Chapter 4

Sustainable Membranes and its Applications

L. Oliveira¹, A.N. Módenes¹, C.C. Triques¹, M.L. Fiorese¹, L.C. Silva², V. Slusarski-Santana^{3*},
L.D. Fiorentin-Ferrari³

¹Postgraduate Program in Chemical Engineering, West Paraná State University, Rua da Faculdade 645, Toledo, 85903-000 PR, Brazil

²Postgraduate Program in Chemical, West Paraná State University, Rua da Faculdade 645, Toledo, 85903-000 PR, Brazil

³Graduation Program in Chemical Engineering, West Paraná State University, Rua da Faculdade 645, Toledo, 85903-000 PR, Brazil

veronice.santana@unioeste.br

Abstract

The utilization of sustainable and high-performance technologies is a growing tendency in industrial processes. The membrane separation process is a clean technology alternative that can be used to separate, concentrate, and/or purify substances. But there is still a great interest in turning this process increasingly sustainable by the structural modification of the membranes using biopolymers and green solvents, and the functionalization with organic and inorganic materials, also improving their performance and anti-fouling characteristics. Thus, this review chapter brings the main concepts about membranes and their main structural modifications to obtain a process that meets the concepts involved in Green Technology.

Keywords

Membrane Separation Process, Polymers, Biopolymers, Green Solvents, Membrane Functionalization, Green Technology

Contents

Sustainable Membranes and its Applications	111
1. Introduction.....	112
2. Membrane separation processes	114

2.1	Morphological classification of the membranes.....	114
2.2	Concentration polarization and fouling	118
3	Fabrication of sustainable membranes.....	120
3.1	Biopolymers, green solvents, and functionalization	120
3.2	Applications of the functionalized membranes	125
4.	Final Considerations.....	132
	References	133

1. Introduction

The membrane separation process is used in food, pharmaceutical, biotechnology, steel, paper, cellulose, and petrochemical industries as a technique to separate, concentrate, and/or purify, and also to decontaminate wastewater, especially those containing emerging pollutants such as antibiotics and hormones, dyes, heavy metals, persistent organic pollutants, in addition to water desalination [1-14].

Due to the operational characteristics, mainly the ones that include low energy consumption during the separation, concentration and/or purification of substances, high solute rejection capacity, no generation of secondary pollutants, and capacity of reusability for multiple cycles, the membrane separation process is included in the concepts of sustainable productive processes defined as Green Technology. In Green Technology, the utilization of ecologically correct alternatives is essential during the transformation of the raw material into a product, with control of the pollution generated and without causing damages to the environment, as is the case of the membrane separation process [11, 15-30, 31].

The membranes used industrially are, mostly, fabricated with ceramic materials that possess the capacity to operate in extreme conditions of pH and temperature, besides having a high lifespan. However, the ceramic membranes possess a high fabrication cost due to the raw material used in their preparation [32-34]. Due to the cost, the ceramic materials used in the membranes are being substituted by natural or synthetic polymeric materials. Depending on the structural characteristics of the polymer macromolecule, the membrane fabricated will present equal or higher mechanical, thermal, and chemical resistance than ceramic membranes. Besides, structural modification in the polymers and mixture of polymeric materials can produce membranes with higher fouling resistance [5, 7, 13, 14, 27].

The polymeric membranes currently commercialized are fabricated with synthetic polymers, mainly from petroleum, and thus, non-biodegradable. The polymeric residues from the processes of fabrication and utilization of the membranes contribute to the increase of residual water pollution, mainly by microplastics [37, 38]. Besides, during the fabrication of the membranes, reprotoxic organic solvents are used, which are harmful to the environment. The substitution of synthetic polymers by biopolymers, such as cellulose acetate and chitosan, which are natural, biodegradable polymers from renewable sources, widely available and at low cost, become a promising alternative. The utilization of green solvents, such as water, ethyl lactate, ionic liquids, and supercritical CO₂ is another possibility to replace commonly used solvents for fabrication membranes [27, 28, 37-39].

Another problem associated with the filtration process with ceramic or polymeric membranes is the fouling development from the accumulation of organic, inorganic, and biological macromolecules that can occur in both the surface and in the membrane pores. Fouling causes a reduction in the selectivity and the permeate flow, and consequently the decrease of the membrane lifespan [9, 40-42, 49]. Several factors affect the fouling development during filtration, however, the superficial characteristics of the membrane, such as high hydrophilicity and low roughness, can contribute to reducing the deposition of foulants agents [5, 40, 44-47].

The morphological and structural characteristics of the membrane can be changed during its fabrication process by its functionalization with materials and/or nanomaterials that present desirable characteristics to the membrane, such as, high surface area, hydrophilicity and mechanical, thermal and physical resistance. The incorporation of organic or inorganic nanomaterials or materials can be performed in the solution or the membrane surface during the fabrication. Due to the physical and chemical characteristics of the incorporated material or nanomaterial, functionalized membranes can present adsorptive, photocatalytic, catalytic, antioxidant, and antimicrobial characteristics. Still, the structural modification by functionalization allows the obtention of membranes with anti-fouling property [19, 48- 55].

In general, the structural modification during membrane fabrication with ceramic or polymeric biomaterials and solvents that are less pollutant, as well as the functionalization with organic or inorganic materials, allow that the membrane separation process meets the sustainable principles becoming a technique closer to the concepts of Green Technology [26, 28, 48, 56]. Thus, this review chapter aims to present general aspects of the conventional membrane separation process and ways of turning the process more sustainable by using biopolymers and green solvents and functionalizing the membranes with organic and inorganic additives. This structural modification, besides keeping the

industrially desired selectivity, influences the anti-fouling properties, promoting an increase in the membrane lifespan.

2. Membrane separation processes

2.1 Morphological classification of the membranes

The membrane separation process is known since 1748 when Abbé Nolet observed that water diffused through a semi-permeable membrane from a dilute solution to a more concentrated one. However, between the 18th and 19th centuries, membranes had no industrial and commercial use and were used exclusively for laboratory applications. Natural membranes were made from the intestine and stomach of animals, or bladders from pigs, cattle, or fish [57-60]. However, a great advance in the membrane separation process occurred in the early 1960s, when Loeb and Sourirajan performed the annealing of commercial acetate membranes and obtained anisotropic reverse osmosis membranes with smaller pore sizes and ten times greater flux than previously existing membranes. In this period, the utilization of reverse osmosis membranes to desalinate water started [2, 18, 61]. After the discovery of Loeb and Sourirajan, many others happened in the following years, such as the fabrication of membranes using ceramic and polymeric materials, which is performed up to now [1-3].

The membrane filtration can be defined as the separation of two or more components through a semi-permeable barrier, based on the particle size difference, in which the permeate is what passes through the membrane, and what is retained in the membrane is the retentate [51, 60, 61]. The membrane separation process is commercially attractive by its technical and economic characteristics, being mainly based on the sieving and electrostatics principles [18]. Often, the membranes are considered a more efficient technology than conventional methods of gravity separation, chemical precipitation, adsorption, and ion exchange [11, 60, 62].

The conventional separation methods that are consolidated in several industrial processes possess unfavorable characteristics, especially concerning the utilization of large physical areas, the necessity of toxic compounds, and generation of secondary pollutants that need adequate treatment [11, 18, 60, 62, 63]. The chemical precipitation method, for example, requires the utilization of a large quantity of chemical products to adjust the pH so that the foulant precipitate, while the gravity separation needs a wide physical area and considerable time to separate the foulant agent. Adsorption is presented as the more viable alternative among the conventional and consolidated techniques, due to the high removal capacity of several types of solutes/pollutants. However, adsorption has as its challenge, be able to reuse of the adsorbent for several cycles keeping efficiency [11, 18, 63]. Thus,

when the characteristics of the membrane separation process are evaluated and compared to the conventional and consolidated methods used up to now, membranes are verified to be able to be used in separation, concentration, and/or purification of several types of substances and several industries.

Membranes can be classified concerning their origin, morphology, structure, fabrication method, and material used [60]. The first classification refers to the nature or origin, which can be biological or synthetic in the liquid or solid form, according to Fig. 1 [40]. Dense and porous polymeric synthetic membranes can be classified into symmetrical and asymmetrical according to the morphology and pore distribution [40, 59, 64]. According to the distribution and size of the pores, dense and porous membranes can be isotropic symmetric when the pores present similar size, and anisotropic asymmetric when the structure is not uniform with pores distributed in different sizes in the membrane [2, 62].

In the dense morphology, the pores are not visible and the solute moves by diffusion through the membrane. The separation of the solutes from a solution is determined by the diffusivity and solubility in the membrane material, thus being able to perform the separation of particles with similar sizes [59]. The microporous morphology aims to reject all the solutes with a size higher than the pore sizes of the membrane. Thus, solutes or particles with similar pore sizes to the membrane can cause the pore blocking, clogging it up, and decreasing the filtration process performance [2, 61].

Figure 1 Classification of the membranes concerning origin, morphology, and structure.
Source: author

Asymmetric membranes have a structure consisting of a very thin polymer top layer (0.1 to 1 μm) supported by a highly porous 100 to 200 μm sublayer that acts only as a support. Thus, the pore size and the material nature of the top layer are responsible for the membrane separation characteristics, while the permeate flow is determined by the thickness and sublayer of the membrane [40, 60, 64]. Thus, asymmetrical membranes possess high flows when compared to the symmetrical ones, and present lower fouling, because the highest

solute rejection happens in the membrane surface, making the internal structure of the pores present low clogging [61,65].

One factor that influences the morphology and structure of the membrane, polymeric or ceramic, is the fabrication technique used. For symmetrical polymeric membranes, the most used methods are sintering, stretching, and track-etching, while the asymmetrical membranes are produced mainly by the phase inversion method from a sole polymer or by the blend of polymeric materials [19, 60, 65].

The phase inversion method basically consists in dissolving a polymer into an adequate solvent and transforming the polymeric solution into a liquid state to a solid state, thus forming the membrane [66, 67]. For such transformation, after the polymer dissolution, the dissolved polymeric solution is spread under inert support as a thin liquid film and the phase inversion of the liquid film can be induced by the contact with a non-solvent or vapor, thermal contact, or solvent evaporation [19, 68]. During the phase inversion, the highest polymer concentration forms the membrane surface with lower pores, while the pores in the sublayer of the membrane are constituted of lower polymeric concentration [40, 64, 68, 69]. Due to the simplicity of the method and the fabrication cost, the phase separation induced by a non-solvent, also known as phase inversion via immersion precipitation, is the most used and reported in the literature fabrication method of asymmetrical membranes [19, 49, 67, 70, 71].

To improve the membrane performance concerning the permeate flow and selectivity, several parameters must be controlled, among them, the polymeric concentration, relative humidity, time of solvent evaporation before the immersion, temperature, and composition of the immersion bath [69]. The choice of parameters that will be controlled will directly influence the final morphology of the membranes, since the process of fabrication must be performed in a way that the membranes are produced with adequate characteristics to the kind of process (separation, purification, or concentration) that they will be industrially subjected. Thus, the property of solute transport through solid membranes can be performed from the application of concentration, pressure, temperature, or electric potential gradient [40, 64, 72].

In general, the lower the pore sizes, the higher the hydrodynamic resistance and the higher the necessary driving force so that permeate flow is not reduced. Thus, the pressure-driven membranes are classified into microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Table 1 shows the main characteristics of these membranes [2, 40, 61, 73].

Table 1 Characteristics of the pressure-driven membranes according to the pores' sizes and rejected material

Membrane	Pressure [bar]	Pore Size [μm]	Retentate
Microfiltration	0.1 - 2	Macroporous pore 0.1 - 10	Bacteria, viruses, pathogens, and suspended particles
Ultrafiltration	1 - 5	Mesoporous pore 0.001 - 0.1	Macromolecules
Nanofiltration	5 - 20	Microporous pore 0.001 - 0.01	Sugars and divalent ions
Reverse Osmosis	10 - 100	Non-porous 0.0001 - 0.001	Monovalent ions

Source: author

Microfiltration membranes are commonly applied in the pharmaceutical, food and beverage, and semiconductor industries to remove bacteria, viruses, pathogens, in addition to the filtration of suspended particles, proteins, and emulsion separation. The microfiltration membranes use the principle of physical separation to reject particles with sizes higher than the range between 0.1 to 10 μm . Compared to the other kinds, the microfiltration membrane presents more open pores and consequently lower operating pressure than the other classifications [3, 31, 59, 60, 74]. The separation of solutes in the ultrafiltration membrane occurs by the pore size difference. This kind of membrane presents high product yield, relative easiness of scale-up, cleaning and equipment sanitation easiness, being mainly applied in the biotechnological and food area, where they are largely used to purify, concentrate, and fractionate solutes such as colloids, microorganisms, proteins, and lipids [3, 51, 75, 76].

The nanofiltration membrane possesses pore sizes between 0.001 and 0.01 μm , being responsible for the separation of particles with molecular weight cut from 200 to 1000 Dalton. Both the nanofiltration and the reverse osmosis membranes require high pressure during the filtration and present a high solute rejection rate, despite the nanofiltration membrane presenting low rejection of monovalent ions, such as chlorides. Due to the high rejection rate of divalent ions and sugars, the nanofiltration membranes have several applications, being the main ones in the potable water, sewage treatment, pharmaceutical, biotech, and food engineering segments. While the reverse osmosis membranes possess pore size between 0.0001 and 0.001 μm and can be applied in the

concentration of a feed flow, due to the rejection of water molecules, or even produce ultra-pure water in the permeate since it possesses a solute rejection higher than 99%. Ultrafiltration membranes are considered porous, while reverse osmosis ones are dense [51, 60, 67, 75, 77-81].

Another factor that influences the performance of the pressure-driven membranes (Table 1) is the kind of material used for the fabrication. The characteristics of the ceramic or polymeric material directly influence the obtention of a membrane that presents a high lifespan, besides thermal, mechanical, and physical stability [2]. The organic membranes are usually made of polymers such as polysulfone, polyvinylidene fluoride, polyethersulfone, polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene, polypropylene, polyamide, chitosan, cellulose acetate, and cellulose [3, 19, 31, 75]. In the fabrication of inorganic membranes are commonly used materials ceramics, zeolites, carbon, glass, or metal [32, 60, 82].

When compared to polymeric membranes, the inorganic membranes possess higher mechanical resistance, thermal, and chemical stability, being thus able to operate in extreme conditions. Besides, ceramic membranes possess easier cleaning and longer lifespan, being able to be used industrially for more than 8 years, while the polymeric membranes need to be replaced every 2 years [2, 32-34]. However, the inorganic membranes do not present good performance during the microfiltration and ultrafiltration processes, besides being too fragile and being easily damaged by improper vibration or fall. Besides, the biggest disadvantage of inorganic membranes is the high initial investment cost [62, 83], while the polymeric membranes are widely used in industrial processes, due to their low cost, easiness of fabrication, and they are available at a wide range of pore sizes [60, 62]. However, a great limitation in the use and commercialization of polymeric membranes occurs due to the fouling development [19, 84, 85].

2.2 Concentration polarization and fouling

Fouling can be defined as the accumulation of particles, colloids, salts, and macromolecules such as proteins and polysaccharides on the membrane surface, inside and/or in the pore walls. The deposition of macromolecules in the membrane surface begins in the first minutes of filtration and over time it causes an additional resistance to mass transfer, causing the phenomenon known as concentration polarization [40,59]. The main consequence of concentration polarization is the drop in permeate flow. Especially in porous membranes, the continuous drop of the permeate flow is commonly observed during the filtration, with a decrease in the solute rejection. At this moment, another phenomenon known as fouling is developed, which is responsible for the lifespan decrease of the

membranes, increasing operating costs of the membrane separation process [19, 31, 51, 86, 87].

Fouling can be reversible when the solutes are retained in the membrane surface forming a gel-cake layer, and irreversible when the membrane pores become obstructed by the solutes [88, 89]. The factors that influence the most in the fouling are the flow velocity, feed composition, concentration of the main constituents, transmembrane pressure, process temperature, feed pH, size and shape of the fouling material, besides the membrane properties such as hydrophilicity/hydrophobicity, roughness, size, and type of pores [31, 89]. Another factor that influences fouling development is the kind of filtration used, dead-end or cross-flow filtration. In the cross-flow kind of filtration, the flow parallel to the membrane surface limits the accumulation of retained material, delaying the development of concentration polarization and fouling [40]. Fouling can occur from the clogging by organic, inorganic, colloidal, and biofouling substances (Fig. 2) [31, 84, 89-93].

Figure 2 Types of foulants that can occur on the membrane during dead-end or cross-flow filtration. Source: author

With the development of fouling and consequent selectivity loss, after a certain filtration time, it is necessary to stop the process and perform a membrane cleaning. This cleaning can be performed physically, chemically, or by backwash, enabling to remove especially the reversible incrustations. The cleaning inefficiency causes a loss in the membrane performance, decreasing the lifespan and leading to a limited condition in which the membrane needs to be discarded. Besides, to perform the cleaning, the membrane needs to

possess mechanical and chemical resistance, and tolerance to chlorine, and different pH ranges [2, 19, 31, 40, 94, 95]. Thus, the choice of the material and technique used to fabricate the membrane together with the knowledge of the incrustation mechanism and kind, as well as the optimization of several cleaning cycles with increase of the lifespan are important topics to still be studied and developed to improve the performance of the membrane separation process.

3 Fabrication of sustainable membranes

3.1 Biopolymers, green solvents, and functionalization

Currently, there is a great search for sustainability in industrial processes due to the accentuated growth of chemical industries, and it is undeniable that the environment has been suffering aggression by this sector. In addition, the requirements from society and environmental protection agencies with their respective legislation have been growing. Thus, the improvement of conventional industrial production processes with green and sustainable strategies, maintaining the quality and productivity required by the consumer market is essential [21, 26, 27, 39, 96-100].

In general, the membrane separation process presents as its main advantages: mild operating conditions with low energy consumption, without the use of additives to promote the separation, concentration and/or purification, operating flexibility, combination with other techniques causing a reduction in the industrial process stages, easiness of scale-up, lower residues generation, and great selectivity during separation, which can occur by the molecular size, or by the physicochemical behavior of the compounds involved. These characteristics make the membrane separation process able to be included in the current concepts of sustainable processes that combine care for the environment and maintenance of productivity. However, much still can be done and improved concerning the processing conditions of the membrane separation process, as well as structural modifications in the membranes to make them more sustainable [15, 16, 40, 101-104].

Normally, membranes are considered sustainable when they use renewable and clean sources in their fabrication, such as the biopolymers and green solvents, or even, when a morphological modification based on synthetic polymers or organic and inorganic additives is performed to increase their performance, anti-fouling properties, and lifespan of the membranes, and consequently, the membrane separation process [10, 22, 28, 36, 37, 41, 105-107]. Among this sustainable tendency, a problem found in the membrane is the polymers used for its fabrication. Polymers are predominantly synthetic, formed by non-biodegradable hydrocarbons, resistant to chemical and biological attack, ensuring longevity, and other properties maintained for long periods [35, 36]. In this context, the

environmental impact caused by the use of synthetic materials in the form of plastics has stimulated the development of membranes from biodegradable biopolymers, produced from raw materials of renewable sources, such as corn, sugar cane, cellulose, and chitin [39,108].

Among the biopolymers, the polysaccharides cellulose and chitin, which are the most abundant natural polymers found in nature, have been the aim of several studies in the last years [22, 37-39, 105, 108-112]. Cellulose is a renewable polymer available in abundant quantity, biodegradable, with low cost, being, thus, another ecologically correct option to be used in the membranes' fabrication [37, 38, 113]. Through the deacetylation of chitin, chitosan is obtained, a biorenewable chemical product that is low-cost, with good stability characteristics, antibacterial activity, chelating properties, hydrophilicity, water solubility (at acidic pH), and is also biocompatible, biodegradable, and non-toxic, contributing to a cleaner and more environmentally correct fabrication process [15, 39, 114-116]. Chitosan can be used in the modification and development of membranes with higher hydrophilicity and performance for the reverse osmosis, ultrafiltration, and nanofiltration processes. Membranes based on chitosan have good separation efficiency, high adsorption capacity, fast kinetics, and present reuse capacity for several cycles, besides anti-fouling characteristics. These features enable chitosan membranes to be used mainly in the treatment of water and effluents containing heavy metals and dyes [114, 117-125].

When the use of synthetic and non-biodegradable polymers is inevitable, solvents less harmful to the environment can be used in an attempt to make the membrane with more sustainable characteristics. Usually, the fabrication of polymeric membranes is based on the phase separation induced by a non-solvent, which used a great quantity of reprotoxic organic solvents such as N,N-dimethylformamide, N-Methyl-2-pyrrolidone, and N,N-dimethylacetamide [126, 127]. In the literature, studies that use green solvents such as ethyl lactate, ionic liquids, supercritical CO₂, and even water are found [27, 28, 106, 126]. Besides, studies point that the membrane fabrication processes that performed the complete substitution of toxic solvents by more ecological solvents reached performances comparable to the ones produced by the classical approach [26, 28, 106].

In order to enable solvent substitution, modifications in the polymer dissolution need to be performed. For the separation of the aqueous phase without the utilization of organic solvents, three alternatives are mentioned in the literature. In the first one, the weak pH-responsive polyelectrolyte in its charged state is dissolved in water and then precipitated using a pH interrupter [27, 100]. In the second alternative, two polyelectrolytes, one weak and one strong with opposed charges, are mixed in a pH, where the weak polyelectrolyte is discharged, and then, a change in the pH induces the phase separation, due to the complexation between both polymers [99]. Lastly, in the third alternative, the

complexation of the polymers occurs due to the mixture of two strong polyelectrolytes of opposed charge at a high salt concentration [128].

A promising alternative to turn the membranes more sustainable is the functionalization of the membrane from structural modification. This structural modification can be performed from the incorporation of organic or inorganic compounds/additives, providing antimicrobial, antioxidant, adsorptive, or catalytic characteristics to the membrane, depending on the kind of functional material employed, besides improving the anti-fouling properties and increasing the lifespan of the membranes [9, 18, 19, 129]. Thus, the structural functionalization allows the fabrication of membranes with morphologies that are more and more adequate to the specific demands of each industrial process, be it separation, purification, and/or concentration. This functionalization with sustainable materials still adds more characteristics associated with the Green Technology concepts to the separation membrane process.

Among the several functionalization techniques of polymeric porous membranes fabricated by phase inversion, the morphological modification from the insertion of organic and inorganic additives in the polymeric solution [89, 130] and under the liquid film in the form of a surface coating of the membrane [18, 48, 51, 89, 125] can be performed. Still, modifications of the macromolecules during the synthesis of the polymer that will be used in the fabrication of the membranes can be done [19, 41, 73, 89]. Thus, physical and/or chemical methods can be used to enable the modification of the membrane surface (Fig. 3).

Figure 3 Functionalization techniques for porous polymeric membranes surface. Source: author

In the physical functionalization, the additive binds to the membrane surface through van der Waals bonds, electrostatic interaction, or hydrogen bonds which has a weaker interaction than the others and may not be stable in the long term. Thus, the membrane is coated by a very thin functional surface layer that provides anti-fouling properties, keeping high performance. Physical surface functionalization is the most used method to modify membranes. In addition, the surface coating technique can be applied to the fabrication of membranes layer-by-layer or double-membrane/in sandwich. However, the disadvantage of this method is the weak interaction between the coated layer and the membrane, which can allow that this layer suffers alteration and be removed during the chemical/physical cleaning and even during the operating process [131-136]. While in the surface adsorption technique, the membrane is modified by the insertion of compounds such as charged polyelectrolytes and surfactants in its surface, able to turn it into hydrophilic and consequently, improve the anti-fouling capacity [134, 137-139]. In the surface modification by blend, it is customary to mix organic and/or inorganic materials in order to transfer the main individual characteristics of each material to the membrane, such as hydrophilicity, thermal, physical, and chemical resistance [71, 140].

In chemical functionalization, the additive is fixed to the membrane surface by covalent bonds that have better chemical and structural stability. The functionalization with polymers, plasma treatment, and graft polymerization are examples of chemical functionalization techniques [18, 89, 134, 138, 141]. The plasma treatment has been widely used to modify the surface of polymeric membranes, due to the quick reaction time, high versatility, and being a process without secondary waste generation. In this method, the plasma species interact with the polymer surface, causing an electronically excited state in atoms with the formation of free radicals and unsaturated bonds. Thus, the reactions with the water and oxygen molecules in the surface of the polymer are eased and consequently, the surface of the membrane becomes with hydrophilic characteristics and higher fouling resistance [89, 133, 135, 142, 143]. Graft polymerization is the most used chemical method to modify the surface, which occurs through a covalent bond between the membrane surface and a polymer with the desired characteristic. This method is attractive due to its simplicity, and for not requiring an extra stage of chemical modification of the polymers during the membranes fabrication [18, 89, 130, 144, 145], which allows its utilization with a wide range of monomers that can be polymerized and grafted onto the porous membrane in a simple way, giving it several physicochemical surface properties [134, 135, 137, 138, 146].

In both chemical and physical functionalization, the use of nanomaterials is a widely used alternative in the membrane separation process. The nanomaterials possess as their main characteristics the high surface area that favors the adsorption, unique surface chemistry,

and the photocatalytic, antimicrobial electrical, and optical properties that are desired in the membranes [7, 13, 21, 53, 107, 147, 148]. Several modifying agents are studied for the membrane functionalization and improvements of the anti-fouling properties, such as the metallic silver (Ag) and copper (Cu) nanoparticles, metal oxides (Fe_2O_3 , ZrO_2 , Al_2O_3 , SiO_2 , ZnO), in addition to various forms of carbon nanofillers, zeolites, $\text{Mg}(\text{OH})_2$, CaCO_3 , and MnO_2 [19, 107]. Comparing all these materials, it is worth mentioning that the carbonaceous materials are ecologically correct, of easy preparation, and abundant availability, besides presenting excellent biocompatibility, and low toxicity [53, 149]. The carbon nanomaterials have unique characteristics, being the main ones the possibility to reach the required pore size, high surface area, and surface functionality, which collaborate to increase thermomechanical stability, water permeability, hydrophilicity and consequently improve the anti-fouling properties of the membrane [52, 150]. Besides, the functionalizing nanomaterials can even provide the membranes antibacterial and photocatalytic characteristics [125, 151-153].

Currently, several studies are approaching the membranes' functionalization using graphene that is a material based on carbon, especially because of the efficiency that the graphene presents in environmental applications, involving the adsorption, catalysis, and photocatalysis techniques [49, 53, 98, 151, 152]. These several studies showed that membranes functionalized with graphene have easy permeate flow recovery after cleaning, chemical and physical stability of the nanomaterials added, and performance improvement concerning the permeate flow and solute rejection. Besides, due to lightness, flexibility, high conductivity, and resistance, the functionalization with graphene gives the membrane desirable characteristics that are closer to the concepts of sustainability [52, 98, 154].

Following the Green Technology principle, the functionalization with agricultural, lignocellulosic, civil construction, wood production, fruit peel, and general disposal residues is a promising and sustainable alternative for the fabrication of composites with minimization of environmental pollution [54, 155-157]. For example, there is eggshell, which is a residue consisting basically of minerals, such as calcium and magnesium carbonate, and lignocellulosic materials extracted from bamboo or other residues, which can be used in functionalization, providing catalytic, adsorptive, and anti-fouling characteristics to the polymeric membranes [50, 157-161].

The possibility of morphological and structural modification of membranes using biopolymers, green solvents, and the functionalization of materials and/or nanomaterials make the membrane separation process to be a technique closer to the sustainability principles, being highlighted as a Green Technology.

3.2 Applications of the functionalized membranes

The membrane separation process is widely used in pharmaceutical, chemical, and food industries, in medical areas, and the treatment of domestic and industrial water. Some examples of applications can be mentioned, such as water treatment; residual water treatment; recuperation/purification of active pharmaceutical ingredients and valuable catalysts; recuperation of proteins and metallic ions; standardization, concentration, and fractionation of proteins; enzymes' purification; concentration of milk, cheese whey, and fruits' juice; whitening and desalcoholization of wines and beers; desalinization and demineralization of waters; as artificial kidneys and lungs in hemodialysis and oxygenators, respectively [3, 38, 66, 67, 112, 162].

In the literature, several relevant studies are found that used synthetic polymers and the combination with biopolymers, green solvents, and functionalization of the membranes with organic and/or inorganic additives to fabricate the membranes in order to make them more sustainable without losing the process efficiency. Rassol et al [28] fabricated nanofiltration membranes by the phase inversion technique using the biopolymer cellulose acetate dissolved in methyl lactate solvent, biodegradable and non-toxic, and in the green co-solvent 2-methyl tetrahydrofuran also from renewable resources. In this study, the cellulose acetate concentration in the casting solution, the addition of co-solvent, and the solvent evaporation time before the coagulation bath were evaluated. The performance of the membrane was evaluated with aqueous solutions of rose bengal or MgSO_4 . The authors observed for the rose bengal, that the increase in the concentration of cellulose acetate from 8 to 20% (wt%) caused an increase in the rejection from 31 to 99.5%, and a decrease in the permeability from 31.8 to 2.4 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively. The addition of 10% (wt%) of co-solvent in the membranes with 10% (wt%) of cellulose acetate promoted rejection of the rose bengal solution higher than 92.0%, and mean permeability of 3.5 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. Concerning the solvent evaporation time, in the membranes with 20% (wt%) of cellulose acetate, the MgSO_4 solution rejection was approximately 93.0% without evaporation and 96.5% with evaporation with a mean flow of 1.3 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. With this study, the authors evidenced that the utilization of biopolymers associated with solvents that are less pollutant is a promising alternative to fabricate sustainable and ecologically correct nanofiltration membranes.

Marino et al [24] employed for the first time the CyreneTM green bio-derived solvent to fabricate two membranes, being one of polyethersulfone and other polyvinylidene fluoride. Both membranes were fabricated by phase inversion induced by vapor and also non-solvent under controlled temperature and relative air humidity. The polyethersulfone membrane presented a structure formed by asymmetrical macrovoids and hydrophilic character with a contact angle lower than 90°. The polyvinylidene fluoride membrane had morphology

with bicontinuous structure and contact angle between 110° and 120° , being, thus, more hydrophobic. The authors ranged the exposition time during phase inversion with vapor and observed that for the polyethersulfone membrane at lower exposition times, the membranes were in the ultrafiltration range, while for longer times, in the microfiltration range. For the polyvinylidene fluoride membrane, the phase inversion with vapor as non-solvent promoted the formation of membranes with pores of $0.03\ \mu\text{m}$ and $0.55\ \mu\text{m}$, respectively. Thus, from these results, the viability of utilization of the green solvent Cyrene™ to fabricate more sustainable and ecologically correct membranes was verified.

Nielen et al [27] investigated an aqueous separation system based on pH change to produce the membranes. The authors chose to use the copolymer polystyrene-alt-maleic acid for having responsive monomers in its structure, which are necessary for the phase separation, and non-responsive hydrophobic monomers, which provide mechanical stability to the resulting membranes. The authors also tested the green solvent acetic acid and water to dilute the copolymer. Porous and dense membranes were fabricated in the microfiltration and nanofiltration range, which presented a rejection higher than 98% to oily waters. However, the membranes with dense and thin layers in the nanofiltration range showed rejections higher than 92% to small micropollutants. Thus, it is possible to observe that nanofiltration membranes can be fabricated to present excellent performance and sustainability characteristics through the separation method by the aqueous phase.

Aiming to improve the anti-fouling ability of the membranes and in the search for the development of sustainable membranes from the functionalization with natural polymers and nanoparticles of biological basis, Goetz et al [37] incorporated chitin nanocrystals in the surface of a membrane of cellulose acetate fabricated by the electrospinning technique. The authors tested the membrane to purify washing water from the process of a food industry containing biological and organic contaminants. The incorporation of chitin nanocrystals to the membrane increased 131% the mechanical resistance, 340% the rigidity, and the flow at 0.5 bar for $14217\ \text{L m}^{-2}\ \text{h}^{-1}$ and decreased the membrane deformation. To complement the excellent results already obtained, the authors observed that the acetate functionalization, which presents a hydrophobic characteristic with a contact angle of 132° , produced a highly hydrophilic membrane, with a contact angle near zero. This alteration contributed to biofouling reduction in the membrane surface, as well as provided better resistance to fouling after the permeation of bovine serum albumin and humic acid solutions.

Most studies found in the literature about the application of the membrane separation process used synthetic polymers of hard biodegradation to fabricate the membranes. On the other hand, several authors fabricated membranes from a blend of polymers and biopolymers and/or performed the functionalization of the membranes incorporating

organic and inorganic additives to make them more biodegradable. Among the organic additives, the chitosan biopolymer was the most used one to fabricate porous membranes, with more than 13,000 research articles published up to 2016 [105]. Another biopolymer that has been widely used is the cellulose acetate for having a low cost, good biocompatibility, and hydrophilicity [38, 108].

Al-Gharabli et al [112] performed the covalent anchorage of chitosan to the hydrophobic surface of polyvinylidene fluoride membranes in order to improve membrane permeability and anti-fouling properties. The membranes with and without chitosan were evaluated concerning the rejection of volatile organic compounds, desalination, and juice concentration. The membranes functionalized with chitosan, called hybrid, presented higher thermal stability, transport performance, selectivity, and fouling decrease when compared to the pure polyvinylidene fluoride membrane. The separation factor increased from 2.3 to 11.1 after the chitosan fixation to the surface of the membrane and the separation index of the process was 6.8 and 90 Kg m⁻² h⁻¹ for the membrane without and with chitosan, respectively. In juice concentration, the membrane without chitosan had a higher flow decrease (50%) than the one with chitosan (20%). The authors also evaluated that the membranes fabricated presented the potential to be used to separate oil in water and residual waters treatment.

Ji et al [109] also fabricated a membrane of a mixed matrix of chitosan with the copolymers 2-ethacryloyloxy ethyl trimethylammonium chloride and 2-hydroxyethyl acrylate. For the membranes with a concentration of 25% of co-polymers, the mechanical properties of elongation at break and tensile strength increased 2.4 and 2 times, reaching maximum values of 4.3% and 61.2 MPa, respectively. The authors observed high hydraulic permeability, salt selectivity, and that the membrane hydrophilicity increased with the concentration of copolymers, causing an increase in the anti-fouling characteristic of the membrane. For the concentration of 50% of the copolymer, the hydraulic permeability was 20.6 L m⁻² h⁻¹, and the rejection of the inorganic salts ZnCl₂ and NaCl was 97.5 and 57.1%, respectively. Thus, this study showed that the mixture of chitosan with the copolymers is a promising strategy to prepare membranes positively charged with mechanical properties and great nanofiltration performances.

Zhou et al [38] fabricated, by the phase inversion technique, ultrafiltration membranes from the blend the polymers cellulose acetate and polyvinylpyrrolidone and the functionalization with cellulose nanocrystals. The results demonstrated that, after the incorporation of the cellulose nanocrystals, the membrane became more porous and the mechanical property of tensile strength increased 47%. However, only for concentrations lower than 0.5% (wt%) of cellulose nanocrystals, the water flow increased and high rejection of bovine serum

albumin (>90%) was verified. The authors also observed that the membrane functionalization reduced the fouling, with a recovery of 68% of the flow.

The functionalization can also be performed by combining organic and inorganic additives. El Reash et al [105] fabricated membranes using the polymeric blend of chitosan and polyacrylamide and functionalized them with silver nanoparticles. The membranes were used for the rejection of Cu (II) ions in aqueous solutions. The composed membranes were efficient in the rejection of the Cu (II) ions, being that the temperature increase from 20 to 40°C accelerated the mass transfer of Cu (II) ions to the membrane surface. The functionalization of the membranes with silver nanoparticles was also verified to have provided antimicrobial properties against Gram-negative, Gram-positive, and *Candida sp.* microorganisms. The authors concluded that the functionalization allowed the lifespan of the membrane to be extended, due to the inability of bacteria to form a biofilm that can cause membrane fouling. Also, with the aim of increasing the anti-fouling property of the membrane and consequently its lifespan, Panda et al [163] fabricated a membrane of a mixed matrix using amine stabilized iron oxide (Fe₃O₄) nanoparticles and polyacrylonitrile (PAN) coated with chitosan. The chitosan coating increased the hydrophilicity of the membrane, however, the impregnation of Fe₃O₄ caused a slight decrease of this characteristic. Besides, the mechanical resistance and the zeta potential of the membrane increased with the concentration of Fe₃O₄ and the membrane became denser and with reduced roughness. The adsorption of humic acid and the fouling characteristic increased with the quantity of amine stabilized magnetic nanoparticles, having a higher value in the concentration of 0.4% (wt%), in which the maximum adsorption capacity of humic acid was reached (70 mg g⁻¹) with flow recovery of 95%.

Alhalili et al [164] used membranes fabricated with the biopolymer cellulose acetate and functionalized with titanium dioxide (TiO₂) and zinc oxide (ZnO) nanoparticles in the rejection of synthetic thiol (dithioterethiol). The TiO₂ and ZnO nanoparticles decreased the contact angle of the cellulose acetate membrane, turning it into more hydrophilic, and, thus, with a greater anti-fouling property. In addition, the permeability that was 8.82 L m⁻² h⁻¹ bar⁻¹ with the cellulose acetate membrane, increased to 20.77 and 21.96 L m⁻² h⁻¹ bar⁻¹ when functionalized with TiO₂ and ZnO, respectively. The rejection of dithioterethiol at 2 mM of concentration and pH 10 with filtration under the pressure of 2 bar was 99.67% for the membrane functionalized with ZnO. The bond ZnO-Sulfur caused a significant reduction of the mobility of sulfur diffusion, while the TiO₂ did not present great effects.

A mixed matrix membrane based on cellulose acetate with the incorporation of mixed metal oxides (Fe - Al - Mn) and chitosan was fabricated by Chaudhary and Maiti [165] with the aim of removing fluoride contamination in groundwater. To achieve that, several parameters were optimized, reaching the optimum conditions of transmembrane pressure

of 6 to 8 bar, pH between 6 and 9, and adsorbent mass of 8%. At these conditions, the membrane with an area of 1 m² was capable of treating 4000 liters of fluoride contaminated water. The fluorine rejection occurred initially by adsorption and posteriorly by electrostatic repulsion, due to the ions adsorbed in the membrane that presented negative surface charges. Besides, the studied membrane presented antimicrobial potential in an aqueous medium, being less susceptible to microbial attack compared to the non-functionalized cellulose acetate membrane.

In Table 2, a summary of several studies that performed the functionalization of membranes to make them more sustainable and improve their performance, especially regarding their anti-fouling capacity, is presented. Among these studies, the incorporation of organic and/or inorganic materials and nanomaterials in the membrane surface is highlighted, which is becoming a promising alternative and able to change the hydrophilicity, mechanical, chemical, and thermal resistance, permeability, and selectivity of the membranes. This combination of organic and inorganic materials and the polymers/biopolymers can also provide the membrane characteristics of adsorption, catalysis, photocatalysis, and antimicrobial. Thus, the membranes are fabricated with characteristics and performance that are desirable to the industrial process in a more biodegradable and sustainable way.

Table 2 Recent studies of the functionalization of porous polymeric membranes.

Polymer	Functionalization	Property	Application	Permeability*	Anti-fouling capacity*	Ref.
Polyvinylidene fluoride	Titanium dioxide (TiO ₂), and zinc oxide (ZnO)	Anti-fouling and Photocatalytic	Wastewater treatment	Increase of 33.5% of the permeability for the membrane with TiO ₂ /ZnO 3:1	Increase of 73% in the anti-fouling capacity for the membrane with TiO ₂ /ZnO 1:3 and under visible light	[21]
Polysulfone modified with polyamide thin film	Natural Clinoptilolite	Anti-fouling	Water desalination	Increase of 33% in the water flow	Increase of 88% in the anti-fouling property	[41]
Polyethersulfone and alumina	Poly(styrene sulfonate) and poly (allylamine hydrochloride)	High rejection of ionic liquids	Recovery of ionic liquid	Permeability of 2.5 L m ⁻² h ⁻¹ bar ⁻¹ for the polyethersulfone membrane and 4.8 L m ⁻² h ⁻¹ bar ⁻¹ for the alumina membrane. Permeability reduction according to the	Increase in the rejection of the sugars Cellobiose, Glucose, Xylose, Fructose, 1-ethyl-3-methylimidazolium acetate, and 1-butyl-3-methylimidazolium chloride according to the increase in the layers of	[166]

				increase in the layers of polymer	polymer for both membranes	
Polyethersulfone modified with polyamide thin film	Acyl chlorided graphene oxide	Anti-fouling and high ions rejection	Water desalination	Increase in the flow from 11.6 to 22.6 L m ⁻² h ⁻¹	Rejection of Na ₂ SO ₄ increased from 95.0% to 97.1%	[167]
Polyethersulfone	Atmospheric pressure argon jet plasma treatment	Anti-fouling	Concentration of whey proteins	Decrease of 86% in the hydraulic permeability of the functionalized membrane	Increase in the hydrophilicity of the membrane and decrease the surface roughness resulting in a membrane with better anti-fouling characteristics. Increase in the flow recovery rate of 70% and high capacity of rejection of the protein	[5]
Polysulfone	Polyamide activated with low pressure nitrogen plasma activated	Anti-fouling	Concentration of fruit juice	Increase in the membrane hydrophilicity and hydraulic permeability (3 times higher)	Decrease of 30% in the time of juice concentration by osmotic distillation for the functionalized membranes. The concentration of the juice from 17.6 °Brix and 18.8 °Brix, reaching up to 60.9 °Brix and 60.4 °Brix in 430 and 340 min, respectively	[168]
Polyamide	Titanium dioxide	Anti-fouling and Photocatalytic	Wastewater treatment	Permeability increase from 6.15 to 7.28 L h ⁻¹ m ⁻² bar ⁻¹	Improvement in the anti-fouling properties due to the increase of hydrophilicity and promotion of photocatalytic activity	[147]
Polyethersulfone	Polyethylenimine and graphene oxide	Anti-fouling	Wastewater treatment	Reduction in the water permeability, being 99.4 L m ⁻² h ⁻¹ bar ⁻¹ for the best rejection result	Rejection of the Blue Corazol dye of 97.8% and flow recovery rate higher than 80%	[8]

Polyethersulfone	Cellulose nanofibers and nanocrystals	Anti-fouling	Wastewater treatment	Highest water flow for the membranes with cellulose nanocrystals, followed by the membranes with cellulose nanofibers	Reduction of fouling and highest rejection for bovine serum albumine and humic acid	[43]
Polyethersulfone	Copper-modified titanate nanotubes	Anti-fouling and antimicrobial	Permeation of bovine serum albumin protein	Highest flow in the membrane with 15% (wt%) of polyethersulfone and highest copper content	Improvement of the anti-fouling property and highest rejection of albumine for the membrane with lower flow	[107]
Polyethersulfone	TiO ₂ @Ni particles	Anti-fouling	Permeation of bovine serum albumin protein	5-times increase of the flow	Rejection of 95.85% of albumine, and flow recovery rate higher than 75%	[148]
Polyethersulfone	Zeolitic imidazolate framework-L nanoflakes and carboxylated graphene oxide	Anti-fouling	Removal of pharmaceutical compounds	Increase in the hydrophilicity of the membrane and increase in the water permeability ($203.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) in the membrane with 0.25% (wt%) of graphene and 0.25% (wt%) of zeolitic.	Improvement in the anti-fouling properties and flow recovery rate of 95.1%. Amoxicillin rejection of 98.9% in laboratory-produced waters	[9]
Polyethersulfone modified with polyamide thin film	Functionalized boron nitride nanosheets	Anti-fouling and high ions rejection	Water desalination	Increase of 25% in the water flow	96.4% rejection of the salt NaCl, and 96% of flow recovery	[10]
Polysulfone	Polyvinylpyrrolidone and silicon dioxide nanoparticles	Anti-fouling and high rejection of amoxicillin	Removal of antibiotics from the aqueous medium	Increase in the flow from $6.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (pure membrane) to $42.28 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (membrane functionalized with 3% of silicon dioxide)	Increase in the separation performance of the amoxicillin from 66.52% to 89.81% in the membrane with 4% (wt%) of silicon dioxide. Improvement in the hydrophilicity and the anti-fouling	[7]

					property of the membrane. The relative flow reduction ratio was 34.14% for the modified membrane	
Polyethersulfone	2-mercaptoethanol capped zinc sulfide quantum dots	Anti-fouling and high rejection of dye	Rejection of dye	Increase in the hydrophilicity of the membrane and the flow with water $249.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for 1% of added nanocomposite	Improvement in the anti-fouling capacity and increase in the flow recovery rate from 52.6% to 87.9% with the addition of the nanocomposite. Increase in the rejection of the Reactive Red 195 dye from 91.3% to 96.1%.	[12]
Polyvinylidene fluoride	Ionic liquid trioctyl (dodecyl) phosphonium chloride	High recovery of platinum group metals	Separation of metals	The isotropic dense membrane achieved lower values of initial flow and transport kinetics slower than the porous anisotropic membrane	Recovery of Pt and Pd higher than 90% for both membranes and excellent chemical resistance property during exposition of 10 days to aggressive chemical products	[14]
Polysulfone and polytetrafluoroethylene	Graphene oxide	Anti-fouling	Removal of lactose and concentration of fats and proteins	Improvement in the anti-fouling capacity and the hydrophilicity of the membranes. Flow recovery of 89% for the PS membrane and 43% for the PTFE membrane	Higher lactose concentration in the permeate for the functionalized membranes	[13]

* compared to the membrane without additive. *Source: author*

4. Final Considerations

This review approached the possibility to improve the membrane separation process from the use of membranes fabricated in a more sustainable way and with similar or higher mechanical, chemical, and thermal resistance characteristics when compared to membranes fabricated with synthetic polymers. Basic concepts that involve the structural and morphological classification of the membranes, as well as problems related to the

fouling development during the filtration process were also presented. Concerning the sustainability concepts, the membrane separation process was observed to be able to be considered as a Green Technology due to the low energy consumption, the non-generation of pollutants, and the possibility to reuse the membranes for several cycles without decreasing its performance regarding the permeate flow and selectivity. However, the studies found in the literature showed that it is possible to improve even more the sustainability concept in the membrane separation process. This improvement is achieved through structural modification of the membranes using biopolymers, solvents that are less harmful to human health, and functionalization of the membranes with organic and/or inorganic additives. Among the biopolymers, chitosan and cellulose acetate are the most used ones to fabricate membranes individually, but mainly as a blend of synthetic polymers, because the biopolymers do not always present adequate chemical, physical, and thermal resistance to be used industrially. Thus, the blend between the polymers and biopolymers is a possibility to have a more sustainable membrane and with desirable characteristics. Concerning the green solvents, water, ethyl lactate, and ionic liquids would be the most indicated. This review also evidences the great volume of studies that were developed in the last 10 years regarding the functionalization of membranes, which was preferably performed inserting organic and/or inorganic materials and nanomaterials in the polymeric solution or the membrane surface. The functionalization of membranes becomes a great alternative to improve the morphology, increase the anti-fouling property, and lifespan of the membranes because it allows associating to the membranes adsorptive, catalytic, photocatalytic, and antimicrobial characteristics. Thus, this review demonstrated that, with the adequate structural modifications in the membranes, the environmentally sustainable Green Technology characteristic that does not harm the environment nor future generations can be associated with the membrane separation process, besides the separation, purification, and concentration efficiency, already consolidated in industrial processes.

References

- [1] J.G. Crespo, K.W. Boddeker, *Membrane Processes in Separation and Purification*, Vol 272, Springer Science+Business Media Dordrecht, 1994.
- [2] A.Y. Tamime, *Membrane Processing: Dairy and Beverage Applications*, first ed., 2013. <https://doi.org/10.1002/9781118457009>
- [3] K. Hu, J.M. Dickson, *Membrane Processing for Dairy Ingredient Separation*, first ed., Wiley Blackwell, 2015.

- [4] M. Omidvar, M. Soltanieh, S.M. Mousavi, E. Saljoughi, A. Moarefian, H. Saffaran, Preparation of hydrophilic nanofiltration membranes for removal of pharmaceuticals from water, *J. Environ. Heal. Sci. Eng.* 13 (2015) 1–9. <https://doi.org/10.1186/s40201-015-0157-3>
- [5] I. Damar Huner, H.A. Gulec, Fouling behavior of poly(ether)sulfone ultrafiltration membrane during concentration of whey proteins: Effect of hydrophilic modification using atmospheric pressure argon jet plasma, *Colloids Surfaces B: Biointerfaces*. 160 (2017) 510–519. <https://doi.org/10.1016/j.colsurfb.2017.10.003>
- [6] S.F. Zakeritabar, M. Jahanshahi, M. Peyravi, Photocatalytic Behavior of Induced Membrane by ZrO₂–SnO₂ Nanocomposite for Pharmaceutical Wastewater Treatment, *Catal. Letters*. 148 (2018) 882–893. <https://doi.org/10.1007/s10562-018-2303-x>
- [7] M. Shakak, R. Rezaee, A. Maleki, A. Jafari, M. Safari, B. Shahmoradi, H. Daraei, S.M. Lee, Synthesis and characterization of nanocomposite ultrafiltration membrane (PSF/PVP/SiO₂) and performance evaluation for the removal of amoxicillin from aqueous solutions, *Environ. Technol. Innov.* 17 (2020). <https://doi.org/10.1016/j.eti.2019.100529>
- [8] N.C. Homem, N. de C.L. Beluci, S. Amorim, R. Reis, A.M.S. Vieira, M.F. Vieira, R. Bergamasco, M.T.P. Amorim, Surface modification of a polyethersulfone microfiltration membrane with graphene oxide for reactive dyes removal, *Appl. Surf. Sci.* 486 (2019) 499–507. <https://doi.org/10.1016/j.apsusc.2019.04.276>
- [9] A. Modi, J. Bellare, Amoxicillin removal using polyethersulfone hollow fiber membranes blended with ZIF-L nanoflakes and cGO nanosheets: Improved flux and fouling-resistance, *J. Environ. Chem. Eng.* 8 (2020) 103973. <https://doi.org/10.1016/j.jece.2020.103973>
- [10] R. Wang, Z.X. Low, S. Liu, Y. Wang, S. Murthy, W. Shen, H. Wang, Thin-film composite polyamide membrane modified by embedding functionalized boron nitride nanosheets for reverse osmosis, *J. Memb. Sci.* 611 (2020). <https://doi.org/10.1016/j.memsci.2020.118389>
- [11] S.A. Gokulakrishnan, G. Arthanareeswaran, Z. László, G. Veréb, S. Kertész, J. Kweon, Recent development of photocatalytic nanomaterials in mixed matrix membrane for emerging pollutants and fouling control, membrane cleaning process, *Chemosphere*. 281 (2021). <https://doi.org/10.1016/j.chemosphere.2021.130891>
- [12] M.R. Ganjali, M.A. Al-Naqshabandi, B. Larijani, A. Badiei, V. Vatanpour, H.R. Rajabi, H. Rezania, S. Paziresh, G. Mahmodi, S.J. Kim, M.R. Saeb, Improvement of dye and protein filtration efficiency using modified PES membrane with 2-

- mercaptoethanol capped zinc sulfide quantum dots, *Chem. Eng. Res. Des.* 168 (2021) 109–121. <https://doi.org/10.1016/j.cherd.2020.12.026>
- [13] A. Morelos-Gomez, S. Terashima, A. Yamanaka, R. Cruz-Silva, J. Ortiz-Medina, R. Sánchez-Salas, J.L. Fajardo-Díaz, E. Muñoz-Sandoval, F. López-Uriás, K. Takeuchi, S. Tejima, M. Terrones, M. Endo, Graphene oxide membranes for lactose-free milk, *Carbon*. 181 (2021) 118–129. <https://doi.org/10.1016/j.carbon.2021.05.005>
- [14] A.T.N. Fajar, T. Hanada, M. Goto, Recovery of platinum group metals from a spent automotive catalyst using polymer inclusion membranes containing an ionic liquid carrier, *J. Memb. Sci.* 629 (2021). <https://doi.org/10.1016/j.memsci.2021.119296>
- [15] W.S. Wan Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: A review, *Carbohydr. Polym.* 83 (2011) 1446–1456. <https://doi.org/10.1016/j.carbpol.2010.11.004>
- [16] E. Drioli, A.I. Stankiewicz, F. Macedonio, Membrane engineering in process intensification-An overview, *J. Memb. Sci.* 380 (2011) 1–8. <https://doi.org/10.1016/j.memsci.2011.06.043>
- [17] Y. Medina-Gonzalez, P. Aimar, J.F. Lahitte, J.C. Remigy, Towards green membranes: Preparation of cellulose acetate ultrafiltration membranes using methyl lactate as a biosolvent, *Int. J. Sustain. Eng.* 4 (2011) 75–83. <https://doi.org/10.1080/19397038.2010.497230>
- [18] M. Padaki, R. Surya Murali, M.S. Abdullah, N. Misdan, A. Moslehyani, M.A. Kassim, N. Hilal, A.F. Ismail, Membrane technology enhancement in oil-water separation. A review, *Desalination*. 357 (2015) 197–207. <https://doi.org/10.1016/j.desal.2014.11.023>
- [19] J.H. Jhaveri, Z.V.P. Murthy, A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes, *Desalination*. 379 (2016) 137–154. <https://doi.org/10.1016/j.desal.2015.11.009>
- [20] C. Santhosh, V. Velmurugan, G. Jacob, S.K. Jeong, A.N. Grace, A. Bhatnagar, Role of nanomaterials in water treatment applications: A review, *Chem. Eng. J* 306 (2016) 1116–1137. <https://doi.org/10.1016/j.cej.2016.08.053>
- [21] N. Li, Y. Tian, J. Zhang, Z. Sun, J. Zhao, J. Zhang, W. Zuo, Precisely-controlled modification of PVDF membranes with 3D TiO₂/ZnO nanolayer: enhanced anti-fouling performance by changing hydrophilicity and photocatalysis under visible light

- irradiation, *J. Memb. Sci.* 528 (2017) 359–368.
<https://doi.org/10.1016/j.memsci.2017.01.048>
- [22] S. Beisl, S. Monteiro, R. Santos, A.S. Figueiredo, M.G. Sánchez-Loredo, M.A. Lemos, F. Lemos, M. Minhalma, M.N. de Pinho, Synthesis and bactericide activity of nanofiltration composite membranes - Cellulose acetate/silver nanoparticles and cellulose acetate/silver ion exchanged zeolites, *Water Res.* 149 (2019) 225–231.
<https://doi.org/10.1016/j.watres.2018.10.096>
- [23] Z. Huang, B. Gong, C. Huang, S. Pan, P. Wu, Z. Dang, Performance evaluation of integrated adsorption-nanofiltration system for emerging compounds removal: Exemplified by caffeine, diclofenac and octylphenol, *J. Environ. Manage.*, 231 (2019) 121–128. <https://doi.org/10.1016/j.jenvman.2018.09.092>
- [24] T. Marino, F. Galiano, A. Molino, A. Figoli, New frontiers in sustainable membrane preparation : CyreneTM as green bioderived solvent, *J. Membr. Sci.*, 580 (2019) 224–234. <https://doi.org/10.1016/j.memsci.2019.03.034>
- [25] S. Samsami, M. Mohamadizani, M. Sarrafzadeh, E.R. Rene, M. Firoozbahr, Recent advances in the treatment of dye-containing wastewater from textile industries : Overview and perspectives, *Process Saf. Environ. Prot.* 143 (2020) 138–163.
<https://doi.org/10.1016/j.psep.2020.05.034>
- [26] W.M. Nielen, J.D. Willott, Z.M. Esguerra, W.M. de Vos, Ion specific effects on aqueous phase separation of responsive copolymers for sustainable membranes, *J. Colloid Interface Sci.* 576 (2020) 186–194. <https://doi.org/10.1016/j.jcis.2020.04.125>
- [27] W.M. Nielen, J.D. Willott, W.M. De Vos, Aqueous Phase Separation of Responsive Copolymers for Sustainable and Mechanically Stable Membranes, *Appl. Polym. Mater.* 2 (2020) 1702–1710. <https://doi.org/10.1021/acsapm.0c00119>
- [28] M.A. Rasool, C. Van Goethem, I.F.J. Vankelecom, Green preparation process using methyl lactate for cellulose-acetate-based nanofiltration membranes, *Sep. Purif. Technol.* 232 (2020). <https://doi.org/10.1016/j.seppur.2019.115903>
- [29] T. Shindhal, P. Rakholiya, S. Varjani, A. Pandey, H.H. Ngo, W. Guo, H.Y. Ng, M.J. Taherzadeh, A critical review on advances in the practices and perspectives for the treatment of dye industry wastewater, *Bioengineered.* 12 (2021) 70–87.
<https://doi.org/10.1080/21655979.2020.1863034>
- [30] E.K. Tetteh, S. Rathilal, D. Asante-Sackey, M.N. Chollom, Prospects of synthesized magnetic TiO₂-based membranes for wastewater treatment: A review, *Materials.* 14 (2021) 11–15. <https://doi.org/10.3390/ma14133524>

- [31] A. Gul, J. Hruza, F. Yalcinkaya, Fouling and chemical cleaning of microfiltration membranes: A mini-review, *Polymers*. 13 (2021).
<https://doi.org/10.3390/polym13060846>
- [32] W. Kujawski, J. Kujawa, E. Wierzbowska, S. Cerneaux, M. Bryjak, J. Kujawski, Influence of hydrophobization conditions and ceramic membranes pore size on their properties in vacuum membrane distillation of water-organic solvent mixtures, *J. Memb. Sci.* 499 (2016) 442–451. <https://doi.org/10.1016/j.memsci.2015.10.067>
- [33] E. Bet-moushoul, Y. Mansourpanah, K. Farhadi, M. Tabatabaei, TiO₂ nanocomposite based polymeric membranes : A review on performance improvement for various applications in chemical engineering processes, *Chem. Eng. J.* 283 (2016) 29–46. <https://doi.org/10.1016/j.cej.2015.06.124>
- [34] C. Li, W. Sun, Z. Lu, X. Ao, S. Li, Ceramic nanocomposite membranes and membrane fouling: A review, *Water Res.* 175 (2020).
<https://doi.org/10.1016/j.watres.2020.115674>
- [35] M. Aider, Chitosan application for active bio-based films production and potential in the food industry: Review, *LWT - Food Sci. Technol.* 43 (2010) 837–842.
<https://doi.org/10.1016/j.lwt.2010.01.021>
- [36] F. Galiano, K. Briceño, T. Marino, A. Molino, K.V. Christensen, A. Figoli, Advances in biopolymer-based membrane preparation and applications, *J. Memb. Sci.* 564 (2018) 562–586. <https://doi.org/10.1016/j.memsci.2018.07.059>
- [37] L.A. Goetz, B. Jalvo, R. Rosal, A.P. Mathew, Superhydrophilic anti-fouling electrospun cellulose acetate membranes coated with chitin nanocrystals for water filtration, *J. Memb. Sci.* 510 (2016) 238–248.
<https://doi.org/10.1016/j.memsci.2016.02.069>
- [38] J. Zhou, J. Chen, M. He, J. Yao, Cellulose acetate ultrafiltration membranes reinforced by cellulose nanocrystals: Preparation and characterization, *J. Appl. Polym. Sci.* 133 (2016) 1–7. <https://doi.org/10.1002/app.43946>
- [39] F. Russo, F. Galiano, A. Iulianelli, A. Basile, A. Figoli, Biopolymers for sustainable membranes in CO₂ separation: a review, *Fuel Process. Technol.* 213 (2021). <https://doi.org/10.1016/j.fuproc.2020.106643>
- [40] M. Mulder, *Basic Principles of Membrane Technology*, second ed., Kluwer Academic Publisher, 1996. <https://doi.org/10.1007/978-94-009-1766-8>

- [41] M. Safarpour, V. Vatanpour, A. Khataee, H. Zarrabi, P. Gholami, M. E. High flux and fouling resistant reverse osmosis membrane modified with plasma treated natural zeolite, *Desalination*. 411 (2017) 89–100. <https://doi.org/10.1016/j.desal.2017.02.012>
- [42] M.T. Alresheedi, B. Barbeau, O.D. Basu, Comparisons of NOM fouling and cleaning of ceramic and polymeric membranes during water treatment, *Sep. Purif. Technol.* 209 (2019) 452–460. <https://doi.org/10.1016/j.seppur.2018.07.070>
- [43] L. Bai, Y. Liu, A. Ding, N. Ren, G. Li, H. Liang, Surface coating of UF membranes to improve antifouling properties: A comparison study between cellulose nanocrystals (CNCs) and cellulose nano fibrils (CNFs), *Chemosphere*. 217 (2019) 76–84. <https://doi.org/10.1016/j.chemosphere.2018.10.219>
- [44] A. Rahimpour, S.S. Madaeni, Polyethersulfone (PES)/ cellulose acetate phthalate (CAP) blend ultrafiltration membranes: Preparation, morphology, performance and antifouling properties, *J. Memb. Sci.* 305 (2007) 299–312. <https://doi.org/10.1016/j.memsci.2007.08.030>
- [45] M.Z. Yunus, Z. Harun, H. Basri, A.F. Ismail, Studies on fouling by natural organic matter (NOM) on polysulfone membranes: Effect of polyethylene glycol (PEG), *Desalination*. 333 (2014) 36–44. <https://doi.org/10.1016/j.desal.2013.11.019>
- [46] R. Krishnamoorthy, V. Sagadevan, Polyethylene glycol and iron oxide nanoparticles blended polyethersulfone ultrafiltration membrane for enhanced performance in dye removal studies, *E-Polymers*. 15 (2015) 151–159. <https://doi.org/10.1515/epoly-2014-0214>
- [47] L.D. Fiorentin-Ferrari, K.M. Celant, B.C. Gonçalves, S.M. Teixeira, V. Slusarski-Santana, A.N. Módenes, Fabrication and characterization of polysulfone and polyethersulfone membranes applied in the treatment of fish skin tanning effluent, *J. Clean. Prod.* 294 (2021). <https://doi.org/10.1016/j.jclepro.2021.126127>
- [48] N. Nady, M.C.R. Franssen, H. Zuilhof, M.S.M. Eldin, R. Boom, K. Schroën, Modification methods for poly(arylsulfone) membranes: A mini-review focusing on surface modification, *Desalination*. 275 (2011) 1–9. <https://doi.org/10.1016/j.desal.2011.03.010>
- [49] L. Zhang, B. Chen, A. Ghaffar, X. Zhu, Nanocomposite Membrane with Polyethylenimine-Grafted Graphene Oxide as a Novel Additive to Enhance Pollutant Filtration Performance, *Environ. Sci. Technol.* 52 (2018) 5920–5930. <https://doi.org/10.1021/acs.est.8b00524>

- [50] G.D. Değermenci, N. Değermenci, V. Ayvaoğlu, E. Durmaz, D. Çakır, E. Akan, Adsorption of reactive dyes on lignocellulosic waste; characterization, equilibrium, kinetic and thermodynamic studies, *J. Clean. Prod.* 225 (2019) 1220–1229. <https://doi.org/10.1016/j.jclepro.2019.03.260>
- [51] F. Yalcinkaya, E. Boyraz, J. Maryska, K. Kucerova, A review on membrane technology and chemical surface modification for the oily wastewater treatment, *Materials*. 13 (2020). <https://doi.org/10.3390/ma13020493>
- [52] H. Saleem, S.J. Zaidi, Nanoparticles in reverse osmosis membranes for desalination: A state of the art review, *Desalination*. 475 (2020). <https://doi.org/10.1016/j.desal.2019.114171>
- [53] M. Jani, J.A. Arcos-Pareja, M. Ni, Engineered Zero-Dimensional Fullerene/Carbon Dots-Polymer Based Nanocomposite Membranes for Wastewater Treatment, *Molecules*. 25 (2020) 1–28. <https://doi.org/10.3390/molecules25214934>
- [54] A.A. Amusa, A.L. Ahmad, J.K. Adewole, Study on lignin-free lignocellulosic biomass and PSF-PEG membrane compatibility, *BioResources*. 16 (2020) 1063–1075. <https://doi.org/10.15376/biores.16.1.1063-1075>
- [55] O.S. Serbanescu, S.I. Voicu, V.K. Thakur, Polysulfone functionalized membranes: Properties and challenges, *Mater. Today Chem.* 17 (2020). <https://doi.org/10.1016/j.mtchem.2020.100302>
- [56] J. Ayyavoo, T.P.N. Nguyen, B.M. Jun, I.C. Kim, Y.N. Kwon, Protection of polymeric membranes with antifouling surfacing via surface modifications, *Colloids Surfaces A Physicochem. Eng. Asp.* 506 (2016) 190–201. <https://doi.org/10.1016/j.colsurfa.2016.06.026>
- [57] H.K. Lonsdale, The growth of membrane technology, *J. Memb. Sci.* 10 (1982) 81–181. [https://doi.org/10.1016/S0376-7388\(00\)81408-8](https://doi.org/10.1016/S0376-7388(00)81408-8)
- [58] K.W. Böddeker, Commentary: Tracing membrane science, *J. Memb. Sci.* 100 (1995) 65–68. [https://doi.org/10.1016/0376-7388\(94\)00223-L](https://doi.org/10.1016/0376-7388(94)00223-L)
- [59] R.W. Baker, *Membrane technologies and applications*, second ed., John Wiley & Sons Ltd, 2004.
- [60] R. Field, E. Bekassy-Molnar, F. Lipnizki, G. Vatai, *Engineering aspects of membrane separation and application in food processing*, first ed., Taylor & Francis Group, 2017. <https://doi.org/10.4324/9781315374901>
- [61] M. Cheryan, *Ultrafiltration and Microfiltration Handbook*, second ed., Taylor & Francis Routledge, 1998. <https://doi.org/10.1201/9781482278743>

- [62] Z.F. Cui, H.S. Muralidhara, Membrane technology - A Practical Guide to Membrane Technology and Applications in Food and Bioprocessing, first ed., Elsevier Ltd, 2010.
- [63] G. Lofrano, M. Carotenuto, G. Libralato, R.F. Domingos, A. Markus, L. Dini, R.K. Gautam, D. Baldantoni, M. Rossi, S.K. Sharma, M.C. Chattopadhyaya, M. Giugni, S. Meric, Polymer functionalized nanocomposites for metals removal from water and wastewater: An overview, *Water Res.* 92 (2016) 22–37. <https://doi.org/10.1016/j.watres.2016.01.033>
- [64] H. Strathmann, Ion-Exchange membrane separation processes, first ed., Elsevier B.V., 2004. https://doi.org/10.1002/14356007.a16_187.pub2
- [65] H. Strathmann, Membrane separation processes, *J. Memb. Sci.* 9 (1981) 121–189. [https://doi.org/10.1016/S0376-7388\(00\)85121-2](https://doi.org/10.1016/S0376-7388(00)85121-2)
- [66] K. Mohanty, M.K. Purkait, Membrane technologies and applications, first ed., Taylor & Francis Group, 2012. <https://doi.org/10.1201/b11416>
- [67] L.W. Jye, A.F. Ismail, Nanofiltration membranes - Synthesis, Characterization, and Applications, first ed., Taylor & Francis Group, 2016. <https://doi.org/10.1201/9781315181479>
- [68] S. Mei, C. Xiao, X. Hu, Preparation of Porous PVC Membrane via a Phase Inversion Method from PVC/DMAc/Water/Additives, *J. Appl. Polym. Sci.* 120 (2010) 557–562. <https://doi.org/10.1002/app.33219>
- [69] K. Scott, Handbook of Industrial Membranes, second ed., Elsevier Science, 1995.
- [70] M. Kumar, Z. Gholamvand, A. Morrissey, K. Nolan, M. Ulbricht, J. Lawler, Preparation and characterization of low fouling novel hybrid ultrafiltration membranes based on the blends of GO-TiO₂ nanocomposite and polysulfone for humic acid removal, *J. Memb. Sci.* 506 (2016) 38–49. <https://doi.org/10.1016/j.memsci.2016.02.005>
- [71] S. Benkhaya, S. M'rabet, R. Hsissou, A. El Harfi, Synthesis of new low-cost organic ultrafiltration membrane made from Polysulfone/Polyetherimide blends and its application for soluble azoic dyes removal, *J. Mater. Res. Technol.* 9 (2020) 4763–4772. <https://doi.org/10.1016/j.jmrt.2020.02.102>
- [72] M.T. Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: a review, *Desalination.* 235 (2009) 199–244. <https://doi.org/10.1016/j.desal.2007.10.042>

- [73] M. Ulbricht, Advanced functional polymer membranes, *Polymer*. 47 (2006) 2217–2262. <https://doi.org/10.1016/j.polymer.2006.01.084>
- [74] J.K. Shethji, S.M.C. Ritchie, Microfiltration membranes functionalized with multiple styrenic homopolymer and block copolymer grafts, *J. Appl. Polym. Sci.* 132 (2015) 1–11. <https://doi.org/10.1002/app.42501>
- [75] W. Ho, K.K. Sirkar, *Membrane Handbook*, Springer Science Business Media New York, 1992. <https://doi.org/10.1007/978-1-4615-3548-5>
- [76] A.K. Pabby, S.S.H. Rizvi, A.M. Sastre, *Handbook of Membrane Separations - Chemical, Pharmaceutical, Food, and Biotechnological Applications*, first ed., Taylor & Francis Group, 2008. <https://doi.org/10.1201/9781420009484>
- [77] T.J. Britz, R.K. Robinson, *Advanced Dairy Science and Technology*, first ed., Blackwell Publishing Ltd, 2008. <https://doi.org/10.1002/9780470697634>
- [78] C. Charcosset, *Membrane Processes in Biotechnology and Pharmaceutics*, first ed., Elsevier B.V., 2012. <https://doi.org/10.1016/B978-0-444-56334-7.00007-1>
- [79] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, *Desalination*. 356 (2015) 226–254. <https://doi.org/10.1016/j.desal.2014.10.043>
- [80] M. Paul, S.D. Jons, Chemistry and fabrication of polymeric nanofiltration membranes: A review, *Polymer*. 103 (2016) 417–456. <https://doi.org/10.1016/j.polymer.2016.07.085>
- [81] M.K. Selatile, S.S. Ray, V. Ojijo, R. Sadiku, Recent developments in polymeric electrospun nanofibrous membranes for seawater desalination, *RSC Adv.* 8 (2018) 37915–37938. <https://doi.org/10.1039/C8RA07489E>
- [82] N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura, *Advanced membrane technology and applications*, John Wiley & Sons, 2008.
- [83] S.K. Hubadillah, M.H.D. Othman, T. Matsuura, A.F. Ismail, M.A. Rahman, Z. Harun, J. Jaafar, M. Nomura, Fabrications and applications of low cost ceramic membrane from kaolin: A comprehensive review, *Ceram. Int.* 44 (2018) 4538–4560. <https://doi.org/10.1016/j.ceramint.2017.12.215>
- [84] W. Zhang, L. Ding, J. Luo, M.Y. Jaffrin, B. Tang, Membrane fouling in photocatalytic membrane reactors (PMRs) for water and wastewater treatment: A critical review, *Chem. Eng. J.* 302 (2016) 446–458. <https://doi.org/10.1016/j.cej.2016.05.071>

- [85] S. Meng, W. Fan, X. Li, Y. Liu, D. Liang, X. Liu, Intermolecular interactions of polysaccharides in membrane fouling during microfiltration, *Water Res.* 143 (2018) 38–46. <https://doi.org/10.1016/j.watres.2018.06.027>
- [86] A. Basile, A. Cassano, N. Rastogi, *Advances in Membrane Technologies for Water Treatment - Materials, Processes and applications*, Elsevier Ltd, 2015.
- [87] B. Huang, Z. Wu, H. Zhou, J. Li, C. Zhou, Z. Xiong, Z. Pan, G. Yao, B. Lai, Recent advances in single-atom catalysts for advanced oxidation processes in water purification, *J. Hazard. Mater.* 412 (2021). <https://doi.org/10.1016/j.jhazmat.2021.125253>
- [88] A.W. Zularisam, A.F. Ismail, R. Salim, Behaviours of natural organic matter in membrane filtration for surface water treatment – a review, *Desalination.* 194 (2006) 211–231. <https://doi.org/10.1016/j.desal.2005.10.030>
- [89] Y. Subasi, B. Cicek, Recent advances in hydrophilic modification of PVDF ultrafiltration membranes – a review: part I, *Membr. Technol.* (2017) 7–12. [https://doi.org/10.1016/S0958-2118\(17\)30191-X](https://doi.org/10.1016/S0958-2118(17)30191-X)
- [90] F. Zhao, K. Xu, H. Ren, L. Ding, J. Geng, Y. Zhang, Combined effects of organic matter and calcium on biofouling of nanofiltration membranes, *J. Memb. Sci.* 486 (2015) 177–188. <https://doi.org/10.1016/j.memsci.2015.03.032>
- [91] L. Weinrich, M. Lechevallier, C.N. Haas, Contribution of assimilable organic carbon to biological fouling in seawater reverse osmosis membrane treatment, *Water Res.* 101 (2016) 203–213. <https://doi.org/10.1016/j.watres.2016.05.075>
- [92] J.N. Hakizimana, B. Gourich, C. Vial, P. Drogui, A. Oumani, J. Naja, L. Hilali, Assessment of hardness, microorganism and organic matter removal from seawater by electrocoagulation as a pretreatment of desalination by reverse osmosis, *Desalination.* 393 (2016) 90–101. <https://doi.org/10.1016/j.desal.2015.12.025>
- [93] S. Jiang, Y. Li, B.P. Ladewig, A review of reverse osmosis membrane fouling and control strategies, *Sci. Total Environ.* 595 (2017) 567–583. <https://doi.org/10.1016/j.scitotenv.2017.03.235>
- [94] H. Chang, H. Liang, F. Qu, B. Liu, H. Yu, X. Du, G. Li, S.A. Snyder, Hydraulic backwashing for low-pressure membranes in drinking water treatment : A review, *J. Memb. Sci.* 540 (2017) 362–380. <https://doi.org/10.1016/j.memsci.2017.06.077>
- [95] N. V Thombre, A.P. Gadhekar, A. V Patwardhan, P.R. Gogate, Ultrasound induced cleaning of polymeric nanofiltration membranes, *J. Ultrason. Sonochemistry.* 62 (2020). <https://doi.org/10.1016/j.ultsonch.2019.104891>

- [96] K. De Sitter, C. Dotremont, I. Genné, L. Stoops, The use of nanoparticles as alternative pore former for the production of more sustainable polyethersulfone ultrafiltration membranes, *J. Memb. Sci.* 471 (2014) 168–178. <https://doi.org/10.1016/j.memsci.2014.06.061>
- [97] P.S. Goh, A.F. Ismail, N. Hilal, Nano-enabled membranes technology: Sustainable and revolutionary solutions for membrane desalination?, *Desalination*. 380 (2016) 100–104. <https://doi.org/10.1016/j.desal.2015.06.002>
- [98] X. Zhu, K. Yang, B. Chen, Membranes prepared from graphene-based nanomaterials for sustainable applications: a review, *Environ. Sci. Nano*. 4 (2017) 2267–2285. <https://doi.org/10.1039/C7EN00548B>
- [99] M.I. Baig, E.N. Durmaz, J.D. Willott, W.M. De Vos, Sustainable Membrane Production through Polyelectrolyte Complexation Induced Aqueous Phase Separation, *Adv. Funct. Mater.* 30 (2020). <https://doi.org/10.1002/adfm.201907344>
- [100] J.D. Willott, W.M. Nielen, W.M. De Vos, Stimuli-Responsive Membranes through Sustainable Aqueous Phase Separation, *ACS Appl. Polym. Mater.* 2 (2020) 659–667. <https://doi.org/10.1021/acsapm.9b01006>
- [101] M. Mondal, S. De, Characterization and antifouling properties of polyethylene glycol doped PAN-CAP blend membrane, *RSC Adv.* (2015). <https://doi.org/10.1039/C5RA02889B>
- [102] A. Said, T.J. Daou, L. Limousy, J. Bikai, J. Halwani, J. Toufaily, T. Hamieh, P. Dutournié, Surface energy modification of a Na-mordenite thin layer treated by an alkaline solution, *Mater. Express*. 5 (2015) 451–456. <https://doi.org/10.1166/mex.2015.1253>
- [103] V.K. Thakur, S.I. Voicu, Recent Advances in Cellulose and Chitosan Based Membranes for Water Purification: A Concise Review, *Carbohydr. Polym.* (2016) 148-165. <https://doi.org/10.1016/j.carbpol.2016.03.030>
- [104] S. Mondal, Carbon Nanomaterials Based Membranes, *J. Membr. Sci. Technol.* 6 (2017) 18–20.
- [105] Y.G.A. El-reash, A.M. Abdelghany, A.A. Elrazak, Removal and separation of Cu (II) from aqueous solutions using nano-silver chitosan/polyacrylamide membranes, *Int. J. Biol. Macromol.* 86 (2016) 789–798. <https://doi.org/10.1016/j.ijbiomac.2016.01.101>
- [106] T. Marino, E. Blasi, S. Tornaghi, E. Di Nicolo, A. Figoli, Polyethersulfone membranes prepared with Rhodiasolv® Polarclean as water soluble green solvent, *J. Membr. Sci.* 549 (2018) 192–204. <https://doi.org/10.1016/j.memsci.2017.12.007>

- [107] K. Szymanski, D. Darowna, P. Sienkiewicz, M. Jose, K. Szymanska, M. Zgrzebnicki, S. Mozia, Novel polyethersulfone ultrafiltration membranes modified with Cu/titanate nanotubes, *J. Water Process Eng.* 33 (2020).
<https://doi.org/10.1016/j.jwpe.2019.101098>
- [108] M.N. Subramanian, *Polymer Blends and Composites: Chemistry and Technology*, John Wiley & Sons, 2017. <https://doi.org/10.1002/9781119383581>
- [109] Y. Ji, Q. An, F. Zhao, C. Gao, Fabrication of chitosan / PDMCHEA blend positively charged membranes with improved mechanical properties and high nanofiltration performances, *Desalination*. 357 (2015) 8–15.
<https://doi.org/10.1016/j.desal.2014.11.005>
- [110] Z. Xu, G. Liu, H. Ye, W. Jin, Z. Cui, Two-dimensional MXene incorporated chitosan mixed-matrix membranes for efficient solvent dehydration, *J. Membr. Sci.* 563 (2018) 625–632. <https://doi.org/10.1016/j.memsci.2018.05.044>
- [111] C.C. De Faria, M. Favero, M.M.M. Caetano, A.H. Rosa, P.S. Tonello, Application of chitosan film as a binding phase in the diffusive gradients in thin films technique (DGT) for measurement of metal ions in aqueous solution, *Anal. Bioanal. Chem.* 412 (2020) 703–714. <https://doi.org/10.1007/s00216-019-02281-4>
- [112] S. Al-gharabli, B. Al-omari, W. Kujawski, J. Kujawa, Biomimetic hybrid membranes with covalently anchored chitosan – Material design, transport and separation, *Desalination*. 491 (2020). <https://doi.org/10.1016/j.desal.2020.114550>
- [113] H. Mahdavi, T. Shahalizade, Preparation, characterization and performance study of cellulose acetate membranes modified by aliphatic hyperbranched polyester, *J. Membr. Sci.* 473 (2015) 256–266. <https://doi.org/10.1016/j.memsci.2014.09.013>
- [114] A. Ghaee, M. Shariaty-niassar, J. Barzin, T. Matsuura, Effects of chitosan membrane morphology on copper ion adsorption, *J. Chem. Eng.* 165 (2010) 46–55.
<https://doi.org/10.1016/j.cej.2010.08.051>
- [115] S.T. Koev, P.H. Dykstra, X. Luo, G.W. Rubloff, W.E. Bentley, G.F. Payne, R. Ghodssi, Chitosan : an integrative biomaterial for lab-on-a-chip devices, *Lab Chip*. 10 (2010) 3026–3042. <https://doi.org/10.1039/c0lc00047g>
- [116] J. Wang, B. Wu, S. Yang, Y. Liu, A.G. Fane, J.W. Chew, Characterizing the scouring efficiency of Granular Activated Carbon (GAC) particles in membrane fouling mitigation via wavelet decomposition of accelerometer signals, *J. Memb. Sci.* 498 (2016) 105–115. <https://doi.org/10.1016/j.memsci.2015.09.061>

- [117] R. Kumar, A.M. Isloor, A.F. Ismail, T. Matsuura, Performance improvement of polysulfone ultrafiltration membrane using N-succinyl chitosan as additive, *Desalination*. 318 (2013) 1–8. <https://doi.org/10.1016/j.desal.2013.03.003>
- [118] A. Akbari, Z. Derikvandi, S. M. M. Rostami, Influence of chitosan coating on the separation performance, morphology and anti-fouling properties of the polyamide nanofiltration membranes, *J. Ind. Eng. Chem.* 28 (2015) 268–273. <https://doi.org/10.1016/j.jiec.2015.03.002>
- [119] E. Salehi, P. Daraei, A.A. Shamsabadi, A review on chitosan-based adsorptive membranes, *Carbohydr. Polym.* 152 (2016) 419–432. <https://doi.org/10.1016/j.carbpol.2016.07.033>
- [120] P.O. Osifo, H.W.J.P. Neomagus, H. Van Der Merwe, D.J. Branken, Transport properties of chitosan membranes for zinc (II) removal from aqueous systems, *Sep. Purif. Technol.* 179 (2017) 428–437. <https://doi.org/10.1016/j.seppur.2017.02.030>
- [121] C.N.B. Elizalde, S. Al-Gharabli, J. Kujawa, M. Mavukkandy, S.W. Hasan, H.A. Arafat, Fabrication of Blend Polyvinylidene fluoride/Chitosan Membranes for Enhanced Flux and Fouling Resistance, *Sep. Purif. Technol.* 190 (2018) 68–76. <https://doi.org/10.1016/j.seppur.2017.08.053>
- [122] A. Shakeri, H. Salehi, M. Rastgar, Chitosan-based thin active layer membrane for forward osmosis desalination, *Carbohydr. Polym.* 174 (2017) 658–668. <https://doi.org/10.1016/j.carbpol.2017.06.104>
- [123] F.F. Ghiggi, L.D. Pollo, N.S.M. Cardozo, I.C. Tessaro, Preparation and characterization of polyethersulfone/N-phthaloyl-chitosan ultrafiltration membrane with antifouling property, *Eur. Polym. J.* 92 (2017) 61–70. <https://doi.org/10.1016/j.eurpolymj.2017.04.030>
- [124] E. Bagheripour, A.R. Moghadassi, S.M. Hosseini, M.B. Ray, F. Parvizian, B. Van Der Bruggen, Highly hydrophilic and antifouling nanofiltration membrane incorporated with water-dispersible composite activated carbon/chitosan nanoparticles, *Chem. Eng. Res. Des.* 132 (2018) 812–821. <https://doi.org/10.1016/j.cherd.2018.02.027>
- [125] N. Li, Y. Tian, J. Zhao, J. Zhang, L. Kong, J. Zhang, W. Zuo, Static adsorption of protein-polysaccharide hybrids on hydrophilic modified membranes based on atomic layer: Anti-fouling performance and mechanism insight, *J. Memb. Sci.* 548 (2018) 470–480. <https://doi.org/10.1016/j.memsci.2017.11.063>

- [126] A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.M. Li, T. He, S. Tornaghi, E. Drioli, Towards non-toxic solvents for membrane: a review, *Green Chem.* 16 (2014) 4034–4059. <https://doi.org/10.1039/C4GC00613E>
- [127] M. Razali, J.F. Kim, M. Attfield, P.M. Budd, E. Drioli, Y.M. Lee, G. Szekely, Sustainable wastewater treatment and recycling in membrane manufacturing, *Green Chem.* 17 (2015) 5196–5205. <https://doi.org/10.1039/C5GC01937K>
- [128] K. Sadman, D.E. Delgado, Y. Won, Q. Wang, K.A. Gray, K.R. Shull, Versatile and High-Throughput Polyelectrolyte Complex Membranes via Phase Inversion, *ACS Appl. Mater. Interfaces.* 11 (2019) 16018–16026. <https://doi.org/10.1021/acsami.9b02115>
- [129] A. Bera, J.S. Trivedi, S. Binod, A.K. Singh, S. Haldar, S.K. Jewrajka, Anti-organic fouling and anti-biofouling poly(piperazineamide) thin film nanocomposite membranes for low pressure removal of heavy metal ions, *J. Hazard. Mater.* 343 (2018) 86–97. <https://doi.org/10.1016/j.jhazmat.2017.09.016>
- [130] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, *J. Membr. Sci.* 327 (2009) 125–135. <https://doi.org/10.1016/j.memsci.2008.11.025>
- [131] D. Zhao, S. Yu, A review of recent advance in fouling mitigation of NF/RO membranes in water treatment: pretreatment, membrane modification, and chemical cleaning, *Desalin. Water Treat.* 55 (2015) 870–891. <https://doi.org/10.1080/19443994.2014.928804>
- [132] J. Sun, L. Zhu, Z. Wang, F. Hu, P. Zhang, B. Zhu, Improved chlorine resistance of polyamide thin-film composite membranes with a terpolymer coating, *Sep. Purif. Technol.* 157 (2016) 112–119. <https://doi.org/10.1016/j.seppur.2015.11.034>
- [133] D.J. Miller, D.R. Dreyer, C.W. Bielawski, D.R. Paul, B.D. Freeman, Surface Modification of Water Purification Membranes: a review, *Angew. Chemie. Int. Ed.* 56 (2017) 4662–4711. <https://doi.org/10.1002/anie.201601509>
- [134] M. Asadollahi, D. Bastani, S.A. Musavi, Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: A review, *Desalination.* 420 (2017) 330–383. <https://doi.org/10.1016/j.desal.2017.05.027>
- [135] M.A.A. El-ghaffar, H.A. Tieama, A Review of Membranes Classifications, Configurations, Surface Modifications, Characteristics and Its Applications in Water Purification, *Chem. Biomol. Eng.* 2 (2017) 57–82.

- [136] N.D. Suzaimi, P.S. Goh, A.F. Ismail, S.C. Mamah, N.A.N.N. Malek, J.W. Lim, K.C. Wong, N. Hilal, Strategies in Forward Osmosis Membrane Substrate Fabrication and Modification: A Review, *Membranes*. 10 (2020) 332.
<https://doi.org/10.3390/membranes10110332>
- [137] Y. Zhou, S. Yu, C. Gao, X. Feng, Surface modification of thin film composite polyamide membranes by electrostatic self deposition of polycations for improved fouling resistance, *Sep. Purif. Technol.* 66 (2009) 287–294.
<https://doi.org/10.1016/j.seppur.2008.12.021>
- [138] M. Rezakazemi, A. Dashti, H.R. Harami, N. Hajilari, Inamuddin, Fouling - resistant membranes for water reuse, *Environ. Chem. Lett.* 16 (2018) 715–763.
<https://doi.org/10.1007/s10311-018-0717-8>
- [139] R.H. Hailemariam, Y.C. Woo, M.M. Damtie, B.C. Kim, K. Park, J. Choi, Reverse osmosis membrane fabrication and modification technologies and future trends: A review, *Adv. Colloid Interface Sci.* 276 (2020) 102100.
<https://doi.org/10.1016/j.cis.2019.102100>
- [140] A. Soleimany, S.S. Hosseini, F. Gallucci, Recent progress in developments of membrane materials and modification techniques for high performance helium separation and recovery: A review, *Chem. Eng. Process.: Process Intensificatio.* 122 (2017) 296–318. <https://doi.org/10.1016/j.cep.2017.06.001>
- [141] D. Li, Y. Yan, H. Wang, Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes, *Prog. Polym. Sci.* 61 (2016) 104–155. <https://doi.org/10.1016/j.progpolymsci.2016.03.003>
- [142] R. Reis, L.F. Dumée, L. He, F. She, J.D. Orbell, B. Winther-jensen, M.C. Duke, Amine Enrichment of Thin-Film Composite Membranes via Low Pressure Plasma Polymerization for Antimicrobial Adhesion, *ACS Appl. Mater. Interfaces*. 7 (2015) 14644–14653. <https://doi.org/10.1021/acsami.5b01603>
- [143] J. Wang, X. Chen, R. Reis, Z. Chen, N. Milne, B. Winther-jensen, L. Kong, L.F. Dumée, Plasma Modification and Synthesis of Membrane Materials - A Mechanistic Review, *Membranes*. 8 (2018) 56. <https://doi.org/10.3390/membranes8030056>
- [144] B.K. Chaturvedi, A.K. Ghosh, V. Ramachandhran, M.K. Trivedi, M.S. Hanra, B.M. Misra, Preparation, characterization and performance of polyethersulfone ultrafiltration membranes, *Desalination*. 133 (2001) 31–40.
[https://doi.org/10.1016/S0011-9164\(01\)00080-7](https://doi.org/10.1016/S0011-9164(01)00080-7)

- [145] E.M. V Hoek, A.K. Ghosh, X. Huang, M. Liong, J.I. Zink, Physical–chemical properties, separation performance, and fouling resistance of mixed-matrix ultrafiltration membranes, *Desalination*. 283 (2011) 89–99.
<https://doi.org/10.1016/j.desal.2011.04.008>
- [146] A. Bhattacharya, B.N. Misra, Grafting: a versatile means to modify polymers: techniques, factors and applications, *Prog. Polym. Sci.* 29 (2004) 767–814.
<https://doi.org/10.1016/j.progpolymsci.2004.05.002>
- [147] R. Bergamasco, P.F. Coldebella, F.P. Camacho, D. Rezende, N.U. Yamaguchi, M.R.F. Klen, C.J.M. Tavares, M.T.S.P. Amorim, Self-assembly modification of polyamide membrane by coating titanium dioxide nanoparticles for water treatment applications, *Rev. Ambient. Água*. 14 (2019). <https://doi.org/10.4136/ambi-agua.2297>
- [148] T. Sun, Y. Liu, L. Shen, Y. Xu, R. Li, L. Huang, H. Lin, Magnetic field assisted arrangement of photocatalytic TiO₂ particles on membrane surface to enhance membrane antifouling performance for water treatment, *J. Colloid Interface Sci.* 570 (2020) 273–285. <https://doi.org/10.1016/j.jcis.2020.03.008>
- [149] O.A. Williams, *Nanodiamond*, Royal Society of Chemistry, 2014.
<https://doi.org/10.1039/9781849737616>
- [150] B.S. Al-anzi, O.C. Siang, Recent developments of carbon based nanomaterials and membranes for oily wastewater treatment, *RSC Adv.* 7 (2017) 20981–20994.
<https://doi.org/10.1039/C7RA02501G>
- [151] C.D. Williams, P. Carbone, Selective Removal of Technetium from Water Using Graphene Oxide Membranes, *Environ. Sci. Technol.* 50 (2016) 3875–3881.
<https://doi.org/10.1021/acs.est.5b06032>
- [152] D.H. Seo, S. Pineda, Y.C. Woo, M. Xie, A.T. Murdock, E.Y.M. Ang, Y. Jiao, M.J. Park, S. Il Lim, M. Lawn, F.F. Borghi, Z.J. Han, S. Gray, G. Millar, A. Du, H.K. Shon, T.Y. Ng, K.K. Ostrikov, Anti-fouling graphene-based membranes for effective water desalination, *Nat. Commun.* 9 (2018). <https://doi.org/10.1038/s41467-018-02871-3>
- [153] H. Yang, R.Z. Waldman, Z. Chen, S.B. Darling, Atomic layer deposition for membrane interface engineering, *Nanoscale*. 10 (2018) 20505–20513.
<https://doi.org/10.1039/C8NR08114J>
- [154] E.F.D. Januário, N. de C.L. Beluci, T.B. Vidovix, M.F. Vieira, R. Bergamasco, A.M.S. Vieira, Functionalization of membrane surface by layer-by-layer self-assembly method for dyes removal, *Process Saf. Environ. Prot.* 134 (2020) 140–148.
<https://doi.org/10.1016/j.psep.2019.11.030>

- [155] J.H. Lora, W.G. Glasser, Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials, *J. Polym. Environ.* 10 (2002) 39-48. <https://doi.org/10.1023/A:1021070006895>
- [156] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, *Carbon.* 40 (2002) 2913–2920. [https://doi.org/10.1016/S0008-6223\(02\)00248-8](https://doi.org/10.1016/S0008-6223(02)00248-8)
- [157] S. Yang, T. Wang, R. Tang, Q. Yan, W. Tian, L. Zhang, Enhanced permeability, mechanical and antibacterial properties of cellulose acetate ultrafiltration membranes incorporated with lignocellulose nanofibrils, *Int. J. Biol. Macromol.* 151 (2020) 159–167. <https://doi.org/10.1016/j.ijbiomac.2020.02.124>
- [158] M. Nasrollahzadeh, S.M. Sajadi, A. Hatamifard, Waste chicken eggshell as a natural valuable resource and environmentally benign support for biosynthesis of catalytically active Cu/eggshell, Fe₃O₄/eggshell and Cu/Fe₃O₄/eggshell nanocomposites, *Appl. Catal. B: Environ.* 191 (2016) 209–227. <https://doi.org/10.1016/j.apcatb.2016.02.042>
- [159] X. Meng, D. Deng, Trash to Treasure: Waste Eggshells as Chemical Reactors for the Synthesis of Amorphous Co(OH)₂ Nanorod Arrays on Various Substrates for Applications in Rechargeable Alkaline Batteries and Electrocatalysis, *ACS Appl. Mater. Interfaces.* 9 (2017) 5244–5253. <https://doi.org/10.1021/acsami.6b14053>
- [160] X. Zhang, X. He, Z. Kang, M. Cui, D.-P. Yang, R. Luque, Waste eggshell-derived dual-functional CuO/ZnO/Eggshell nanocomposites: Photocatalytic reduction and bacterial inactivation, *ACS Sustain. Chem. Eng.* 7 (2019) 15762–15771. <https://doi.org/10.1021/acssuschemeng.9b04083>
- [161] C. Senthil, K. VEDIAPPAN, M. Nanthagopal, H. S. Kang, P. Santhoshkumara, R. Gnanamuthub, C. W. Lee, Thermochemical conversion of eggshell as biological waste and its application as a functional material for lithium-ion batteries, *Chem. Eng. J.* 372 (2019) 765–773. <https://doi.org/10.1016/j.cej.2019.04.171>
- [162] K. V. Peinemann, S.P. Nunes, L. Giorno, *Membrane Technology: Membrane for Food Applications*, Vol. 3, Wiley-VCH, 2010. <https://doi.org/10.1002/9783527631384>
- [163] S.R. Panda, M. Mukherjee, S. De, Preparation, characterization and humic acid removal capacity of chitosan coated iron-oxide-polyacrylonitrile mixed matrix membrane, *J. Water Process Eng.* 6 (2015) 93–104. <https://doi.org/10.1016/j.jwpe.2015.03.007>

- [164] Z. Alhalili, C. Romdhani, H. Chemingui, M. Smiri, Removal of dithioterethiol (DTT) from water by membranes of cellulose acetate (AC) and AC doped ZnO and TiO₂ nanoparticles, *J. Saudi Chem. Soc.* 25 (2021) 101282. <https://doi.org/10.1016/j.jscs.2021.101282>
- [165] M. Chaudhary, A. Maiti, Fe–Al–Mn@chitosan based metal oxides blended cellulose acetate mixed matrix membrane for fluoride decontamination from water: Removal mechanisms and antibacterial behavior, *J. Membr. Sci.* 611 (2020) 118372. <https://doi.org/10.1016/j.memsci.2020.118372>
- [166] A.M. Avram, P. Ahmadiannamini, A. Vu, X. Qian, A. Sengupta, S.R. Wickramasinghe, Polyelectrolyte multilayer modified nanofiltration membranes for the recovery of ionic liquid from dilute aqueous solutions, *J. Appl. Polym. Sci.* 134 (2017) 45349. <https://doi.org/10.1002/app.45349>
- [167] P. Wen, Y. Chen, X. Hu, B. Cheng, D. Liu, Y. Zhang, S. Nair, Polyamide thin film composite nanofiltration membrane modified with acyl chlorided graphene oxide. *J. Memb. Sci.* 535 (2017) 208–220. <https://doi.org/10.1016/j.memsci.2017.04.043>
- [168] P.O. Bagci, M. Akbas, H.A. Gulec, U. Bagci, Coupling reverse osmosis and osmotic distillation for clarified pomegranate juice concentration: Use of plasma modified reverse osmosis membranes for improved performance, *Innov. Food Sci. Emerg. Technol.* 52 (2019) 213–220. <https://doi.org/10.1016/j.ifset.2018.12.013>