinium nitrate to the aspiration of the moderator pump. Gadolinium nitrate is not added directly to the moderator, therefore, the results are not immediate.

Gd(III) is also used, together with organic chelators, as a contrast agent in magnetic resonance imaging (MRI) and magnetic resonance angiography (ARM) to improve contrast as a functional material in magnetic refrigeration and to obtain optical fibers.

Corrosion is always undesirable, but often it can not be prevented. Corrosion products are formed even in plants made of stainless steel or zirconium alloy and are released as impurities in the fluid that circulates the pipes. As these impurities cross the flux of neutrons in the reactor core, they are transformed into radioactive species that emit gamma radiation, thus causing a radiological problem for staff during operation. Some of these corrosion products are soluble and, as ionic species, cause a supple problem of increasing the radiolysis process. High levels of ionic impurities tend to prevent the natural recombination reaction between D_2 and O_2. The resulting extra oxygen is available to further support the corrosion process. Moreover, both oxygen and deuterium in radiolysis are released into the moderator's covering gas (helium). The circulation of the coating gas through the recombination units maintains an acceptably low concentration of deuterium if the radiolysis process is under control. [1]

The methods of separation from Gd(III) extracted from the literature study are: extraction with ion exchange resins, extraction with ionic solvents, extraction with solvent-impregnated resins, extraction with chelating agents and extraction by magetic interaction, applicable both in the nuclear field and for the purification of water / soil, for the selective recovery of rare elements from secondary sources. In the nuclear field, gadolinium extraction is carried out through the Moderator Purification System, based on ion exchange columns.

Therefore, concentrations of ionic impurities in the moderator are kept to a minimum to control the radiolysis process and prevent the trip of deuterium into the moderator coating gas and the danger of explosion. For this, the methods used consist in the continuous extraction of ionicimpurities, by means of ion exchange columns that make up the Moderator Purification

System, and the maintenance of an effective chemical control. The Moderator Purification System controls the value of the moderator's reactivity by removing soluble neutron poisons: gadolinium nitrate. [1] For gadolinium to serve as a neutron absorbent, it should be present in dissolved form, and the medium should be slightly acidic. However, the pH cannot be reduced to very low values due to increased corrosion of structural materials when increasing acidity. Thus, the technical specifications for the pH of the moderator system is in the range of 5-5,5, the purity of heavy water should be maintained by removing carbonates and silica to avoid any gadolinium precipitation. Gadolinium extraction is normally done using commercially available ion exchange resins, as opposed to special substrates used to remove lanthanides and other metal contaminants from aqueous solutions. [21-24]

Ionic liquids have become extremely popular compounds in recent separation research due to their unique physico-chemical properties. Compared with conventional organic compounds, ionic liquids are characterized by low volatility, low toxicity, high thermal and chemical stability, high polarity, high viscosity, high hydrophobicity and high surface activity due to the presence of both cations species and anions in the same molecule. [16,17]

The accumulation of lanthanides in the soil, water and food chain must be taken into account in environmental studies. Several methods are available for the extraction of lanthanide elements, includingusive adsorption, ionic exchange,precipitation reactions and evaporation. The impregnation technique is a type of selective ion exchanger based on solvent extraction. The impregnation process has a potential advantage over solvent extraction, such as minimal use of organic solvent, less waste accumulation, simple operation and reduced costs. The concept of solvent-impregnated resin is based on the incorporation of the extractant into a matrix of porous material either by a physical impregnation technique or by introducing the extractant during the synthesis of the porous matrix. Some considerations must be taken in the impregnation process, such as: the solubility of the extractant in water must be low to prevent the loss of the impregnated extractant during the extraction process, the extractant should have an adequate viscosity so that the extractant can easily penetrate into the pores of the matrix, and the impregnation process should not affect the chemical and physical structure of the supporting material. [18]

The sorption properties of gadolin (Gd) by an acrylamide polymer based on carbamoilmetilfosfonate (cmp), which combines both chelating andthermosensitive properties, namely poly-(diethyl-6-(acrylamido)hexyl-carbamoil-methylphosphonate) (P (CPAAm6C)). New retention processes, such as ultrafiltration enhanced with polymers or polymer-assisted ultrafiltration (PEUF/PAUF), which pair a functionalized polymer (soluble

or insoluble) to complex metals with a membrane ultrafiltration step to recover the polymer after complexation. For example, Ricoux et al. reported the development of a retention process for palladium using a functional polymer of insoluble phosphine oxide. Another more interesting example is Graillot et al. TEMF (Thermosensitive Enhanced MicroFiltration) process that allowed the removal of metals from water by using water-soluble copolymerS P (NnPAAm-stat hMAPC1). NnPAAm exhibited thermosensitive properties, while MAPC1 monomers allowed for the complexation of metals. The use of this type of complexed thermosensitive polymer has two advantages: (i) the thermosensitive polymer is soluble in solution at a temperaturelower than the point ofdew (CP) thus favoring the complexation of metals, and (ii) the polymer becomes insoluble at a higher temperature of CP, which leads to an increase in particle size and thus to an easier filtration stage, that allows for an energy saving. In an earlier paper, the first thermosensitive-complexed homopolymer (P(CPAAm6C)) was reported.

B-cyclodextrin magnetic devices, which are synthesized in three stages, could be easily regenerated while retaining good adsorption performance for organic pollutants and heavy metals in wastewater (Hu et al., 2020; Zhang et al., 2017). [51]

Although a good retention yield of Gd(III) is achieved, the disadvantages of these separation methods are: high costs, large space requirements, large inventory of solvents, poor sealing of the system, long waiting time, high consumption of heavy water used for deuterization of the resin, the need to deuterization of the resin after exhaustion, large amount of waste.

Chapter II of the thesis corresponds to the first objective of the research,which is achieved by presenting a new method, revolutionary and facile, for the evaluation of the process of separation bya membrane , based on changing the color of the membrane surface during the separation process. For this purpose, a cellulose acetate membrane was modified in several steps – initially with the amino-propyl-triethoxysilane, followed by the reaction with glutaraldehyde, and functionalization with calmagite – indicator with a double role,that of facilitating the separation process of Gd(III), as well as of changing the color of the membrane surface and implicitly of demonstrating the separation the desired cation .

Complexed solutions and gadolinium-based salts are used for two main applications: as contrast agents for clinical magnetic resonance imaging and research (MRI) [83,84] and as poison for nuclear reactors, to control the nuclear reaction [85]. The problem of toxicity with Gd (III) is given by the fact that traces of this element or other complex solutions based on Gd

(III) can remain in the brain, causing toxic effects [86,87]. In addition to being an extremely toxic element, one of the biggest   challenges of using this element in its application, currentlyknown, is given by the practical situation thatit cannot affect   the environmentl , because MRI contrast agents are subject to very strict regulations, and also water that is used as a moderator of nuclear reactors with poison content by the moderator is maintained in a closed circuit and well controlled, without harming the environment, due to the same strict regulations. For these reasons, the retention of Gd(III) in water is limited to a single practical application: to regulate the concentration of Gd(III) in the heavy water used to moderate fission nuclear reactions.   For this application, only one separationsolution isused: ion exchange resins. Most of the resins used are based on polystyrene [88], with degrees of retention ranging from 150 to 178 mg Gd (III) / g resin. Higher yields for the retention process can be obtained using a mixed bed resin   (MB) ion exchanger column, consisting of strongly acidic cationic resin (SAC) and strongly basic anionic resin (SBA) [89], obtaininga retention degree of 250 mg Gd(III) /g of resin. New systems based on functionalized mesoporous silica [90,91] or on composites with magnetic nanoparticles [92] were tested, but ion exchange remains the technical solution with the highest retention efficiency. So far, even if we consider a separation process, no membrane material has been reported to be used for gd(III) retention. We propose inthis study a membranematerial, which not only has the ability to separate Gd(III) din the water used to moderate nuclear reactions, but also with the remarkable property of changing its color, visually indicating the separation from Gd(III).

Membrane materials are unique of all the materials known and used at the moment because, in addition to their structural and functional characteristics and properties, they hold a unique property: selectivity [93]. A membrane is a functional material that essentially acts as a barrier to a particular type of ions, molecules and particles, but is permeable to the rest of the species in a multicomponent system [94]. The development of membrane separation processes was based both on technical factors such as separation selectivity, reliability of technology, energy efficiency and productivity, and on economic factors such as the cost of the plant, equipment [95-97],   operation, maintenance   [98] and the cost of raw materials [99]. Membranes and membrane processes are an interdisciplinary field whose explosive evolution has been determined by the unlimited involvement of materials science, mathematics, physics, physical chemistry, biology and engineering at every stage, from theory to industrial process. Proof of this are the multiple applications in different fields, such as biomedical sciences: hemodialysis [100-102], protein separation [103,104], osseointegration [105-107], fuel cells [108-110], environmental decontamination [111]. After carrying out a membrane separation

process, a very important step is to evaluate the separation efficiency. For this, different methods of analysis are applied to the solution with separate species, such as UV-V IS spectroscopy [112], atomic absorption [113] and induced plasma coupled with ICP-MS mass spectrometry [114].

The basic principle of this research was to find a substance that simultaneously has two roles: the separation of gadolini from aqueous solutions and the indication that gadolini was separated, by changing a membrane property that can be easily observed, namely the color of the membrane surface. For this purpose, an indicator was sought that meets both conditions and can be immobilized on the surface of the membrane. The principle of operation of this indicator is based on the reaction of complexion of metal cations generated by the two hydroxyl groups and the two nitrogen atoms [119]. The degree of novelty of this research is given by the fact that without additional instrumental methods of analysis, the efficiency of the separation can be visibly observed by the operator by changing the color of the membrane surface.

The synthesized materials were characterized by Fourier transformant infrared spectroscopy (FT-IR), thermal analysis (TGA-DTA), X-ray photoelectronic spectroscopy (XPS) and Raman spectroscopy, proving material synthesis membranar with self-indicatory properties . When separating Gd (III), having as its source gadolinium nitrate, used as moderator poison in nuclear reactors, the membrane has changed its color from blue to pale pink, ICP-MS analyses showing a gd(III) separation process efficiency of 86%, relative to the initial supply solution, after 5 recirculation cycles.

SEM microscopy has revealed several important aspects regarding the morphological changes in the surface of the synthesized membranes. Unlike the standard cellulose acetate membrane, the functionalized membrane with APTES has a low surface porosity due to the crosslinking effect induced by the covalent interaction between APTES and the free hydroxyl groups on the membrane surface. In addition, in the case of the membrane functionalized with APTES, on the porous surface, a series of agglomerations are observed due tothe polymerization of aptes, inthe presence of traces of water in the alcohol, during the functionalization reaction.

As a result of the immobilization of calmagite, the surface structure of the membrane increases greatly, which is most likely due to the rejection of calmagite molecules (a large number of non-participating electrons in nitrogen atoms and oxygen atoms in sulfonic groupse). After filtering the gadolini, the morphology ofthe surface changes. This is due to the complexation reaction that occurs between the non-participating electrons in the nitrogen atoms and the hydroxyl groups in the adjacent molecules, which leads to a reticular and re-tightening

of the surface. In addition, on the porous surface, we can observe the presence of large gadolinium crystals, which probably formed around the growth sites, which arose from the initial complexation of calmagite.

Aspect of the optical of the synthesized membranes revealed that the basic principle, from which the idea of this research originated, works. In the hrydrolysis phases of membrane functionalization - the immobilization of APTES and glutaraldehyde - the surface of the membrane remains white. After immobilizing the calmagite, the surface of the membrane is dark blue in color. After filtering gadolinium nitrate, a radical change in color from dark blue to pink can be observed, visible to the naked eye; in addition to its separating properties, the membrane also exhibits self-indiction properties.

Spectrelay FT-IR shows major changes, proving the functionalization of the membranes used. Thus, after partial hydrolysis of cellulose acetate membranes, in order to increase the number of hydroxyl groups at the surface of the membrane, the specific band for the $C = O$ groups decreases in intensity, since the number of acetyl groups was reduced during the hydrolysis process. In addition, the functionalization with APTES causes a movement of all bands,due tothe presence of Si atoms. Immobilization of the calmagite caused a change in the intensity of all bands (due to the change of the functional groups in relation to the total surface of the membrane: the presence of the groups $-N = N-$ and $-SO_3H$), as well as their slight displacement (for the same reasons). The band from 1750 cm^{-1} attributed to the $C=O$ groups, has the highest intensity in cellulose acetate, and is very diminished after hydrolysis with sodium hydroxide. The tape is still present in the case of other membranes, which indicates that the hydrolysis of the membrane is not complete, leaving behind fewer $C=O$ groups. In addition, another decrease in intensity can be observed for the 1250 cm^{-1} band, attributed to ethereal C-O groups. This is also due to the partial hydrolysis of acetyl groups in cellulose acetate, but it may also be due to the hydrolysis of polymer chains, as indicated by thermal analysis. However,the formation of new connections with ether occurs and by immobilization of APTES on the surface of the membrane. The decrease in the intensity of the band can be explained by the breaking of several links instead of the formation of new bonds, as well as by the steric tripping generated by the large molecular volume of APTES. Other changes occur in the region of 3200–3600 cm

$^{-1}$, which are specific to hydrogen bonds in water and hydroxyl groups. In the case of cellulose acetate, after treatment with sodium hydroxide (to increase the number of groups -OH), the intensity of the tape increases due to the increase in the number of hydroxyl groups. The

intensity is also very high for ca/aptes/ga membrane due to the crosslinking effect on the membrane and high water retention [126–129].

The immobilization of the calmagite on the surface of the functionalized membrane can be observed in the IR spectrum of the CA/ APTES / GA / CAL membrane where, in addition to the bands corresponding to cellulose acetate, the presence of two additional bands at 1579 and 1520 cm^{-1} of the CAL structure can be observed. and are consistent with the values reported in the literature [130]. These results were further supported by the bad spect Raman respectively. Several new peacks attributed to the presence of new functional groups on the original membrane were clearly visible. The intensities of the peacks of the initial membrane were higher after functionalization, which led to an improved surface area, demonstrated by the Raman spectra [122].

More evidence that the functionalization process took place is showninthe XPS curves. XPS analysis was performed to observe the change in the chemical composition of the CA membrane surface after the functionalization process. The XPS spectrum of the CA membrane shows two allocated peaks C 1s and O 1s located at 284.72 eV and 531.34 eV, respectively. The functionalization of the CA membrane surface leads to somechanges, both in the atomic percentage of C 1s and in O 1s, as well as the emergence of new peacks in the XPS spectra. For example,in the XPS spectra of CA/APTES membranes, the C 1s percentage increases from 45.16% to 64.96%, and the O 1s percentage decreases from 44.8% to 20.49%. In addition to the peack corresponding to the CA, a new peack located at 102.12 eV could be observed, attributed to Si 2p (8.64%). Thisindicates that the binding to APTES to the membrane surface has occurred. The additional functionalization stage involves the reaction with GA, which has the following atomic percentage: 62.69% for C 1s, 28.64% for O 1s, 5.34% for N 1s and 3.7% And 2p. Immobilization of calmagite is demonstrated by an increase in the percentage of O 1s to 25.04% and a decrease in the atomic percentage of C 1s to 63.27%, this is due to the orientation of the calmagite molecules on the surface, recorded by the XPS equipment. In addition, the decrease in the atomic percentage N 1s to 3.24% is due to the shield ofitsplane ofthe steric daddy induced by the polarity of the ice-flavoredrings. The XPS results demonstrate that the modification process has been achieved.

To demonstrate the functionalization of CA membranes, high-resolution spectra of C 1s, O 1s, N 1s and Si 2pwere recorded. D up thefunctionalization with APTES, a peack appears at 281 eV, which is assigned to the C-Si group. In addition, in the CA/APTES membrane, the peack of 288 eV is assigned to a C -N bond. The intensity of the O–C–O peack (at a binding energy of 289 eV) is high in the case of the CA/APTES membrane, due to the increase in

these bonds after the immobilization of APTES. The next step of the functionalization (reaction with GA) was demonstrated by the presence of a new peack at 288 eV, which is attributed to the link C = N [49-51].

In plus, the O 1s spectrum shows three peacks centered at 530, 531 and 532 eV,allocated to the O = C, O – C and O – H bonds, for the CA membrane. In the case of the CA/ APTES membrane, the appearance of a peack specific to the O-Si group at 529 eV suggests immobilization of APTES at the surface of the membrane. After immobilization of the calmagite, the connection O=S at 534 eV is present only in the structure of the indicator used [131–133].

Spectreles for N 1s show the presence of N–C bonds in ca/aptes, CA/APTES/GA membranes, respectively CA/APTES/GA/CAL, at 399 eV and N=C bonds in ca/aptes/ga and CA/APTES/GA/CAL membranes at 402 eV [134]. Regarding the spectra for Si 2p, we can observe the Si-O bonds (at 103 eV) and the Si-C bonds (at 102 eV) in APTES, uset as a linker, present in the ca / aptes membranes, CA / APTES / GA and CA / APTES / GA / CAL [135].

For industrial applications, the thermal stability of the material is also an important parameter. With this in mind, the thermal stability and degradation profile of pure CA membranes and modified CA membranes were evaluated by thermal analysis. Pure CA membranes show the typical two-stage decomposition profile of degradation attributed to solvent evaporation and polymer chain degradation [30]. In the case of modified CA membranes, thermal degradation profiles illustrate a similar trend as for the pure CA membrane, which means that the synthesized materials are thermally stable. An increase in mass is observed in the case of ca/aptes membrane, which could be attributed to SiO_2 fragments of the APTES structure and could prove that the immobilization of the silane coupling agent on the surface of the CA membrane was achieved [136].

The lowest waste mass (2%) was recorded in the case of CA/APTES/GA/CAL membrane and is due to thermal degradation due to organic moisture on the surface of the CA membrane. There are many studies that demonstrate that the degradation temperature depends on the functional groups grafted on the cellulose acetate surface [137].

The temperature at which the mass loss is 5% ($Td_{5\%}$) was recorded to show the thermal stability of the synthesized membrane. The data reported in Table 1 indicate a significant increase in the thermal stability of the modified CA membrane after each stage of change. The improvement of the thermal stability of the CA/APTES membrane is attributed to the chemical interaction between the hydroxyl groups in CA and APTES. Moreover, this increase in thermal stability could be a consequence of a slight cross-linking effect induced after the

immobilisation of APTES on the ca membrane surface, also supported by SEM images [138]. In the case of CA/APTES/GA membrane, the improvement of thermal stability corresponds to the strong bonds obtained in the ca/aptes/GA membrane, as observed in our previous studies [123]. The greatest thermal stability was recorded in the case of the membrane with calmagite immobilized on the surface of the CA. This could be attributed mainly to aromatic rings with high thermal stability and to strong bonds built on the surface of cellulose acetate. Similar behavior was observed by Abdel-Naby et al. when they managed to chemically modify cellulose acetate with dialylamine [139]. The results of DTG referential thermogravimetry do not show any significant changes.

The thermal behavior of the membrane is not radically altered, which indicates the stability synthesized during the transformation process. Small changes can be explained by multiple chemical changes in the synthesized membranes, which have an effect not only on the immobilizationofthe squidt , but also on the partial hydrolysis of the polymer that constitutes the material. The greatest thermal stability in the case of CA / APTES / GA / CAL membranes is attributed to the presence of covalent bonds in the entire structure of the material.

Also, the fluxes throughthe synthesized membraneswere studied,and the retention capacity of the membrane was evaluated by five successive passes of 500 ml of 1 g/L solution concentration of gadolinium nitrate. In the case of cellulose acetate membrane, the initial water flow was about 160 L / m^{2}h, but after functionalization with calmagite, the flow increased to about 600 L / m^{2}h. This can be explained by the hydrophilic character of the calmagite molecule, which also induces a higher hydrophilic character of the material membranar.

After the first recirculation cycle, the decrease in flow can be explained by hydrodynamic stabilization of the polymer layers in the membrane structure.

The totalretention, assessed by ICP-MS, was 86% for the functionalized membrane, compared to 64% for the standard cellulose acetate membrane. This difference can be explained by the reaction of complexion of the calming indicator to the surface of the membrane. In addition, as a result, with higher retention values, there is a change in the color of the surface, visually indicating the retention of Gd (III). Subsequentstudies, related to this new generation of membrane materials, will consider and validate quantitative methods to visually indicate the concentration of the retained cation, depending on the color of the surface.

Chapter III of the thesis was developed to fulfill the second objective of the thesis, according to which the surface of a cellulose acetate membrane was modified in several stages: initially with amino-propyl-triethoxysylane, followed by the reaction with glutaraldehyde and

immobilization of ether crown. The synthesized materials were characterized by Fourier transformant infrared spectroscopy (FT-IR) and X-ray photoelectronic spectroscopy (XPS), which demonstrates membrane synthesis with gd (III) separation properties. The retention performance of the membrane was tested by induced plasma analyya coupled with mass spectrometry (ICP-MS), demonstrating a separation process efficiency of 91 % in relation to the initial feed solution.

Polysulfone is one of the most widely used polymers for obtainingmembranes, due to its remarkable properties,suchas: chemical stability,mechanical andthermal properties andthe possibilityof producing a wide range of polymeric membranes with differentapplications. Membranefunction isthe key process to obtain high-quality membrane materials. The field of membrane materials andtechnology is one of the most important in the area of interest of polymers andtheir applications,due tothe various applicationscurrently used in everydaylife,from water purification [140] to advanced medical processes, such as controlled release of medicines [141], hemodialysis [142] or osseointegration [143]. There are two main methods of using the propertiesof polymeric membranes – preparation of composite membranes [144], respectively thefunctionalizationof their surface[145]. In general, polymeric composite membranes are obtainedwiththeaimof improvingtheir thermalproperties [146],mechanical properties[147] and separationproperties[148], especiallyinparticular in in the case of carbon nanotubes [149, 150] or graphenes as fillers [151, 152]. Polysulfones represent a class of amorphous thermoplastic polymers,characterizedby high values of the temperature of the glassy tranceandsticloas, good mechanicalresistance,outstanding thermal characteristics andresistanceto oxidizing environments. Due to their properties, thesepolymers are increasingly usedinvarious commercial applications. A basic repetitive unit of any polysulphone consistsofasulfonicgrouping, one or more aryl-type countries,an ether-type group andotherfunctionalgroups. Aromatic polysulfones have many key characteristics, such as: a high point of sticles and transceiroment (Tg, generallylower than 170ºC) anda high degree of thermal and oxidativestability. By their nature, they have optical transparency,are resistant to hydrolysis inhotwater or steam, to medium temperatures, andto acids or bases ina wide range of concentration and temperatures [153].

Functionalized PSF-based anion exchange membraneswereobtainedby workingonthe polymerwith trimethylamine andN, N, N, N'-tetramethyl-1,6-hexandiamin,usingchloromethylate, amination and alkalization [154]. The main advantage of the synthesis strategy chosen is given by the fact that N, N, N, N'-tetramethyl-1,6-hexadiamine presents a long alkyl chainthat is used somuch for crosslinking andfor amination

ina single step andalsothat intensifys physico-chemical properties of the membrane. The reported ionic conductivity is superior to other double-layered membranesand anion exchangebased on polysulphone functionalized with hydroxyl – 23.6 mS/cm [155] or graphene 10.7 mS/cm [156].

Based on the experiments carried out inasingle $H_{2/O2}$ fuel cell,it can be concluded thatthe corresponding proportionsofamination andreticularagentscan lead to the obtaining ofmembranes withbalanced performance ofionic and ion transport i stability. Also, reticulation has been used to obtaintheexchange membranesof polysulfon cations with different sulfonation vents for electrodialysis. Thecross-linking response was realized ina UVenvironment, using 2,4,6-trimethylbenzoyl-diphenyl-phosphine (TPO)oxide asphoto-initiator and triacrylate-triacrylatetriacrylate (TMPTA) as a cross-linking [157]. The cross-cross-link membranes of the polysulfone sulfonate changed by cations obtainedby this method have demonstrated an increase instabilitybetween 40-70°C anda high performance in electrodialysis with a separation efficiency for NaCl of 89.1%. Inrecent years, composite polysulfone/TiO2aminated membranes have been synthesized for the separation from Cr(VI) fromaqueous solutions, based onthe ionic exchange capacity(IEC) of the membrane [158]. It is well known that the initial polysulphone membranes presentnegligible IEC [159]. After amination, the IEC increases considerably. The percentage of separation from Cr(VI) was affected by the formation of ion pairs inthesupplysolution,the fixed load of the membrane andthecompetitionof interferingions [158]. Polysulfones functionedonalized with phosphorous acid andphosphorous ester (reticulated and unticulated) have been used as an extractant for the extractionofchlorinated hydrocarbons (CHC) from water [160]. The membranes werefunctionalized usinga two-cellprocedureand– chlorometry followed by theMichaels – Arbuzov reaction[161]. Chloromethylated polysulfones have been used as precursors for variousapplications[162-164], includingtheobtainingof PEM for alkaline fuel cells [165, 166]. The exchange membranes of poly(aryl-ether-sulfon)anionswere obtainedby polycondensation of monomer mixtures with aninut content ofhexamethyldihydroxybiphenyl with copolymers with high molecularmass, followed by bromine complete benzilice andMenshutkin reactions, resulting inpoly(arilen-ether-sulfonicmembranes) withrandomly distributed diphenyl units and dithanyl, linked with exactly as imidazole groups.

These membranes provide a good retention capacity for aromatic CHCs, due to theincreased hydrophilicity and interactions of the donor-acceptor electron π between the polymeric matrix and the aromatic groups e [167].

The synthesized membranes showed a higher capacity for ionic exchange at a smaller amount of water,being suitable forelectrochemical applications, such as redox flow batteries. Forthe samepurpose, composite membranes based on quaternized polysulfone (QPSF) anddouble-layered hydroxide (LDH) were synthesized [168]. Polysulfone was dissolved indimethylacetamide (DMA) and, before casting,it was addedto N, N, N, N'-tetramethyl-ethylenediamine (TMEDA) inthe polymersolutionas a cross-linking agent to cause joint reticulation of membranes. LDH was obtainedby controlling theconditionsforhomogeneous precipitation of urea [169], the composite membranes being made by dispersion of LDH inthe polymer solution, followed by casting andprecipitation. The QPSF/5% LDH nanocomposite membranes havea low degree of adsorption,improved resistanceto resistance anda higherionic conductivitythan theQPSF membranes. Theanti-deposition properties of PSF membranes have been improvedby introducingamino groups intothe polymer chain. Polysulphone was ily chloromethylated,this functional groupbeing later replaced by metansulfonamide or benzensulfonamide [170].

The functionalizedmembranes demonstrated a lower degree ofadsorptionfor BSA, compared to simple PSF membranes, due to the formationof thetoweror hydrogen bond between the water molecules andthe hydrophilicsulfonamidegroups polymer.

In order toobtainmembranes exchangeof anions, composite membranes were synthesized onthe basis of functional PSF andgraphene oxide. The polymer was modified in twostrawsand:chloromethylamin anddimethylaminaddition, respectively,with the formation offunctionalazidylamine groups. During a process of jointingat 160 ºC, a covalent structure was formed and cross-linking between the lateralchainswithazidandrGO withalchenilgroup without sacrificing group ionices. Thus,a composite membrane with rGO was obtained, inwhich the filling isthe sameandwith thereticular agent [171]. Also, the membranes of polysulfonwith metal catalyst quaternized with metallic catalyst are used for the production of biodiesel from soybean oil, which prove a very good conversion. In order to obtainmembranes functionalized by PSF withcatalyticapplications, the initial membraneswerefunctionalized inthree cellsand– chlorometry, quaternization andalkalini zare [172]. The applicationsof alkaline oxideSr/MgO in theprocess ofansesterification ofbiodiesel production have been investigated anda conversionof 90% to30 min [173] has been converted. The membranes operating with active catalyticcomponents have attractedconsiderable attention inthe productionprocessofbiodiesel [174]. Although modified biomass has proven to be effective andeconomicalfor the separation and recovery of metal ions from aqueous medium, it presents technical limitsin theapplicationson the scale wide andcontinuousprocesses. For the

separation of biomass insuspension from theaqueous phase,the difficulthandlingandpossible clogging of lines andfilters intheproduction provedto be a real challenge for adsorbansin powderform [175, 176]. Inorder to supporttheresearch topic of ion exchangemembranesbased on polysulfon function, polysulfon-based membranes have been obtainedas a polysulfon-based adsorbent Inthe state of performance, resistant in acidicenvironment for the retentionof platinummetalgroups (PGM) inwastewater. A ps composite membrane was prepared with biomass (Escherichia coli) coated with polyethylenemin (PEI) (PEI-PSBF), by mixing the PS-biomass membranes in thewater andcrosslinkingof the glutaraldehyde with glutaraldehyde . The presence of biomass in the membrane has led to an improvement inthe retention capacity for Pt(IV) of the PSBF andplaysthe role of linkbetweenpsbf andPEI by donating the group functional countrieswith a negative load for theassociationof functionalcountrieswith positive amino-type loadin PEImolecules [177]. Atthe sametime, a new nanocomposite catalytic membranewas obtainedbased on chemically modified PS andpalladium particles. Followingthe analyses ofFT-IR, ^{1}HNMR, TGA, DSC, UV-VIS andSEM, these membranes demonstrated good catalytic activity andhigh stabilitywhen reusing them 30 times, withouta significant loss of productivity ess[178]. One ofthepractical reactions catalysed by the palladium isthe Suzuki coupling response. TheC-C links formed inthis reactionhave a substantialimportance in theindustryproducing medicines, heterocycles, agro-chemical products andperfumes. Suzuki coupling reactions have been carried out inthe presence of homogeneous palladium catalysts that differinscope. Limited reuse of the catalyst, which causes contamination of the product with residual palladium anda high cost, represents the main defect of this type of catalyst. The catalytic membranes described above represent a method of exceedingthis limit[179].

Based onprevious research, it has been shown that there are two strategies for obtainingsolid membranes withchiralresolution. The first strategy entens the formation of the membrane from a synthetic or natural polymer containingactive chiral carbon atoms inits fields: cellulose oritsderivative, sodium malginate, chitosan, etc. [180-182]. Anotherstrategy is to introduce directly the modified chiral selectorsonthesubstrate [183]. Thus, a PSF membrane was modified with polydopamin (PDA), and β-cyclodextrin (β-CD) was subsequently integrated onthe surfaceof themembrane [184].

Chlorometry is noteasyto control, andthe number ofchloromethyl floss and polymer groups can be very small, which affects the conductivity of the membrane. Reactionoften causes the appearance ofa gel, ifit is not properly controlled. Usinga suitable quaternization, the conductivity of the membrane can be optimized for theproductionof alkaline membranes

anion exchange (AAEM) [195-197]. Whilethe accessibility of thefunctionalgroupsofchlorometil used is limited, chlorometlylation can be improvedby adjusting the temperature andthe reaction time[198].

A novelty element is thesynthesis of a hybrid membrane, based on cuaternized PSF with immobilized graphene oxide (GO) (Q-PSF/GO), by inversion of the phase,usingGO as anadditive andtriethanolamine(TEOA) asaminating agent. The FT-IR images showed that GO was immobilized by thequaternary ammonium group, and thequaternary ammonium groupions andthecharitable GO gogroupsformed on the Q-PSF/GO$_{0.5}$membrane, which showeda good asset capacity for capacity and retention[204]. The performanceof the membrane isgiven by theincorporation of GO[205-208], due to the hydrophilicfunctionalgroup(hydroxyl, carboxyand epoxy) [209, 210]. However, the homogeneous dispersion of graphene derivatives is restrictedby their strong tendency to form aggregates [211, 212]. Liken, to obtainmembranes with mixedmatrices, derivative polysulfone andzeolite particlesareused. APTMS (aminopropyltrimethoxysylene) has been used as a coupling agent to bind covalently, without resulting in mebran defects, mebranparticles zeoliti of the polymer modified with acrylate. The results of the analyses showeda considerable improvement intheaffordabilityof pure gases or gas mixtures with selectivity for H 2/CO$_2$, depending on themixture in the supply gas or theoperating temperature [213].

More recently, there is along-lasting stabilityforthe development of proton conductive membranes at high aperture as electrolytesfor the cleanenergy conversionof fuel cells. In order to optimize the stability of the polymer dependingon the imidazole grafted structure,thesetypes of imidazole-polysulfone with different compositionsandimidazole and polysulfone chloromethylate were also used, preferencebeinggiven to types with a group hydrophobic alkyl ri acceptors of the longest electrons, due to the establishedsuperior chemical. Membranes witha long end of the lateral chainof decil inimidazole have demonstrated the highest conductivity [219].

Complexed solutions and gadolinium-based salts are used for two main applications - as contrast agents for clinical magnetic resonance imaging (NMR) [220, 221] and as poison for nuclear reactors to control the nuclear reaction [222], but traces of this element or other complexed solutions based on Gd (III) may remain in the brain, causing toxic effects [223, 224]. The retention of Gd (III) in water is limited to the unique practical application of the regulation of the concentration of Gd (III) in the water used to moderate nuclear reactions, since the residues resulting from clinical use are strictly controlled and regulated. Atthis time, adjusting the concentration of Gd (III) in the water used to moderate nuclear reactions, a single

solution is used: ion-exchange resins, especially those based on polystyrene [225], with performances ranging from 150 to 178 mgGd (III) / g resin. Higher yields for retention can be obtained using a mixed bed resin (MB) column consisting of strongly acidic cationic resin (SAC) and strongly basic anionic resin (SBA) [226], achieving a retention of 250 mg Gd (III) / g of resin. New systems based on functionalized mesoporous silica [227, 228] or composites with magnetic nanoparticles [229] were tested, but ion exchange remains the technical solution with the highest retention. More recently, a membrane system forGd(III) retention has been developed, based on cellulose acetate functionallyfunctional with calmagite, a membrane with two adjacent remarkable properties– theretentionof Gd(III) bythe reaction ofcalmagite complexation and i change in the color of the membrane,thusindicating thecompletion oftheretention process[230].

Membrane materials are unique of all the materials known and used at the moment because, in addition to their structural and functional characteristics and properties, they hold a unique property: selectivity [231]. A membrane is a functional material that essentially acts as a barrier to a particular type of ions, molecules and particles, but is permeable to the rest of the species in a multicomponent system [232]. Many fields have beendeveloped inthe last period, havingin the centerpolymeric membranes, others thanthe separative ones. Applicationssuch as tissue engineering [233-236] or membrane reactors for oxidative photodegradation of organic compounds andhave increasinglypronouncedapplicability between classical membrane processes [237,238]. Methods for modellingthe separative properties ofmembranes include the use of surfactants and addedtothe polymer solution [239], the synthesis of composite membranes inwhich the filling plays an active role inthe separation process [240-243], or the synthesis of functional membrane materials[244-246].

This study was conducted to separate Gd (III)from aqueous solutions usingcellulose acetate membranes functioned andderivedwith chorearaethers. Gadolinium nitrate is one of the most used chemical compounds for the control of nuclear reactions which, in the last year, has successfully replaced boric anhydride for this type of application [247–249]. The basic idea of the current research was to find an easy way to remove gadolini from aqueous solutions. As the solutions used in nuclear energy are very pure solutions, the possibility of having other interferences to be separated into the system was eliminated from the start [250]. Excess gadolinium must be separated to control the nuclear reaction at the desired parameters.

Between thepolymers usedto obtainpolymeric membranes, cellulose andits derivatives occupy a special place, the first membraneseverobtainedbeing obtainedfromnitrocellulose. Cellulose derivatives havethe great advantage of being soluble ina wide rangeof

solventsandpolymers,thisfact offering versatility when obtainingmembranes by inversion of phaseor evaporation of solvent. However,thescope of these membranes are limited due totheir lowchemical andmechanicalresistance, and there isin particularthe danger of hydrolysis inenvironments that are tooacidic or too basic, with the breakingof polymer chains anddecreasingresistance its mechanical andhydrodynamic membrane.

Atthe chemical andmechanical strength,theselectivity of membranes incellulose derivatives can also be improvedby the functional andderivatisationactions. The use of APTES has proven to be an ideal method for immobilizing other species oncellulosederivative membranes,which is also theadvantage of reticulating the surfaceof the membrane with arole in n its stabilisation [256]. APTES has been used for the immobilization of magnetic particles [257], the compatibility of nanocellulose with polyetersulphone [258] or polyvinyl alcohol [259], the hydrophobicization of cellulose-based tissues [260, 261], orthe reactive retention of dyesandfor waste water purification [262-265].

For theapplicationpresented inthis study, cellulose acetate,despite the chemical or mechanical propertiesnot necessarily remarkable, can be an ideal candidate, since, froma chemical point of view,thesolution of moderator of a nuclear reactor isascleanas possible in terms of thecompetition, which could vary the acidity or the basicity, being in fact a solutionthat containsthe majorityof Gd(III).

FT-IR spectra show major changes, proving the functionalization of the membranes used. Thus, after partial hydrolysis of cellulose acetate membranes, in order to increase the number of hydroxyl groups at the surface of the membrane, the specific band for the group C = O decreases in intensity, since the number of acetyl groups was reduced during the hydrolysis process. In addition, the functionalization with APTES causes a displacement of all the bands due to the presence of Si atoms. Immobilization of the crownether caused a change in the intensity of all the bands (due to the change of the functional groups in relation to the total surface of the membrane), as well as their slight displacement (for the same reasons). The band from 1750 cm^{-1}·attributed to the C=O groups, has the highest intensity in cellulose acetate, and is very diminished after hydrolysis with sodium hydroxide. The tape is still present in the case of other membranes, which indicates that the hydrolysis of the membrane is not complete, leaving behind fewer C=O groups. In addition, another decrease in intensity can be observed for the 1250 cm^{-1} band attributed to the etheric C-O groups. This is also explained by the partial hydrolysis of acetyl groups in cellulose acetate. Inany case, the formation of new connections with the ether also takes place by immobilizing APTES on the surface of the membrane. The decrease in the intensity of the band can be explained by the breaking of several bonds instead

of the formation of new bonds, as well as by the steric tripping generated by the large molecular volume of APTES. Other changes occur in the region of 3200–3600 cm^{-1}, which are specific to hydrogen bonds in water and hydroxyl groups. In the case of cellulose acetate, after treatment with sodium hydroxide (to increase the number of groups -OH), the intensity of the tape increases due to the increase in the number of hydroxyl groups. The intensity is also very high for the CA/APTES/GA membrane due to the crosslinking effect on the membrane and high water retention [265,266].

The immobilization of the choreath ether on the surface of the functionalized membrane can be observed in the IR spectrum of the CA/APTES/GA/EC membrane where, in addition to the bands corresponding to the cellulose acetate, the presence of two additional bands at 1070 and 1140 cm^{-1} of the EC structure can be observed. These peaks correspond to the stretching vibration of the C-O and C-O-C amide bonds and are consistent with the values reported in the literature [266]. More evidence that the functionalization process is taking place is showninthe XPS curves. XPS analysis was performed to observe the change in the chemical composition of the CA membrane surface after the functionalization process. The XPS spectrum of the CA membrane shows two allocated peacks C 1s and O 1s located at 284.72 eV and 531.34 eV, respectively. The functionalization of the ca membrane surface leads to some changes in both the atomic percentage of C 1s and O 1s, as well as the emergence of new peacks in the XPS spectra. For example, in the XPS spectra of the CA/APTES membrane, the C 1s percentage increases from 45.16% to 64.96%, and the O 1s percentage decreases from 44.8% to 20.49%. In addition to the peak CA, a new peak at 102.12 eV attributed to Si 2p (8.64%) could be observed, and this indicates that aptes binding to the membrane surface has occurred. The additional functionalization step involves the reaction with GA, which presents the following atomic percentage: 62.69% for C 1s, 28.64% for O 1s, 5.34% for N 1s and 3.7% For 2p. The immobilization of the ether crown is demonstrated by an increase in the percentage of O 1s to 25.04% and a decrease in the atomic percentage of C 1s to 63.27%, this being due to the orientation of the surface-based ether crown molecules recorded by the XPS equipment. In addition, the decrease in the atomic percentage N 1s to 3.24% is due to the shield of steric flatness induced by the polarity of the ice-flavoredrings. The XPS results demonstrate that the modification process has been achieved.

The thermostability of the materials wasstudied by means oftheTGA and DTG curves. Thesamples illustrate the same decomposition profile havingtwo stages of degradation:thefirst due to the evaporationof the solvent, and the second due tothe decompositionof thepolymeric chain. In order to observe the thermostability of the membranes,

thetemperature values at which they lose the mass ettention wererecordedwas5% (Td5%). Thus, an increase inthethermostabiiteof themembranes could be observed after the first two stages of modification, andthen it will decrease in the case of themembranethat containsthe ECmolecules immobilized at the surface. The best thermostability was inthe case of ca/APTES/GA membrane, and this is due to the crosslinking effect obtainedatthe surfaceof themembrane followingabilysisGA. O sthat dere significant dere of the thermo-stablenesshas been observed inthe case of CE membranes, this being due to the breakage of ga molecules following derivatizationwith CE. Similar results were obtainedin a previous study where we managedto immobilizm molecules of resveratrol on the surfaceof theCA membrane. Asfor theDTG curves, no significant changes could be observed,whichmeans that the synthesized membranes are stable during themodification process.

Also, the streams through synthesized membraneswerestudied, and the retention capacity of the membrane was evaluated by five successive passages of 500 ml of 1 g / L aqueous solution of gadolinium nitrate. In the case of the cellulose acetate membrane, the initial water flow was about 160 L / m^2h, but after functionalization with choreath ether, the flow increased to about 682 L / m^2h. This can be explained by the hydrophilicity of the chorear ether molecule , which also induces a higher hydrophilic character of the membrane material. After the first recirculation cycle, the decrease in flow can be explained by hydrodynamic stabilization of the polymer layers in the membrane structure.

The totalretention, assessed by ICP-MS, was 91% for the functionalized membrane, compared to 64% for the standard cellulose acetate membrane. This difference can be explained by the complexing reaction with ether crown immobilized at the surface of the membrane.

Chapter IV of the thesis highlights the third objective of the thesis, which was achieved by obtaining composite membranes with silica nanowires for gadolinium retention. For this, a solution of 12% cellulose acetate (mass) in dmf was prepared. Silica nanowires were subsequently dispersed into cellulose acetate solution in different concentrations (1.25, 2.5 and 5%). The synthesized membranes were characterized by SEM, water contact angle, FT-IR and TGA-DTA, proving the obtaining of the membranematerial, and the ICP-MS analyses demonstrated an efficiency of the Gd(III) separation process of 75%, for the membrane with the highest content of silica nanowires, compared to 58%, for the initial CA membrane.

The use of SiNW as a filler brings several advantages in terms of pore formation and their stability, due to the interface interactions with the polymeric matrix, which significantly affects the formation of pores.

The synthesis of this type of membranes is based on cellulose acetate (CA) as matrix and SiNWs as fillers.

In recent decades, polymer membranes have reached their status as highly advanced materials due to their use in a variety of applications in various fields, such as water purification [267], electronics [268], sensors [269], environmental decontamination techniques [270], separations [271], biomedicine [272], hemodialysis [273] or osseointegration [274,275].

The most well-known polymers for membrane synthesis include: polysulfone (PSF) [276], polyetersulfone [277], ketone polyether [278], polyphenylene oxide [279], polyphenylene sulfate [280], cellulose [281], nitrocellulose [282] and cellulose acetate [283]. The shape, distribution and diameter of the pores can be adjusted by choosing the solvent, the concentration of the polymer solution, the coagulation temperature or the addition of additives to the polymer solution [268].

One of the most used techniques to improve the properties of polymeric membranes, both structural and functional, is the preparation of composite membranes [284, 295]. Among the different fillers used, carbon nanotubes (CNTs) [286, 287] and graphene and its derivatives [288, 289] are widely used due to their outstanding properties [290], such as thermal [291], electrical [292], mechanical and induced properties of composite materials [293-295].

The latest approaches in the field of polysulphone composite membranes with carbon nanotubes or graphene are presented from both perspectives – synthesis and applications.

To overcome the disadvantages associated with acid treatment, to increase the hydrophilic character of multi-walled carbon nanotubes (MWNT), they were coated with polydopamine (Pdop). Using different concentrations of Pdop-MWNT, between 0.1 and 0.5% (percentages by mass), several PSF/ Pdop-MWNT membranes were synthesized by the phase inversion method. The nanocomposite membranes obtained show an increase in water permeability compared to the membrane of the initial PSF, due to the increase in the hydrophilic character of the membrane by adding the Pdop-coated MWNT to the polymeric matrix. At the same time, the increase in the hydrophilic character of the membrane due to the functionality with MWNT through the coating process led to an increase in the anticoagulation properties and the breaking resistance of the membrane. Also, morphological changes in the membrane show a decrease in pore diameter correlated with an increase in the concentration of CNT. Due to their superior mechanical properties, these membranes could be used for ultrafiltration processes. The optimal concentration of Pdop to improve hydrophilic properties was 0.1% (percentages by mass) Pdop [296].

The incorporation of several concentrations of oxidized MWNT (oMWNT), by treatment with a mixture of acids, into the PSF matrix to obtain improved membranes has also been studied. The results of the water flow tests carried out on the membranes obtained showed a similarity of the three concentrations of psester staple fibres (16, 18 and 28% respectively), due to an initial increase in the flow of water, followed by a gradual decrease with an increase in the concentration of oMWNT. The analyses recorded a decrease in the contact angle with the increase in the concentration of the reinforcing agent, due to the high hydrophilic character of the membrane surface. The introduction of hydrophilic oMWNT into the polymer matrix has led to a change in pore size, which tend first to increase and then decrease. [297]

On the other hand, the effect of the carboxylate reaction of carbon nanotubes (MWNT-COOH) on the properties of the PSF-based ultrafiltration membrane was studied, and a change in the hydrophilic character and its permeability was observed depending on the degree of carboxylate obtained. It has been observed that the addition of MWCNTs in a mixture of sulfuric acid : nitric acid (3:1) does not lead to a 100% degree of functionality. This is demonstrated by X-ray photoelectronic spectroscopy (XPS). Significant amounts of hydroxyl groups and carbonyl groups are observed on the structure of MWCNTs. The presence of MWNT-COOH led to an increase in the tensile strength of the membrane when the carboxylate degree was less than 2.56%, followed by a decrease in the resistance of the membrane to tensile strength to a higher degree of functionality, compared to pure MWNT. It has been observed that a degree of carboxylate above this value has a negative effect on the mechanical properties of the membrane, resulting in a decrease in the retention efficiency of the membrane and a fractionation of CNT in membranes, due to the destruction of the bonds in the CNT structure as a result of the modification process. [298]

At the same time, the functionalization of amino groups was studied by dispersing MWCNTs (f-MWCNT) in 1.3-phenylenediamine solution, to synthesize thin-layer nanocomposite membranes (TFN), with applications in direct osmosis, by polymerization at the interface. A change in membrane roughness and an increase in hydrophilic character was observed in direct proportion to the amount of f-MWCNT embedded in the polymer matrix (0.01, 0.05, 0.1%). The membrane performance was evaluated using a 10 mM NaCl feed solution and a 2 M NaCl filtration solution. A permeability increase of approximately 160% (95.7 L/m$^{2 \cdot h}$) was observed for TFN with f-MWCNT, compared to the initial TFN [299].

Using another method, with solvents, several MWCNT-PSF nanocomposite membranes were synthesized, with different concentrations of MWCNT. Thermogravimetric analyses (TGA) have demonstrated an increase in the thermostability of the nanocomposite,

following the addition of the reinforcing agent. This increase was due, on the one hand, to the high thermal stability of MWCNT and, on the other hand, to the prevention of heat transfer in nanocomposite membranes by dispersing MWCNT. Synthesized nanocomposite membranes have also been studied in terms of electrical properties. Dielectric studies were carried out at several frequencies (10 Hz - 1 MHz), using the CSF meter, observing an increase in dielectric constant and dielectric losses directly proportional to the content of MWCNT, due to polarization at the interface between the conductive MWCNT and PSF. A decrease in the resistivity of dielectric constants (DC) in the discontinuous fibers in pure polyester was also observed, from $10^{14}\,\Omega$ cm to $10^4\,\Omega$ cm, after adding a concentration of 1% MWCNT, followed by a decrease to $10^2\,\Omega$ cm, after increasing the content of MWCNT to a concentration of 7% [300].

In the same direction of research, the influence of two types of CNT (crude and oxidized) on the physico-chemical properties and filtration performance of composite membranes of PSF/CNT type was studied. Composite membranes were obtained by the phase inversion method, using polyester staple fibers as a polymer. During the manufacture of the membrane, a loss of CNT was observed, which appears to be greater in the case of oxidized CNT (fCNT) compared to crude CNT (rCNT). According to Raman spectroscopy, the dispersion of CNT in the polymer matrix changes in the microenvironment ofnanotubes. Porosity tests showed an increase in membrane porosity by 54 % after the addition of rCNT and by 68% after the addition of fCNT to the polyester staple fibre matrix. At the same time, the presence of fCNT in the polymer matrix also led to an improvement in the thermostability of the membrane and its mechanical properties. There was a significant increase in the flow of water through composite membranes with an inorganic content of 2%, compared to the initial membranes. 2-naphthol permeation tests for synthesized membranes demonstrated a twice-improving permeation capacity for composite membranes compared to initial membranes [301].

Using the solvent evaporation method, several symmetrical PSF-type membranes with CNT were synthesized. To obtain symmetrical membranes, the functionalization of amino groups on the surface of CNT membranes with ether crown derivatives was initially carried out using a polymeric membrane. Composite membranes were characterized by various advanced methods of analysis [302]. The new PSF polymeric membranes with functionalized N and P CNT (fP-CNT and fN-CNT), with high permeability and selectivity, have been successfully developed using a modified phase inversion process. These membranes were characterized in terms of morphological, hydrophilic character, permeability and retention, and

a dependence on the amount and type of CNT embedded in the polymer matrix was observed. Thus, the results obtained showed a significant improvement in the hydrophilic character and flow of water in the case of composite membranes. At the same time, the dispersion of CNT gives the membrane a better degree of permeation and better selectivity, due to the increase in the size of the membrane's pores and its hydrophilicity in direct proportion to the addition of CNT. A 30% improvement in retention properties was reported when small fractions of fN-CNT or fP-CNT were introduced into the psyster staple fiber matrix. This improvement could be due to functional groups, which led to an electrostatic rejection between the functional groups present on the membrane surface and the humic acid (cross-linking agent) molecules [303].

In addition, the new nanocomposites made of carbon nanofibers and polysulphone (PSF) were synthesized by the mixing method of the solutions and the effect of the dispersion and concentration of added carbon nanofibers (CNFs) on the properties of polyester staple fibres was studied. Fesem analysis of the nanocomposite with a CNF concentration of 5% shows several agglomerations, which may be due to the high concentration of CNF in the PSF matrix. To improve the polarization at the interface between CNF and PSF, CNFs have been functionalized by oxidation to air. The presence of CNF in the polymer matrix led to an improvement in the thermostability of materials with the increase in the concentration of inorganic agent, due to the impeding of heat transfer of the polymeric matrix and the intermolecular bonds of hydrogen between the psester and CNF staple fibers. A decrease in the resistivity of the dielectric constant (DC) was observed from 1.08×10^{14} to 1.2×10^5, after the addition of a CNF concentration of 1%. A dependence of the resistivity of alternating current (AC) on frequency was also observed at low concentrations of CNF (0.5 and 1%), but at high concentrations of CNF (1, 3 and 5%) the resistivity was no longer affected by frequency, as a conductive CNF network was formed. The synthesized materials were also characterized from a dielectric point of view, and a remarkable increase in the dielectric constant was observed after the addition of cnf. Its highest value was 6.9×10 11 and was obtained at 10 Hz for composite membranes with the highest amount of CNF. Due to the remarkable improvement in material properties, they could be used in various industrial applications, such as electromagnetic interference and electrostatic discharges [304].

The influence of reinforcing agents on the properties of composite membranes based on polyester staple fibers has also been studied. Subsequently, these membranes were used to obtain new thin-layer polyamide membranes (TFM), the performance of which was tested in direct osmosis, using distilled water and 0.6 M NaCl solution as a solvent. Pure MWCNT,

functionalized MWCNT, graphene oxide (GO) and carbon-tio$_2$ composite were used as reinforcing agents. Compared to pure PSF, the presence of pure MWCNT in the polymer matrix favors the formation of a hydrophobic support, while MWCNT functionalized with GO leads to a hydrophilic material with high porosity and interconnected pores. After the addition of the reinforcing agent (polyvinylpyrrolidone (PVP)) and carbon-thiO$_2$ composite to the PSF, an improvement in membrane porosity and hydrophilicity was observed. These membranes have also been tested for permeability. The test results showed that PSF membranes containing MWCNT functionalized with GO show the highest water permeation and retention of the solution, compared to those containing pure MWCNT or simple PSF. The presence of PVP in MWCNT hydrophilic membranes allows for the passage of a high water flow compared to those containing GO and MWCNT, due to the interconnected structure, which allows for low selectivity at NaCl. A significant improvement was also observed in carbon-TiO$_2$ and PVP composites. The best permeation was obtained for membrane containing 0.5% GO-TiO$_2$ and PVP (9.6-12.5 L $\cdot$ m^{-2} $\cdot$ h^{-1}). However, the best results were achieved when GO was replaced by the functionalised MWCNT (8,4-20,3 L $\cdot$ m^{-2} $\cdot$ h^{-1}) [305].

Similarly, new nanostructured composite membranes based on polyester staple fibres and various types of carbon nanotubes (single-walled carbon nanotubes – SWCNT and multi-walled carbon nanotubes – MWCNT) were obtained as reinforcing agents. For membrane synthesis, two types of solvents (N-dimethylformamide (DMF) and aniline) were used for polymer powder solubilization. The covalent binding between MWCNT and the polymer matrix has also been studied. For this, mwcnt carbon nanotubes were functionalized with amino acid groups, and PSF was formed. The forsimilation of psyster staple fibres was carried out using the Vilsmeier-Haak method [306]. The analyses carried out showed a significant improvement in the properties of the composite membrane compared to the pure membrane [307].

On the other hand, the influence of series of treatments for the functionalization of CNT, such as cholesterol (octaneamine (OCA) and octadylamine (AOD)) and nitric acid have been studied to improve their stability in three types of solvents (n-vinylpyrrolidone (NMP), trinitrophuran (THF) and DMF). By the solution method, by varying the concentration of CNT in the polyester staple fiber matrix, 4 types of polymer composites (0-5%) were synthesized The analyzes performed showed an improvement in the stability of CNT after the modification processes, with a greater increase in NMP and DMF compared to THF. Both mechanical and thermal tests confirmed the presence of a residual solvent in all samples, resulting in a significant reduction in glass transition temperature (Tg) [308].

Subsequently, symmetrical polymer membranes were obtained and characterized, instead of asymmetric membranes, by the method of solvent evaporation, using polysulfona as a polymer and CNT-amino as additives. Obtaining symmetrical membranes was the result of the presence of CNT. After this, the polymeric membrane was used as a support for the functionalization of CNT with ether crown derivatives [309]. The symmetrical character was given by the chosen synthesis method – evaporation of the solvent at 40°C. Due to the low evaporation rate of the solvent at the formation of the membrane, and also the presence of CNT in the structure of the polymeric film, a symmetrical structure with the same pore diameter was generated on both sides of the membrane.

Later, to eliminate the disadvantage of CNT agglomeration due to the strong Van der Walls interactions between CNT tubes, organic molecules were bound to their surface. New types of PSF, with different structural units in the polymer structure, were used as dispersion media for MWCNT. Based on the analyses, it was observed that the presence of sulfide-type groups in the PSF favors the dispersion of MWCNT in the polymer matrix, due to the donor-acceptor interactions between the sulfide and MWCNT groups of the Π-Π interactions between the aromatic units and the MWCNT. The homogeneous dispersion of MWCNT in the polymer matrix led to an improvement in the mechanical and thermal properties of composite materials, compared to pure polymeric membranes [310].

Similarly, using the solution method, several polyester-based staple fiber composites were synthesized using different types of modified CNT. Hildebrand solubility parameters were used to investigate the potential modification methods applied to increase interface interactions and improve CNT dispersion in the solvent. The TNs tested were: pure, chemically treated with a mixture of acids, physically related to the 1-octylamine surfactant (OCA), functionalized covalently with OCA, pure CNT, treated with acid and subsequently modified with polymethyl methacrylate (PMMA). Studies have shown a substantial change in the length and diameter of the carbon tube for all treatments applied, except that involving the physical adsorption of surfactant to the surface of the CNT. However, of all the types of CNT studied, the lowest degree of leach (3%) and the best mechanical properties resulted for the composite membrane containing CNT functionalized with OCA. The thermogravimetric analysis (TGA) confirmed the presence of a high level of residual solvent for all applied treatments, the concentration of which is influenced by the type of treatment used. The smallest percentage of residual solvent was found in the pure composite containing CNT, due to the presence of pores in the CNT, which helps to remove the solvent [311].

As a result of the variation in the concentration of CNT, by the solution method, new polycrystalline polycrystalline polysulphone (PU)/PSF/CNT membranes were obtained. These composite membranes were characterized morphologically, structurally and thermally, and it was observed that the presence of CNT in the polymer matrix led to an increase in the crystallineness of the materials and their thermostability, compared to pu and PSF films [312].

Subsequently, several composite membranes of the PSF/CNT type were synthesized by the phase inversion method. Before the synthesis of composite membranes, they were doped with silver nanoparticles (Ag-CNT), by wet impregnation to increase the hydrophilic character of CNT. The PSF/Ag-CNT composite membranes showed a slight decrease in water flow, but an increase in stability during compaction. For membranes with an Ag-CNT concentration of 0,2 % in the polymer matrix, the highest flow recovery of approximately 80 % and the smallest total flow loss of 56 % was observed, with an irreversible reduction in R_{ir} resistance = 21 %. [313]

Aromatic electrostatic replacement in the presence of $AlCl_3$ was used for direct coupling to a commercial sample PSF and C60 for the preparation of new C60-polymeric materials. Subsequent studies were based on the hydrophobic filling effect on the phase inversion process, with morphological changes and separation properties demonstrating that a good dispersion of the filler in the polymer matrix induces an increase in the viscosity of the mixture when casting. The covalent interactions between C60 and polymer have been demonstrated by ^{1}H-NMR, FT-IR and UV analysis. At the same time, it was observed that C60 was randomly distributed along the polymeric chain. The presence of C60 in the polymer matrix in concentrations between 0.5 and 3.2% led to high thermal stability and superior optical properties [314].

Last but not least, the new psf/fulerene and PSF functionalized nanoparticles with magnetic nanoparticles have been synthesized with applications in the pre-evaporation of volatile amino acids resulting from the pharmaceutical and paint industry and in the removal of Pb and Hg from wastewater. PSF/C60 type membranes were obtained by the phase inversion process, using chloroform and DMF as solvents. Pre-evaporation tests of the residual aniline solution recorded the best results for C60 membranes, which use chloroform as a solvent. The value of the pre-evaporation flow for PSF/C60 membranes was $9 \cdot 10^{-6}$ g / s $\cdot$ cm^2, greater than that obtained with initial PSF membranes $2.3 \cdot 10^{-6}$ g / s $\cdot$ cm^2. The composite membranes with staple fibers made of polyester / magnetic nanoparticles-ether crown were synthesized by the solvent evaporation method and tested for their retention capacity of Pb and Hg. Test results

showed outstanding performance, these composite membranes being suitable for the processes of decontamination of heavy metal wastewater [315, 316].

The interesting combination of polymer properties such as low density, flexibility, low cost, chemical resistance and simple methods of handling and processing made them easy to choose [317-320]. Indeed, polymer-based materials are widely used for a number of applications, and in recent years a significant amount of studies have been devoted to improving the existing properties of polymers [321-334]. The use of nanomaterials in combination polymers offers a number of applications in the fields of biomedicine (as artificial kidney [335], artificial liver [336], artificial pancreas [337], artificial lungs [338], diet [339]) and controlled release of medicines [340-343]. Among the various such functionalized materials widely used today, both in industrial and laboratory practice, composite membranes have evolved as promising new materials, since they offer a wide spectrum of applications in terms of active participation in the separation process. In membrane materials, the use of fillers provides two main advantages (i) increases mechanical strength and (ii) improves the separation properties of the membrane by modifying porosity or the presence of polymers, significantly improving their efficiency for different applications [344-346]. For example, hemodialysis membranes based on polysulfide and covalently linked carbon nanotubes to the polymer showed high performance for separation, but production costs, operational and manufacturing risks limit their extensive applications [347].

Various composite cellulose acetate-based membranes have been reported with different fillers, such as heavy metal retention zeolite [348], silica nanowires for reverse osmosis [349], materials with photoluminescence properties [350], gas separations [351], hydroxyapatite to improve osseointegration processes [352,353] or TiO_2 nanoparticles [354]. Composite membranes of cellulose acetate with polyvinyl alcohol [355], polyurethane [356], poly (hidorxibutirate) [357], polyester [358], polyamide [359] and polyaniline [360] have been studied. Transparent membranes for ultraviolet radiation applied in the manufacture of photovoltaic devices were obtained from cellulose acetate and graphene oxide [361]. Also, graphene oxide has been used to improve the bovine serum albumin retention of cellulose acetate membranes [362]. It has been shown that at a concentration of 1% graphene oxide in the polymeric membrane, the degree of retention increased from 78% to 99%. This was explained by the modification of the pores of the membrane due to a crosslinking effect between the polymer and the filler (soft chemical interactions that stabilize the structure of the membrane). Increased attention was paid to cellulose acetate composite membranes with carbon nanotubes, due to their remarkable properties that improve the performance of

composite membranes (high degree of retention, improved mechanical or thermal properties). The retention of NaCl increases from 64% to 96%, the improvement being explained by the modification of the membrane pores and also by the adsorption of salts at the surface of carbon nanotubes in the membrane structure [363].

The use of carbon nanotubes as fillers in the field of polymer membranes for water purification is suitable for salt retention, since the large area of free nanotubes in the pores of the membrane shows a high adsorption capacity. The electrons located at the surface of these species interact with the cation improving separation. The presence of functionalized carbon nanotubes with carboxyl groups and sulfonic groups in the cellulose acetate membrane has been shown to improve the retention capacity of the membrane [364]. The membranes tested for reverse osmosis processes showed a lower flow, of 57%, with alginate solutions due to the repulsive forces of alginate compared to the original cellulose acetate membrane.

Recently, a new class of nanowires with 2D-1D interconnected structure (silica gel/SiNWs nanowires) has been discovered that have the potential to overcome the disadvantages induced by carbon nanotubes (NTBs) and even replace NTTs in certain particular applications. SiNWs generally consist of particles with dimensions over 1 μm long and about 20 nm in diameter. The entire structure of the SiNW consists of the 2D-1D interconnected architecture [365, 366]. Silica nanowires can be obtained on 2D layers of clay particles, resulting in hybrid particles with a large surface area. The final yield of the SiNW product was over 78%. Based on the reaction yield and sodium tetraortosilicate/montmorillonite ratio, SiNW consist of more than 75% 1D segments (nanowires) and slightly less than 25% 2D segments (mineral clay layers). The synthesis of such nanowires can be carried out even at room temperature, without the use of additional agents. Despite the well-established synthesis and the reaction mechanism [366], so far only limited applications of such nanowires have been available. The ability of SiNW to form large supramolecular structures based on amino acid salts has been reported. These types of nanowire-based fillers have the potential to bring more advantages in terms of separation performance, costs, mechanical properties and biocompatibility [367] for more economical polymers (such as cellulose-based) known for the membrane manufacturing process and other applications [368].

Among the different membranes used in biomedical applications, cellulose-based membranes offer a number of advantages, in particular in terms of biodegradability and environmental protection [369-371]. Cellulose or cellulose (CA) acetate-based membranes were used in hemodialysis and in the production of controlled release patches of the active

substance [372]. In this context, the current study provides the viability of the successful use of Pure Silica Nanowires (without 2D units) as reinforcing agents in polymeric materials with low mechanical properties, such as cellulose or cellulose acetate membranes. The nanocomposite polymeric material would bring new cost and versatility-related benefits, already known for obtaining polymeric membranes. Therefore, the current study provides insight into the use of SiNWs in CA membranes for biomedical applications. Different concentrations of SiNW in CA were studied, and composite membranes were well characterized in terms of mechanical properties, thermal stability, wetting, hydrodynamic characteristics and retention of bovine serum albumin. In addition, cytotoxicity studies were also conducted on nanocomposite membranes to assess the occurrence of cytotoxic effect in the presence of SiNW, as the first evidence on biocompatibility. This subsequent problem has a double significance for future biomedical applications [373,374].

All chemicals were used without any further purification. Sodium montmorillonite was obtained from southern clay, Inc., tetraortosilicate, and N,N′- dimethyl formamide (DMF), dimethyltiazole, 5-diphenyltetrazolium bromide and 2-propanol were purchased from Sigma Aldrich. Ethanol and ammonia solution were obtained from Chimopar, while bovine serum albumin (BSA) and cellulose acetate were obtained from Merck.

In the current study, SiNWs were synthesized using the sol-gel method reported in the literature [375]. In short, a typical reaction mixture consisting of: a solution of 400 ml of water with a concentration of 1% dispersed sodium montmorillonite, 38 g of tetraortosilicate, 600 ml of ethanol and 80 ml of 25% ammonia solution was obtained. The reaction was performed at 75°C for 7 hours at 900 rpm magnetic stirring. After the completion of the reaction, the final product was left for several days for drying at room temperature. Subsequently, the final powder was washed several times with deionized water and separated by centrifugation. The powder obtained by SiNW consists of amorphous silica nanowires (1D), with an average diameter of about 20 nm and a length of over 1 μm and layers of mineral clay (2D) [376].

To obtain the nanocomposed membranes, a 12 % cellulose acetate solution in DMF was originally prepared by dissolving for 1 hour under intense stirring. The polymer solution was left for 24 hours to degass to prevent the formation of voids in the membrane at the later stage. SiNWs were subsequently dispersed into the cellulose acetate solution, in an ultrasonic bath, at different concentrations (1.25, 2.5 and 5%) at the CA polymer. Ca nanocomposite membranes, with a thickness of 300 μm, were then obtained by pouring the polymeric solution onto a glass substrate, followed by dipping it in a coagulation bath with deionized water. After

pouring, the membranes were washed with ethanol and water and kept in deionized water to prevent the growth of microorganisms on the surface.

The morphology of composite membranes was observed by smallelectronic scattering roscopy, with SEM images showing a decrease in pore size in the presence of SiNW, compared to the original CA membrane.

The effect turned out to be even more noticeable on the surface of the porous membrane. The pores of the active surface of the membranes treated by CA were barely visible, since the initially large interconnected pores of wet membranes shrink during drying (treatment required before SEM analyzes). As a result, the contraction of the CA membrane, following drying, causes the presence of spherical pores. Upon the addition of SiNW, the actual shape of the membrane pores began to be visible in the SEM images. On the porous surface, the diameter of the pores turned out to be about 10 times smaller for the siNW membranes, compared to the original CA membrane. SEM images have also suggested a certain increase in pore density with the presence of SiNW, but this will be clarified by the next analysis carried out, since the SEM analysis shows a high limitation when the details are extrapolated to the entire macroscopic material.

The pore size distribution on the porous surface of the membranes varies from 40 μm, for the cellulose acetate membrane, to 30 μm, for the CA membrane with a concentration of 1.25% SiNW, to 15-20 μm, for the CA membrane with a concentration of 2.5% SiNW, respectively to 5-10 μm, for the CA membrane with a concentration of 5% SiNW. The pores of the membrane-active surface have a diameter of about 100 nm, for the cellulose acetate membrane, being extremely difficult to detect for composite membranes (inset).

At the synthesis of polymeric membranes by phase inversion, the solvent in the coagulation bath extracts the solvent from the polymeric membrane. The distribution of pore size depends on various factors, such as: extraction balance between solvent and non-solvent, polymer solution or non-solvent temperature. A high miscibility between the polymeric solvent and the non-solvent will increase the speed of the non-solvent through the polymeric membrane, resulting in the formation of smaller pores and the formation of a thicker layer of membrane. In the case of our synthesis method, the polymeric solvent was represented by DMF and the non-solvent was represented by water. The presence of silica nanowires (with their hydrophilic character) will increase the speed of water at the synthesis of the membrane through the polymeric membrane, which will lead to the formation of smaller pores and a thinning of the membranes.

This can also be observed by measuring the thickness of membranes in cross-section. For CA membranes, the measured thickness was between 71.7-74.2 μm, for CA membranes with a concentration of 1.25% of SiNW was between 49.7-55.3 μm, for CA membranes with a concentration of 2.5% of SiNW it was between 41.3-41.7 μm, respectively, of 38.5-39.3 μm for CA membranes with a concentration of 5% of SiNW. With the increase in the concentration of silica nanowires, the thickness of the membrane decreases.

Studies on awater contact cannonball, determined on dry membranes, have shown a decrease in the contact angle. These results were largely in line with sem observations, as pore conservation is more pronounced in the presence of SiNW. Preservation of pores in the dry membrane, favored the sorption of water on the surface of the membrane. The increase in pore density, confirmed by SEM analyses, influenced the surface properties of the membrane and a significant decrease in the contact angle for composite membranes was observed [377]. The initial CA membrane showed a contact angle around 65°, with a difference of almost 10° between the right and left angles. In the case of membranes with SiNW, the contact angle values decreased due to the more hydrophilic dupra facets (contact angle of 45° and 37° – for concentrations of 1.25; 2.5 and 5% of SiNW). In addition, the dynamics of adsorption of droplets depends on the concentrations of SiNWs. A drop of water of 6.5 μL was adsorbed in about 7.5 min. for the initial CA membrane, while for a concentration of 5% of SiNW, less than 2 min. were required. The difference between the angle of left and right contact can be explained by sliding the droplets on the rough surface of the membrane induced by large pores. The effect of siNWs on the decrease in size and distribution of pores has been confirmed by the small difference between the right and left contact angle of up to 1°. This behavior confirmed the compact morphology observed in SEM images for nanocomposed membranes. The properties of the surface are confirmed by improving the permeation properties of water and indirectly by increasing the density of pores.

MWCO is a specific parameter for polymer membranes indicating the minimum molecular weight of separated solutes at a degree of rejection of 90% [378]. For ultrafiltration membranes, THE MWCO values can be in a wide range, between 10000 and 300000 Da [379]. For the synthesized membranes, the MWCO determined was set at 50 kDa for the initial CA membrane, 32 kDa for CA membranes with a concentration of 1.25% of SiNW, 31 kDa for CA membranes with a concentration of 2.5% of SiNW and 29 kDa for CA membranes with a concentration of 5% of SiNW. These values are largely in line with the results obtained from the retention of BSA and are also correlated with observations from the SEM analysis and water flows.

Water flows were determined at different temperatures for composite membranes with the highest concentration of SiNW (5% at CA content). By increasing the temperature of the feed solution, the flow through the pores of the membrane should increase due to the expansion of the pores. This rule applies to all cellulose acetate membranes (increased flow of water from 9800 L/m^{2}h to 20 °C to 12000 L/m^{2}h to 60 °C). When nanocomposite membranes were analyzed, pore expansion was considerably reduced (from 9100 L / m^{2}h to 20 °C to only 9300 L/m^{2}h at 60 ° C). This behavior indicated a significant increase in the stability of the pores, attributed to the presence of SiNW. The greater stability to temperature changes in the water, compared to the initial CA membranes, can be explained by the non-covalent interaction, but on a large surface area, between SiNW and CA.

The porous morphology of SiNW presents a large interface, rich in hydroxyl functional groups, that are capable of interacting with the polar molecular chain of CA. Interaction has also been confirmed by subsequent analyses. For use in biomedical applications, stability at temperatures higher than 40°C is notrequired, but in membrane processes such as hemodialysis, for blood filtration, high stability of the membrane structure is required. Due to the continuous recirculation of biological fluids for more than 4 hours, it is important that the membrane structure is stable, in order to maintain all the parameters of the constant separation process.

BSA retention studies have also been conducted on synthesized membranes. BSA retentions were carried out using a protein synthetic solution of 10^{-5} M in 500 mL deionized water, the retention determination being carried out by UV-VIS analysis [380]. After continuous recirculation for 120 min, retention for the cellulose acetate membrane was 62%. In the case of composite membranes with a concentration of 5% of SiNW, it was found that the retention of BSA increased to 94%. The large difference between BSA retention for the initial CA membranes and the membranes containing SiNW also indicates an interaction between nanowires and proteins, since such a difference can not only be explained by a decrease in the porosity of the membrane. The experimental data obtained are largely in line with those previously reported, indicating the ability of silica nanowires to interact with proteins and metalloproteins [381]. This property of silica nanowires makes these synthesized membranes to be used in different types of biological separations for: proteins, amino acids and peptides or biological fluids or in different types of purification processes such as hemodialysis.

The study of thermal properties revealed several interesting aspects about the physical interaction between fillers (SiNW) and the polymeric matrix (CA). The associated water losses have not been influenced much by the content of SiNW and this is in line with previous

discussions on the adsorption of water, mainly in the pores of the membrane. Thermo-oxidative degradation (in air) presented two stages, both depending on the content of SiNW. The second stage of thermo-oxidative degradation seems to reveal a more compact arrangement of the cellulose acetate matrix in the vicinity of the filler forming an interphase. The total residue at 700 °C increases in direct proportion to the SiNW content. General TGA measurements have shown a clear stabilization of CA membranes due to the presence of SiNW structures. This was quite predictable, since both units of montmorillonite contained in SiNW were described in the literature as beneficial for stabilizing cellulose acetate membranes in thermo-oxidative degradation. The mechanism is based on the steric forebearing effect induced by clay layers for volatile degradation products, in the diffusion process from ca membranes.

The physical interaction between the SiNW filler and the CA membrane observed in the TGA analyses has been further confirmed by the FT-IR spectra. The FT-IR spectra showed a decrease in the intensity of the peacks for the hydroxyl groups in the initial CA membrane, with the increase in the SiNW content. The tape from 3450 cm^{-1} decreased in intensity and its position was displaced by 30 cm^{-1} when a concentration of 1.25% of SiNW was used, and then remained unchanged, regardless of the SiNW content. The band modification clearly indicates an interaction with "mobile" and adsorbed water, without significantly affecting the "bound" water, from ca membranes with SiNW. Vibrations from 1638 cm^{-1} decrease in intensity with increasing the concentration of SiNW, but the frequency remains unchanged.

The dispression of SiNW in ca membranes led to an increase in rigidity and strength properties, compared to the initial cellulose acetate membranes.

For nanocomposed membranes with a concentration of 1.25% of SiNW, the standard deviation was greater than in the case of nanocomposite membranes with a concentration of 2.5% of SiNW. This behavior can be explained by a less uniform distribution of the low filler content of SiNW (1.25%) in the matrix of the cellulose acetate membrane. For a higher concentration of SiNW (5%), the standard deviation increases even more (10%), which indicates the agglomeration of the siNW filler particles in the matrix of the cellulose acetate membrane. The optimum dispersion of SiNW in the case of the membrane with a concentration of 2.5% silica nanowires was also confirmed by the results of the TGA, where the greatest thermal stability was achieved. Even at lower concentrations of SiNW (1.25%), young's module growth was substantial, followed by a moderate increase, directly proportional to the subsequent increase in SiNW concentration. The tensile strength decreases in direct proportion to the decrease in the concentration of SiNW, which indicates a clear reinforcing effect and an interaction between the fill material (SiNW) and the cellulose acetate (CA) membrane.

The membrane with the highest content of silica nanowires separated 75% Gd(III), compared to 58% for the initial CA membrane (from the 1g/L feed solution), this being due more to the crosslinking effect of the membrane and less to the interaction that can occur between the silica nanowire filler and Gd(III).

The use of SiNW as a filler brings several advantages in terms of pore formation and their stability, due to the interface interactions with the polymeric matrix, which significantly affects the formation of pores.

The synthesis of this type of membranes is based on cellulose acetate (CA) as matrix and SiNWs as fillers.

The future perspectives for this PhD thesis are based on the evaluation of the possibility of developing the results obtained so far for the implementation on an industrial scale, with the aim of streamlining moderator purification system from the point of view of: economic, handling and demanding conditions of resin retention in ion exchange columns (tightness of the columns), the minimisation of the amount of waste resulting from the resin replacement process, the decrease in the consumption of heavy water used to deuterize a fresh resin introduced into the column, of eliminating the dedeutery process after depletion of the resin and minimizing the associated radiological dangers, of minimizing the moderator heavy water purification plant.