



Application of nanotechnology and nanomaterials in water and wastewater treatment: membranes, photocatalysis and disinfection

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ABSTRACT

In recent decades, the introduction of novel and promising nano-materials for development of next generation of membranes of advanced antifouling and anti-scaling properties as well as for disinfection and photo-catalysis has been observed. Membranes made of these materials enable to obtain significantly higher water/permeate fluxes than thin film composite membranes currently used in membrane separation processes. Nano-materials such as silica, zeolites, metals (Ag, Zr and Ti) and metal oxides (TiO₂, ZrO₂, ZnO, Al₂O₃), metal-organic compound, and carbon-based materials, that is, carbon nanotubes (CNTs) and graphene-based materials are the most often applied for membrane modifications. In the paper, the state of the art in progress and challenges related to preparation of membranes made of nano-materials is presented. Novel composite membranes can be divided into two categories: (i) membranes made of only from graphene-based materials also known as freestanding membranes and (ii) polymeric/ceramic membranes modified with nano-materials. Modification of polymeric membranes can be made either by introduction of nano-material on a membrane surface or its addition to a membrane casting solution followed by membrane formation from a mixture of a polymer and a nano-material. The future prospect of membranes based on nano-materials in regard to the final separation efficiency and commercial scaling up has been discussed.

Keywords: Nano-materials; Membranes; Disinfection; Photo-catalysis; Review; Water and wastewater treatment

1. Introduction

The fresh water scarcity observed around the world forces science and industry to seek and develop more efficient and cheap strategies of water production from alternative resources, while these methods need to be environmental friendly and harmless to living organisms. An important role in this respect can play membrane separation processes, which, in recent decades, have become one of the non-conventional techniques used to solve fresh water scarcity issues [1]. In comparison with conventional water

and wastewater treatment processes, membrane processes are environmental friendly and energy efficient. Moreover, they can be used in combination with conventional methods as well as single-stage processes [2]. Crucial features of membrane water treatment and water reclamation include high automation level, compact installation sizes, lower consumption of chemicals and module configuration enabling flexible design [2]. Ideal membrane should characterize with controllable pore size, high hydraulic permeability, high selectivity and chemical resistance in wide pH range. The dependence between membrane selectivity and

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permeability is a serious challenge for membrane technologies exploitation. Not only membranes fouling and lifetime of membranes themselves are significant issues but also modules are significant issues, as they affect energy consumption and complicate design and exploitation of the overall treatment system [2]. Energy consumption is very important in regard to commercial use of pressure-driven membrane processes. The efficiency of membrane systems depends mainly on membrane material and membrane thickness as well as on the possibility of membrane physico-chemical properties.

Different membrane techniques such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), electro-dialysis, membrane distillation and extraction, pervaporation, capacitive deionization, and forward osmosis (FO) can be used for water and wastewater treatment [2,3]. RO process is a crucial method of water desalination and it is more and more often used in water reclamation as the third stage of municipal wastewater treatment [1–4]. Despite relatively good recognition and advantageous features of water and wastewater treatment, including operational costs, environmental impact and limited possibilities of water pretreatment as well as used membrane recovery, the growing interest in development and modification of these processes is observed [4].

The crucial area of research in membrane desalination and water and wastewater treatment is focused on the development of novel, semipermeable membranes of improved separation efficiency and antifouling character [3,5]. The next generation of membranes should meet requirements of treatment of specific water types by their proper design or rather tailoring, what includes structure and physicochemical properties, hydrophilicity, porosity, charge and thermal and mechanical stabilities as well as introduction of novel features such as antibacterial, photocatalytic and adsorptive ones. The recent analysis has shown that for example RO membranes of three times higher water permeability allow for 15% of energy saving and 44% decrease of volume of pressurized tanks currently used in seawater desalination plant [6]. In case of wastewater treatment, even higher savings can be obtained (e.g., 45% decrease in energy consumption and 63% decrease in pressurized tanks volume) [6]. Moreover, the selectivity improvement results in production of water of better quality. Additionally, membranes of improved antifouling features allow for the decrease of cleaning frequencies and elongate membrane lifetime.

In recent years the growing interest in the use of nano-materials to development of next generation of membranes of advance antifouling and anti-scaling properties for water and wastewater treatment has been observed [7–14]. The development of nano-materials and nanotechnology enables improvement of both membrane structure and transport characteristics. The most popular materials used for membrane modifications are silica, zeolites, metals (Ag, Zr and Ti) and metal oxides (TiO_2 , ZrO_2 , ZnO , Al_2O_3), metal-organic compound [8], aquaporin (AQP) type proteins [11] and carbon-based materials, that is, graphene and graphene oxide [9,10] as well as CNTs [12,13]. These modern materials assure new possibilities for design and manufacture of next generation of semipermeable membranes. The introduction of functional nano-materials to a membrane

structure allows for improvement of permeability fouling resistance, mechanical and thermal stability as well as self-cleaning.

2. Conventional and novel membrane materials

The first asymmetric RO membranes were made of cellulose acetate and next they were mostly replaced by thin film composite (TFC) membranes with of polyamide (PA) skin layer [15]. In comparison with cellulose acetate membranes, polyamide TFC membranes characterize with higher water permeability and better salts rejection (e.g., for some RO membranes NaCl rejection may be >99.9%), wider temperature range (0–45°C) and better tolerance to operational pH (pH 1–11). Typical TFC membrane comprises of three layers (Fig. 1): dense, polyamide retention layer (skin/active layer), porous support usually made of polysulfone (PSF) or polyethersulfone (PES) and non-woven fabric for mechanical stability enhancement. PA skin layer, which defines that water permeability and rejection of salts may be prepared by interfacial polymerization (IP) of amine monomer in water phase and acyl chloride monomer in organic phase. Different methods of optimization of structure and chemical nature of TFC polyamide membranes are used in order to increase their separation efficiency and anti-fouling properties. Typical methods cover change of type and concentration of monomer, modification of a membrane surface and final processing of manufactured membrane [16,17]. However, many of these methods allow for insignificant improvement of separation properties, while permeability of water of currently used TFC membranes remains relatively low. Except for that, other disadvantages of commercial TFC membranes are low selectivity and high affinity to fouling [18] as well as mechanical and chemical instability [19]. For example, water permeability of typical RO membranes of TFC type varies from about 1 to 2 L/m²h bar for RO membranes used in seawater desalination (SWRO) and ~2 to 8 L/m²h bar for RO membranes used in brackish water desalination (BWRO).

The significant improvement of TFC membrane, developed in 2007, relied on introduction of porous zeolite nanoparticles (NaA) of pore size ~0.4 nm to polyamide skin layer during IP process [20]. In the membrane structure, which was named as thin film nano-composite, porous zeolite nanoparticles assured preferable water transportation pathways, lowered hydraulic resistance and influenced on retention of dissolved salts according to sieving mechanism, that is, the ratio of particles size to membrane pore size. In Fig. 1, the structures of TFC membrane and thin film nano-composite (TFN) membrane are compared.

3. Membranes with inorganic nanoparticles

Inorganic nano-materials usually used in TFN membrane synthesis comprise of zeolites [20], titanium dioxide [21], titanium-magnesium oxide [22], silicon dioxide [23], magnesium oxide and aluminum, silver [24], zirconium [25] and other. The production of membranes with inorganic nanoparticles is based either on introduction of nano-materials to active layer of TFC membranes by means of surface modification method or on their introduction to membrane matrix

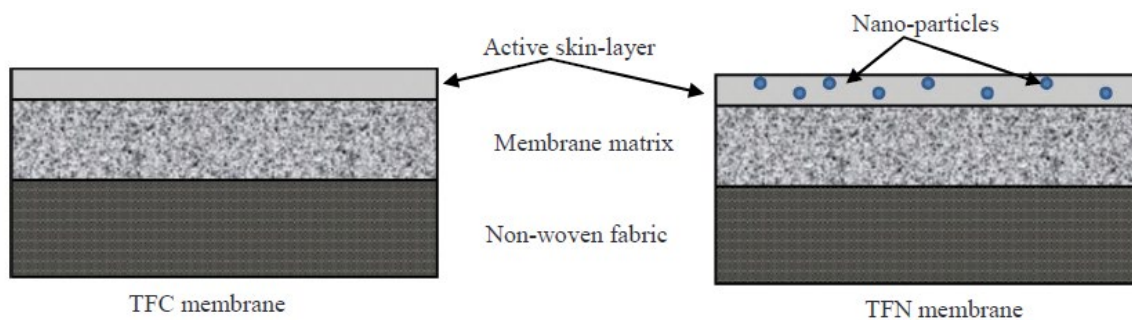


Fig. 1. Schemes of structures of thin film composite (TFC) membrane and thin film nanocomposite (TFN) membrane.

during phase inversion production process [1,5]. Membranes modified with nano-materials often show improvement in water permeability, higher hydrophilicity, surface charge change, proper salt retention and antibacterial, antifouling and anti-scaling properties in comparison with non-modified, reference membranes. The impact of nanoparticles on permeability and selectivity of a membrane depends on type, size and amount of added nanoparticles [5].

3.1. Metal oxide nanoparticles

Nano-zeolites are the most often used in TFN membrane preparation, as they allow the formation of more permeable, negatively charged and thicker active layer of polyamide [26], due to large specific surface, hydrothermal stability and high number of micropores. The permeability of water revealed by TFC membranes containing zeolite is almost twice as high as the one of conventional TFC membranes (without zeolite). Moreover, NaCl retention coefficient remains unchanged ($93.9\% \pm 0.3\%$ for TFN vs. $93.4\% \pm 1.1\%$ for TFC) [20]. Nano-zeolites have also been used as antibacterial substances carriers, including Ag^+ ions, which give antifouling properties to a membrane. Dong et al. [20] introduced zeolite to PSF membrane, which allowed for membrane hydrophilicity improvement and limitation of growth and reproduction of microflora, and thus the membrane gained bacteriostatic properties. Zeolites are also widely applied as nano-fillers in gas separation and pervaporation membranes [27]. The addition of zeolite nanoparticles can be simply adapted to existing membranes manufacturing lines, which are originally designed to produce polyamide TFC membranes [5]. Hence, TFN membranes with zeolite have gained early commercialization stage (e.g., zeolite-based membranes LG NanoH2O®). QuantumFlux TFN membranes for seawater desalination by means of RO method are also available on the market [5].

Nano-silica is an inorganic material of narrow particles pore size distribution and large specific surface. Its introduction to a membrane structure is expected to improve membrane lifetime and chemical resistance. Kebria et al. [28] have prepared ultra-thin composite NF membranes by adding nano-silica to membrane casting solution. The measured water flux has equaled $13.3 \text{ L/m}^2 \text{ h}$, but the removal of crystal violet had slightly decreased in comparison with the reference membrane. Yin et al. [29] have found that by using mesoporous silica particles of pore size up to 3 nm, TFN membranes of increased water flux can be obtained, whereas

the retention remains unchanged compared with reference TFC membranes. For example, composite membrane made of polyvinylidene fluoride (PVDF) containing silica nanoparticles are highly stable at high temperature and more selective in water treatment [30]. Another example covers embedding of silica nanoparticles in PSF membrane, for which increased gas permeability is observed [31]. Membranes made of polybenzimidazole conjugated with silica nanoparticles may be used in selective gas separation [32]. Zhang et al. [33] have described the synthesis of composite NF membrane of tetra-*n*-butyl titanate/polyethyleneimine/silica type by means of mineralization. The obtained results suggest that the presence of nanoparticles in active layer of the composite membrane increases the resistance to organic solvents, improves retention, does not affect solvent permeability and promises long-term exploitation stability.

Mollahosseini and Rahimpour [21] have developed thin film nano-composite NF membranes by covering the PSF matrix with thin skin containing nano-titanium dioxide (TiO_2) using IP (with trimezoyl phenyldiamine chloride). Antifouling properties of the developed membrane have been investigated during water and pepsin solution filtration. NaCl retention of the NF membrane has increased from 70% to 84% for membrane modified with TiO_2 . Antibacterial, antifouling and photocatalytic properties as well as permeability have been improved by introduction of TiO_2 nanoparticles. Hoseini et al. [34] have used TiO_2 nanoparticles containing different amounts of cobalt (12–15 nm) to prepare photocatalytic membranes made of PES by means of phase inversion. The impact of nanoparticles concentration on membrane's separation efficiency and photocatalytic degradation has been observed. Permeability tests have confirmed that the addition of TiO_2 nanoparticles containing 1.34 wt.% Co to PES matrix improves 2,4-dichlorophenol degradation and permeate flux. The best separation results (flux: $7.62 \text{ L/m}^2 \text{ h}$ and retention: 96.62%) have been reached for a membrane containing 1 wt.% of Co/ TiO_2 nanoparticles (1.34 wt.%), which has been radiated with visible light. Kowalik-Klimczak et al. [35] have presented results of the research on the modification of polyamide membranes with the use of titanium dioxide (TiO_2) nanoparticles and zinc oxide (ZnO) nanotubes, in order to make the membranes resistant to biofouling. To activate the flat-sheet membranes plasma processing in argon (Ar) and mixture of argon and oxygen (Ar/ O_2) has been applied. It has been found that due to applied modification, the obtained membranes are characterized with more advantageous

filtration properties than the native materials. Moreover, membranes modified with nano-ZnO reveal stronger antibacterial properties than membranes modified with nano-TiO₂. Esfahani et al. [36] have investigated properties of UF membrane made of PSF with admixture of nano-TiO₂ and single-walled CNTs. The results have shown that the membrane changes its properties in dependence of the amount of introduced nanoparticles. When the ratio of nano-TiO₂ and single-walled CNTs equals 1:1 (1 wt.% in total), the obtained membrane characterizes with the highest permeability, the highest humic acid retention coefficient and antifouling character.

Membranes made of nano-ferric oxide and mixed polymers, that is, PES and polyaniline nanoparticles have been prepared using phase inversion method and the amount of nanoparticles has been modified [1]. It has been noticed that membrane containing 0.1 wt.% of nanoparticles reveals the maximum removal of copper(II) at the lowest pure water flux. It is caused by the fact that nanoparticles placed in surface pores of a membrane during its preparation block the pores entrance. The research with scanning electron microscope and atomic force microscope has showed that separation mechanism is based on adsorption. Szymański et al. [37], by using wet-phase inversion method, have prepared PES membranes modified with nanoparticles of Fe₃O₄-trisodium citrate (FeCTNC). It has been found that the addition of 1 and 2 wt.% of FeCTNC results in the maximum permeate flux obtained during UF of pure water in reference to results obtained for non-modified membrane. The analysis of fouling in BSA presence has shown that membranes modified with 1 and 3 wt.% of FeCTNC were characterized with much improved permeate flux in reference to non-modified membranes. In case of membranes modified with higher amount of FeCTNC (4 wt.%), significant fouling has been observed. Atomic force microscope and SEM analysis have enabled to find that membranes modified with 1 and 2 wt.% of FeCTNC contain small aggregates of nanoparticles, while membrane modified with 4 wt.% of FeCTNC contains large aggregates.

Zinc oxide (ZnO) is one of the main multifunctional semiconductor and due to its excellent electrical, mechanical, optical and chemical properties it is very important photocatalyst and antibacterial material. Advantageous features of nano-ZnO are low costs and high surface to volume ratio. Due to these characteristics, which is accompanied with high thermal stability, nano-ZnO is used in modification of TFC membranes. Moreover, introduction of nano-ZnO to a membrane matrix may solve fouling issues of a membrane [1]. The recent research have shown that UF membranes made of a mixture of ZnO nanoparticles and PVC are characterized with low contact angle and higher hydrophilicity, what results in high water flux [38]. However, inorganic nano-materials have a tendency to agglomerate in polymeric matrix and even in a solvent. One of the methods of limitation of agglomeration and nanoparticles dispersion improvement is their mixing with graphene, carbon nanotubes (CNTs) or other materials [7]. Composite hollow fiber (CHF) NF membranes have been modified by introducing ZnO nano-spheres to poly(piperazine-amide) layer during IP [39]. Active layer has been formed on an internal surface of PSF membrane by means of double coating. The impact of ZnO

nano-spheres on membrane capacity, including hydrophilicity, separation efficiency and resistance to chlorine has been investigated. The results have shown that modified CHF membranes of low concentration of ZnO nano-spheres (1.5 wt.%) have characterized with higher capacity (33.8 L/m² h) and good retention of MgSO₄ (92.2%) at 0.7 MPa pressure. ZnO nano-spheres have also allowed for better resistance of NF composite membrane to chlorine in regard to reference membrane, which have not contained ZnO. Novel composite membranes composed of chitosan/ZnO nanoparticles (CS/nano-ZnO) have been prepared by casting of solution containing all components, whereas nano-ZnO have been dispersed in chitosan matrix [40]. The results of the research have shown that nano-ZnO influences on mechanical properties of CS/nano-ZnO membrane and antibacterial resistance of membranes containing 6–10 wt.% of ZnO toward *Bacillus subtilis*, *Escherichia coli* and *Staphylococcus aureus* are significantly improved.

Modified UF membranes made of PVDF have been obtained by means of phase inversion method using solution containing dispersed nanoparticles of aluminum oxide (Al₂O₃) [41]. The impact of Al₂O₃ nanoparticles concentration in polymeric solution on permeation efficiency, mechanical strength and antifouling features of a membrane has been investigated. The experimental results have indicated that composite Al₂O₃-PVDF membranes reveal significant differences in surface and transport properties in regard to reference PVDF membrane. The research on UF membranes made of PES containing Al₂O₃ in regard to fouling prevention in membrane bioreactors, has been carried out [42]. The efficiency of the membrane has changed due to the addition of Al₂O₃ nanoparticles to membrane casting solution and the capacity decrease has not been as significant as in case of PES only membrane. The increase of permeate flux observed for modified membrane has been assigned to surface hydrophilicity and increased filtration surface caused by addition of hydrophilic Al₂O₃ nanoparticles. The higher hydrophilicity of the composite membrane has also improved its antifouling features. Additionally, the permeate flux increased at 0.1 MPa filtration has corresponded to only 18.2% of the decrease noted for non-modified membrane.

3.2. Metal nanoparticles

Nanoparticles and ions of silver are historically found as efficient antibacterial agents and are used for the modification of membranes and biofouling prevention [43]. Such an effect is obtained due to release of Ag⁺ ions and generation of products containing reactive oxygen species [44]. Antibacterial action of silver nanoparticles can be controlled and in contrast to silver ions it is permanent.

Ben-Sasson et al. [45] have presented a novel method of introduction of Ag nanoparticles on TFC RO membrane surface. The reaction of silver salt with a reducer on a membrane surface has resulted in uniform and irreversible coating of the surface with Ag nanoparticles. Retention of salts as well as surface roughness, hydrophilicity and zeta potential has remained unchanged after Ag nanoparticles introduction, while slight decrease in permeability (to 17%) has been observed. The layer of nanoparticles formed at the membrane surface has resulted in strong antibacterial

properties, what has been confirmed by 75% reduction of amount of three species of model bacteria attached to the surface.

Yang et al. [46] have proposed modification of RO membrane surface as well as spacers in the membrane module with nano-silver layer. Modified membranes and spacers have been tested in regard to their antifouling properties in flat-sheet module operated. The obtained results have shown that permeate flux decrease during filtration has been much lower in case of coated membrane than in case of non-modified one, while the retention of salts has been slightly higher. Additionally, the antibacterial effect of membranes coated with silver has been obtained and neither on the membrane nor on spacer any growth of bacteria has been detected, while bacteria cells attached to the membrane has been quickly deactivated.

Zodrow et al. [47] have introduced silver nanoparticles to the UF membrane made of PSF (nAg-PSF) in order to make the membrane efficiently resistant to wide range of bacteria, including *E. coli* K12, *Pseudomonas mendocina* KR1 and bacteriophages MS2. The introduced nano-silver has also increased the membrane's hydrophilicity making it less susceptible to another type of fouling. XPS analysis has shown some silver losses on the membrane surface after relatively short filtration, what has caused significant losses of antibacterial and antiviral efficiency.

Antibacterial UF membranes made of PSF have been prepared by introduction of different silver nanoparticles to the casting solution [48]. Additionally, SEM analysis has also shown that addition of silver nanoparticles causes decrease of pores entrance. From the SEM images, it can be observed that dense spots in membrane cross section are formed after addition of 2 wt.% of nanoparticles of 30 nm size. Moreover, it has been found that silver nanoparticles of size 70 nm increase roughness of the membrane surface in contrast to silver nanoparticles of size 30 nm. The filtration of bacteria containing solution has showed that membrane with smaller silver nanoparticles possesses better antibacterial activity.

Moziak et al. [49] have investigated the impact of titanate nanotubes modified with silver (Ag/TNT) on transport and antibacterial properties of UF membranes made of PES formed by means of wet phase inversion method. For membrane modification, Ad/TNT of different silver content equal to 2.83, 4.72, 7.26, 11.44 and 13.21 wt.% has been used. In order to determine antibacterial efficiency of Ag/TNT, the research with *E. coli* and *Staphylococcus epidermidis* used as model bacteria has been carried out. The highest antibacterial activity has been revealed by membranes containing 11.44 and 13.21 wt.% of Ag, whereas for non-modified membranes any zone of antibacterial activity has not been observed. The permeability of non-modified membrane has been measured as 147 L/m²h bar, while for membranes containing 11.44 and 13.21 wt.% it has been 178 and 195 L/m² h-bar, respectively.

In order to minimize biofouling, MF membranes made of PES have been prepared by means of phase inversion method, while silver nanoparticles (AgNps) have been synthesized by chemical reduction and introduced to MF membranes [50]. Antibacterial properties have been analyzed in reference to *Pseudomonas fluorescens*. 20%–30% limitation of

activity of microorganisms has been observed. The permeate has been analyzed in regard to total number of bacteria of coli group and the removal rates have been established at 99.9% and 99.999% for non-modified and modified membranes, respectively.

3.3. Summary

Despite the fact that inorganic nanomaterials possess many advantages in regard to water treatment, their application is limited to laboratory scale. Membranes, which are to be used in food and water production industries must additionally correspond to specific industry standards and safety rules. Hence, the impact of discussed inorganic nanomaterials on human health and safety in reference to amount/concentration of nanoparticles acceptable for human bodies [51,52]. The use of nanoparticles of less toxic substances, such as Mg(OH)₂, CaCO₃ and hydrated MnO₂ has been recently discussed in literature [53–55]. However, more available and less toxic materials such as carbon-based nanotubes have dominated other nano-materials in membranes production.

In Table 1 the use of some inorganic nanomaterials to improve efficiency of NF membranes of desalination is shown [20–24].

4. Membranes made of carbon-based nanomaterials

Allotropic forms of carbon, that is, CNTs [56–59], graphene-based nanomaterials [60,61], that is, nanoporous graphene (NPG) [60–63] and graphene oxide (GO) [64,65] are novel nano-materials, which possess huge potential in sustainable development of membrane technologies, especially in regard to desalination and water and wastewater treatment. They have also been found to be very promising membrane materials, due to their unique and advantageous features such as water transport rate through films containing CNT, NPG and GO (Table 2) [66–68]. Additionally, they characterize with high chemical, thermal and mechanical resistance, high conductivity, low density and specific optical properties. Retention properties of films containing carbon-based nanomaterials are strongly dependent on size of channels to water transport as well as on chemical modifications (e.g., presence of functional groups) [67,68]. Characteristic dimensions of channel in CNT and NPG are regulated with proper pore sizes. In contrast to CNT and NPG, for which channels dimensions are related with synthesis conditions, characteristic GO channels dimensions mostly depend on its oxidation and solution properties [68]. Unique hybridization features of carbon-based nanomaterials enable preparation of membranes for different separation processes.

Novel composite membranes to desalination and water and wastewater treatment made of CNT, NPG and GO can be divided into two categories [66]:

- Membranes made only of CNT, GO or NPG, known also as freestanding,
- Polymeric membranes modified with CNT, GO or NPG.

In the first group, nanomaterial is directly used as a separation layer, while in the second nano-material is used for

Table 1
Inorganic materials introduced to polymeric membranes and their effectiveness

Nano-material	Nanoparticles size	Nanomaterial properties	Membrane polymer	Nanoparticles effect	Membrane efficiency
Zeolites	80 nm	Porous structure	Polysulfone, polyamide	Increases surface roughness and number of pores	Increases water permeability
TiO ₂	20 nm	Hydrophilicity photocatalysis	Polysulfone	Increases hydrophilicity and antibacterial activity	Increases salts retention, antibacterial antifouling properties
MgTiO ₃	80 nm	Hydrophilicity	Polysulfone, polyamide	Increases hydrophilicity and roughness	Increases flux and salts retention
SiO ₂	235 nm	Hydrophilicity	Polysulfone, polyamide	Increases hydrophilicity and roughness	Increases salts retention and selectivity of ions
ZrO ₂	20 nm	Hydrophilicity	Polyacrylonitrile	Uniform (10–20 nm) active layer of high hydrophilicity	Increases flux and bivalent ions retention
Titanate	8–12 nm	Porous structure	Polyetherimide	Increases hydrophilicity, density and surface of pores	Increases salts retention and antifouling properties
Silver	35–45 nm	Antibacterial	Polysulfone	Strong antibacterial efficiency	Improves antibacterial activity
ZnO	50 nm	Hydrophilicity	Polysulfone	High hydrophilicity	Increases salts retention and antifouling properties

Table 2
Properties of membranes made of polyamide, CNT, nanoporous graphene and graphene oxide

Feature	Polyamide	CNT	Nanoporous graphene	Graphene oxide
Material	Cross-linked polymer	1D carbon material	2D carbon material	2D carbon material
Transport mechanism	Solution-diffusion	Sieving and electrostatic repulsion	Sieving and electrostatic repulsion	Sieving and electrostatic repulsion
Characteristic dimension of channel	Non regular pores random in matrix, pore size ~0.4–0.58 nm, sometimes non uniform pores distribution	Well-defined pores, e.g., 1.3–2.0 nm. Pores density $<2.5 \times 10^{11}/\text{cm}^2$, length ca.3 μm .	Nanopores across graphene layer of 1 atom thickness, non-uniform pore size possible (e.g., ones obtained by plasma digestion ~5–10 Å)	Channels formed from neighbor hooding GO layers, channels dimensions depend on oxidation rate and surrounding properties
Separation properties	~1 to 2 L m ⁻² h ⁻¹ bar ⁻¹ for SWRO and ~2 to 8 L m ⁻² h ⁻¹ bar ⁻¹ for BWRO; NaCl retention ~>99% (basing on cross-flow tests)	Permeability of gases >10 times higher than one resulting from diffusion model. Permeability of water 1,000 times higher than one resulting from hydrodynamic model	~3.6 × 10 ⁶ L m ⁻² h ⁻¹ bar ⁻¹ ; practically 100% KCl retention (40°C sample of diameter 5 μm , dead-end system)	Water permeability 10 ¹⁰ times higher than for helium; water permeability and retention depend on distance between layers
Antifouling properties	Susceptible to fouling	Antibacterial	No data	No adhesion of substances and micro-organisms

the modification of membrane surface or nanoparticles are introduced to polymeric matrix.

4.1. Freestanding GO/NPG membranes

Freestanding membranes made of GO/NPG may be described as a set of nano-sheets, which are arranged in a series of layers, packed and situated one on another and properly distanced from each other [4]. Water/solvent molecules are transported through neighbor hooding nano-channels, while dissolved substances are retained (Fig. 2). The effective thickness of one nano-sheet of GO/NPG equals 0.5 nm, while the site thickness may vary from hundreds of nanometers to dozens of micrometers [65]. Freestanding GO/NPG membranes are flexible and mechanically stable [69–71].

The most often used methods of preparation of freestanding membranes based on GO/NPG cover filtration, self-assembly, layer by layer (LBL), spray or spin coating, GO/NPG nano-sheets casting or electric field induced method [9,64,69,71–74]. Filtration method comprises of covering of GO/NPG on porous membrane (usually UF or MF) at pressurized or vacuum conditions followed by filtration and drying [75,76] in order to obtain membrane with porous layer. This method can be used for the preparation of GO/NPG containing membranes of thickness from several nanometers to several microns, however the connection between neighbor hooding layers is weak and thus the stability of a membrane is poor. Self-assembly layer by layer method of films preparation relies on alternate imposing of charged substances on oppositely charged substrate surface [77]. The sequential adsorption of charged polymers and/or nanoparticles is a valuable technique of formation of thin multilayers.

Different techniques of vacuum filtration have been used for the preparation of GO/NPG membranes with proper distances between nano-sheets [78]. Nair et al. [79] have minimized distances between GO/NPG to 1 nm using spray or spin coating method and stable solutions of GO/NPG are dispersed in water. The prepared membranes are completely impermeable to gases, vapors and liquids, including helium, while the permeation of water has been unlimited. Additionally, the permeability of water through the membrane has been 10^{10} times higher than for helium

due to almost frictionless flow of monolayer of water through 2-D capillaries between graphene sheets placed in close distance one from another [79]. It has also been shown that hydroxyl and epoxide functional groups attached to GO/NPG nano-sheets are responsible for keeping distance between sheets [80].

Permeability of water in GO/NPG membranes is a function of pore size and distance between sheets. Boehm et al. [81] have shown that distances between nano-sheets elongate after immersion in polar liquid, for example, sodium hydroxide solution. Xu et al. [82] have stated that water flux and selectivity of GO/NPG membranes depend on interlayer nanostructure of a membrane. The increase of porosity and surface of edges of nano-sheets may influence higher permeability of freestanding GO/NPG membranes. The action of OH^* radicals on GO/NPG sheets causes elimination of carbon atoms placed at edges (as CO_2) and inside GO sheet (as CO) and lace like edges and nano-pores on membrane surface are formed [83].

The elongation of distances between GO/NPG sheets can be partially prevented by thickening of films, what allows for filtration of hydrated ions of smaller radius. To water desalination, distances between GO sheets should be shorter than 0.7 nm in order to reject hydrated Na^+ ions [65]. Mi [84] have stated that distances between nano-sheets can be decreased by GO reduction or by covalent binding of small particles with GO sheets, what allows for overcoming of hydration forces. For example, GO membrane after carboxylation with glycine (GO-COOH) reveals higher retention of salt and permeability as negative GO-COOH surface favors electrostatic repulsion, characterizes with increase hydrophilicity and higher number of channels for water transport [85].

Freestanding membranes made of GO can be used in water desalination process [86]. They allow for complete retention of salt whereas water permeation is twice as high as one observed for commercial RO membrane due to very low thickness of GO membrane (ca. 10 nm). Cohen-Tanugi and Grossman [87] have suggested that layer of graphene with nano-pores of diameter below 0.55 nm can be used for water desalination and retention of salt is higher than one of the commercial RO membranes. They have also stated that permeability of water through ultrathin freestanding GO membranes of up to 10 nm thickness equals to

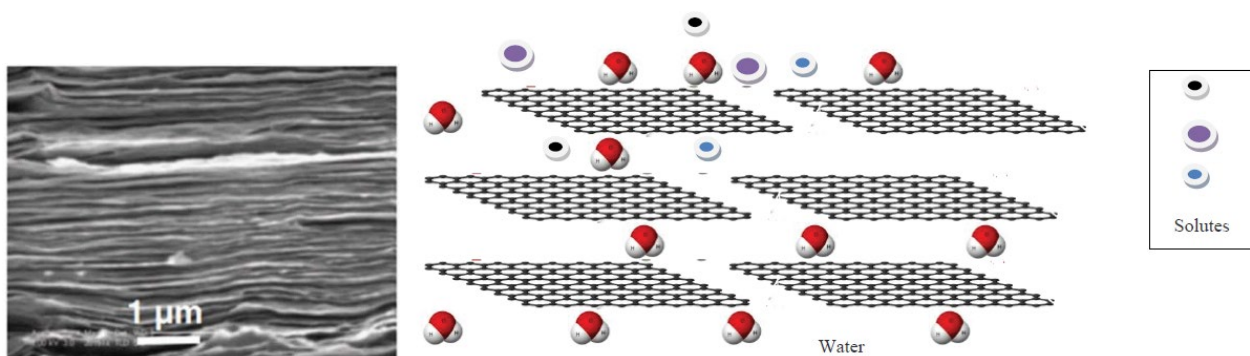


Fig. 2. Scheme of graphene oxide, SEM image of graphene oxide and the scheme of transport mechanism through graphene oxide system (<https://commons.wikimedia.org/wiki/File:Graphite-sheet-side-3D-balls.png>).

400 L/m² d MPa, that is, several orders of magnitude more than in case of commercial RO membranes. On the other hand, Han et al. [88] have stated that NF GO membranes are characterized with the water flux of 21.8 L/m² h and 40% salt retention. The poor retention has been explained by the presence of open cracks, the appearance of which has been related with GO sheets preparation. Hu and Mi [65] during their research with graphene membrane have also obtained low retention of salt, which has varied from 6% to 46%, but it has been accompanied with high flux in the range of 80 to 276 L/m² h·MPa in dependence of a number of GO nano-sheets. However, at the presence of NaCl and Na₂SO₄ distance between GO layer decrease in regard to solution ionic strength (ca. 1–2 nm at 100 mM) due to their hydration and impact of charge, which compresses electric layer, what often allows for transport of K⁺ and Na⁺ disabling its use to water desalination [89].

Xu et al. [90] have used vacuum filtration technique to form GO/TiO₂ membranes by introduction of TiO₂ nanoparticles between GO nano-sheets. The presence of oxygen containing functional groups enables easy dispersion of GO nano-sheets in water. The average pores diameter of prepared membrane has been equal to 3.5 nm. It has been found that TiO₂ nanoparticles interact with GO nano-sheets what finally elongates distance between nano-sheets and enlarges channels dedicated to water transport through the membrane. GO-TiO₂ nanofiltration membranes are characterized with complete retention of methyl and rhodamine B what confirms their usability for the removal of dyes from water.

4.2. Freestanding CNT membranes

Two main types of CNT freestanding membranes may be distinguished, that is, isoporous and buckypaper ones [91]. Isoporous membranes are formed from adjusted cylindrical pores in impermeable matrix, what forces the flow of liquids only through empty interiors of CNTs. On the other hand, buckypaper membranes may be described as randomly distributed CNTs in non-woven structure similar to paper [91]. The main advantages of such CNT membranes are the presence of very large porous 3D net and large specific surface.

Isoporous CNT membranes have been first manufactured by Hinds et al. [12]. The obtained membranes have been characterized with the fluid flux 2–3 orders of magnitude higher than the one resulted from fluids flow theory. Vertically oriented CNTs have been introduced to polymeric foil forming nano-porous membrane structure, what has been confirmed by SEM images, gas permeation and investigations on transport of ions [12]. It has also been noted that CNT selectivity and fluids flow control through CNT pores may be increased by CNT edges functionalization [92]. Holt et al. [67] have examined isoporous CNT membranes of pore size 2 nm and they have stated that gas flux exceeds values predicted by Knudsen diffusion model by the order of magnitude, whereas water flux is three orders of magnitude higher than the value predicted by hydrodynamic model. Similarly, water permeability through isoporous CNT membranes has been several orders of magnitude higher than the one determined for polycarbonate commercial membranes despite the pore

size has been order of magnitude smaller, what increases selectivity and flux of these membranes [67]. Hummer et al. [92] have shown that the chain of water particles may permeate fast, frictionless through CNT, what results from hydrogen bonds present in water particles chain, which are introduced to hydrophobic interior of CNT, while interactions between carbon and water particles occurring inside CNT are insignificant. Thomas and McGaughey [93] have been found that increase of CNT diameter from 0.66 to 0.93 nm decreases retention ions from 100% to 95%. On the other hand, decrease of CNT radius from 0.34 to 0.39 nm assures permeation of water to CNT interior, and causes retention of sodium and chloride ions [94].

CNT membranes of “buckypaper” type are prepared with the use of methods such as vacuum filtration [95], layer by layer (LBL) [96] or electrospinning [97]. Peng et al. [95] have formed freestanding CNT membranes using vacuum filtration of suspension of oxidized SWCNTs through polycarbonate membrane (Fig. 3). After immersion in ethanol ultrathin films have been removed from polycarbonate (PC) support. The obtained CNT membranes have had thickness of several dozens to several hundred nanometers. The authors suggest that freestanding CNT films with well-defined nanostructure may potentially be widely used in membrane separation, sensors and catalysis [95].

Dumée et al. [98] have prepared freestanding CNT membranes to direct contact membrane distillation. Self-supporting membrane has been prepared using MWCNTs of diameter range 10–15 nm and length 150–300 μm. Vacuum filtration through 0.2 μm PES support followed by flaking of imposed layer has resulted in the formation of freestanding CNT membranes. They have been characterized with higher porosity (90%), hydrophobicity (contact angle 113°), heat flux (2.7 kW/m² h) and salt retention equal to 99% and distillate flux equal to 12 kg/m² h (seawater 35 g NaCl/L) in comparison with polytetrafluoroethylene (PTFE) membrane [98]. Bhadra et al. [99] have used MWCNTs functionalized with –COOH groups for the preparation of freestanding CNT membrane dedicated to membrane distillation (MD). The use of MWCNTs with carboxylic groups increases polarity and interaction between membrane surface and water vapor, what results in the increase of MD-based desalination. Distillate flux equal 19.2 kg/m² h measured for MWCNT membrane is higher than the one obtained for conventional membranes made of PVDF.

4.3. Modification of polymeric membranes using CNT/GO/NPG

If nano-material (CNT/GO/NPG) is properly connected with polymeric [100] or ceramic [58] matrix, that properties of obtained composites are more advantageous in regard to non-modified membranes and novel material can be used in various membrane processes, that is, RO, nanofiltration, ultrafiltration, gas separation and pervaporation [101,102]. Nanomaterial can improve mechanical, antifouling and surface properties in hybrid polymeric membranes. This improvement of CNT/GO/NPG containing membranes is related to hydrophilic character of some functional groups present in nanomaterial [103].

A modification of polymeric membranes may be made by introduction of a nanomaterial either to a membrane's

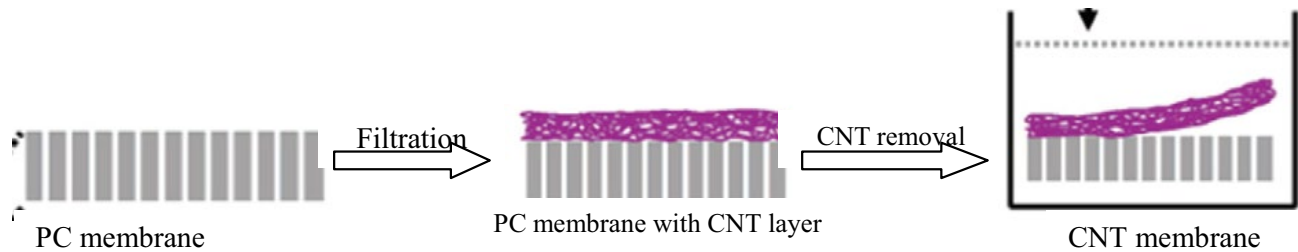


Fig. 3. Preparation of freestanding CNT membrane.

surface or to casting solution followed by membrane formation from the mixture of a polymer and a nano-material [66].

4.3.1. Modification of polymeric membranes surface

Modification of a membrane surface may be performed by direct imposition of nanomaterial by means of layer by layer method, vacuum filtration [64,73] or IP with TFC membrane surface resulting in the formation of TFN membrane [104]. Preparation of membranes by introduction of nanomaterial on membrane surface by means of covalent [105], electrostatic [106] or coordination bonding in order to increase separation efficiency may also be applied. Modification of polymeric or ceramic membrane surface using graphene and its derivatives may improve membrane properties, including antifouling and antibacterial ones [107]. Additionally, membranes with modified surface are more resistant to chlorine, while the effectiveness of membrane process is maintained. Modification of membrane surface requires relatively low amount of nanomaterial, what is economically beneficial and limits the impact of nano-material production on environment.

Wang et al. [64] have prepared membranes containing GO on support made of polyacrylonitrile nano-fibers using vacuum filtration of GO suspension. The obtained membranes have revealed high retention of dyes (ca. 100% of Congo red) and moderate retention of bivalent ions equal 56.7% for Na_2SO_4 , while water permeability has been measured at 2 L/m^2 h bar. Similarly Xu et al. [108] have made membranes by vacuum filtration of GO suspension through aluminum oxide support coated with polydopamine, and the prepared material has been burned in order to improve connection with support and increase stability of the produced membrane. The finally obtained membranes have revealed high water flux equal 48.4 L/m^2 h at NaCl retention 99.7% and temperature 90°C.

Hu and Mi [65] have used GO crosslinking by using 1,3,5-benzenetricarbonyl chloride (TMC) to covalently bond GO nano-sheets on PSF support coated with polydopamine. The obtained GO membrane has been characterized with water permeability equal from 8 to 27.6 L/m^2 h-bar at relatively low retention of mono- and bivalent ions (6%–46%) and high retention of dyes (93%–95%). What is more interesting is that the permeability of water and retention of salts have not changed with increase in number of GO layers. The authors have explained this unique phenomenon by frictionless transport of water between GO layers.

Except for the discussed methods, GO membranes enriched with carboxyl, hydroxyl, epoxide and amide

groups may be prepared using self-assembly layer-by-layer (LBL) method. Carboxylic and amine groups on GO surface are responsible for negative charge of GO particles dispersed in water, thus they can move in electric field, what causes the formation of self-assembly film. Kim et al. [109] have modified PES RO membranes using amine groups and LBL method. They have coated membrane surface with negatively charged GO nanoparticles and next deposited positively charged nanoparticles functionalized with amine groups GO layer on the negative layer. The modified membrane has revealed high water flux equal to 28 L/m^2 h and 98% retention of salt. Choi et al. [106] have also used LBL technique to modify polyamide (PA) membrane surface with GO and amine functionalized GO (aGO) nano-sheets. The modified membrane has shown good resistance to chlorine degradation due to the presence of protective GO layer on PA membrane surface. Also, the resistance to fouling of modified membrane has significantly increased and the flux has been 10% higher, while NaCl retention measured during filtration of water solution containing 2,000 mg/L of salt has decreased by 0.7%.

GO may be used for covalent modification of desalination membranes surface. Covalent bond may be formed with the use of amide bond between carboxylic groups attached to nano-sheets with other carboxylic groups present on thin polyamide layer (PA) of TFC membrane [105]. Functionalization of PA surface in TFC membranes causes that nano-sheets are better arranged on membrane surface, what has strong and positive effect on antibacterial and hydrophilic properties of modified membranes. It has been found that surface hydrophilicity does not increase membrane water flux, as water flux is regulated by solution-diffusion mechanism in active PA layer (TFC), independently of surface modification [3]. Despite covalent bonding, GO can be attached with membrane surface by electrostatic interaction using LbL method [17]. Choi et al. [106] have modified polyamide (PA) membranes by LbL deposition of positively charged GO containing NH_3^+ groups and negatively charged, non-functionalized GO (Fig. 4). Due to ultrafast water permeation in GO nano-sheets, surface modified TFC membranes do not show decrease in permeability when compared with reference, non-modified membranes. Additionally, membranes containing GO have lower tendency to foul and higher chlorine resistance. The authors relate improved antifouling features with more hydrophilic and smoother membrane surface after modification with GO.

One of the main issues in membrane exploitation to water treatment is fouling, which significantly limits the wide use

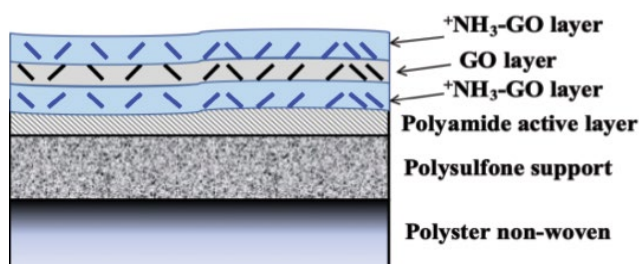


Fig. 4. Scheme of layer by layer coating of polyamide TFC membrane surface with positively charged amine GO (AGO) and GO using electrostatic interaction.

of membrane technologies. The vulnerability of membrane to fouling significantly depends on membrane material selection, chemical features of its surface and structure porosity [110]. It has to be additionally pointed that NPG and GO reveal the ability to inactivate bacteria in direct contact with their cells [111,112]. Perreault et al. [105] have investigated the impact of modification of membrane with GO to improve the antibacterial features of TFC membranes made of PA. GO nano-sheets have been bonded with membrane surface using amide and carboxylic groups interactions. It has been shown that 65% of *E. coli* cells become deactivated during direct contact with the membrane within 1 h. It has been found that GO deactivates bacteria by initiation of physical damage of cell's membrane [107] followed by eventual extraction of lipids out of the cell [113]. SEM images show that cells, which are in contact with GO membrane seem to be flattened or shrunken in comparison with cells observed on reference membrane. Hence from the SEM images, antibacterial behavior of the modified membrane does not cause any losses in its transport properties.

Sun et al. [114] have presented research describing preparation of composite membranes made of cellulose acetate (CA) modified with graphene containing silver nanoparticles (GO-AgNP) of anti-biofouling properties. Microscopic analysis had shown that silver nanoparticles (AgNPs) maintain their nanostructure on the membrane surface. The research has shown that after 24 h filtration the decrease of relative permeate flux of composite GO-AgNP has reached 46%, that is, much less than in case of CA reference membranes (88%). Additionally, the capacity of composite GO-AgNP membrane is higher than one measured for membranes modified only with GO or only with AgNP. Composite GO-AgNP membranes efficiently prevent bacterial growth and formation of biofilm on the membrane surface causing 86% *E. coli* inactivation after 2 h contact with the membrane.

Ma et al. [115] have introduced copper nanoparticles (CuNPs) on polyamide RO membrane in order to decrease its biofouling. To increase the amount of CuNPs on the membrane surface and to improve antibacterial membrane properties, cysteine (Cys) and graphene oxide (GO) may be used as agents, which form covalent bonds between CuNPs and membrane surface. GO increases hydrophilicity of the membrane modified with CuNPs what causes the increase in water flux at simultaneous insignificant impact on retention of salts. Inactivation of bacteria revealed by functionalized Cys-Cu and GO-CU membranes has been 25% higher

than one of the membranes coated only with CuNP, what has also been confirmed by membranes testing.

Zhang et al. [116] have connected GO with oxidized CNT to modify PVDF membrane. The presence of long and curled CNT allows to prevent GO aggregation, as they reveal the tendency to bind with neighbor hooding GO nano-sheets. Modified GO-CNT membrane has shown much higher hydrophilicity and antifouling properties than membranes modified only with GO or only with CNT. Water flux of membranes modified with GO and CNT in weight ratio equal to 1:1 has been increased by 252% in comparison with PVDF reference membrane.

Due to difficulties related with preparation of membranes containing vertically oriented CNT, which characterize with proper retention of solutes, many researchers have focused on preparation of TFN membranes based on CNT, in which CNT are introduced to retention layer (e.g., during IP of polyamide) [117,118]. As CNTs are hydrophobic and non-reactive, what often causes incompatibility with polymeric matrices, a number of methods of chemical or physical modification have been developed to improve CNT dispersion in coating solution [119]. Among them the use of an acid is found to be the most efficient method as it allows to form hydroxyl ($-OH$) and carboxylic ($-COOH$) groups at CNT ends making them more hydrophilic and more reactive [120]. Functionalized CNT may be next introduced to thin skin layer made of polyamide [117], what may significantly influence on physico-chemical properties of membranes (e.g., hydrophilicity, porosity, charge density and additional water channels) [121]. A number of investigations have also shown that TFN membranes based on CNT are characterized with improved antifouling properties [13] as CNT possess strong antibacterial properties.

Chan et al. [122] have introduced positively and negatively charged CNT using vacuum filtration to produce high-quality RO membranes. The obtained CNT containing membranes have been characterized with four times higher water permeability ($1.3 \text{ L/m}^2 \text{ h bar}$ for TFN vs. $0.3 \text{ L/m}^2 \text{ h bar}$ for TFC) and retention almost identical than non-modified membranes (98.6% for TFN vs. 97.6% for TFC). The authors have related increased permeability of modified membrane to ultrafast transport through CNT, which has been uniformly distributed on ultrathin skin layer. Xue et al. [117] have functionalized MWCNTs with three different functional groups, that is, carboxyl (MWCNT-COOH), hydroxyl (MWCNT-OH) and amine (MWCNT-NH) ones, and next they have introduced functionalized CNT to aqueous solution of piperazine (PIP) in order to prepare TFN membranes. At the optimum concentration 0.01% (m/v) of MWCNT, all membranes have revealed higher permeability of pure water and higher retention of salts. Among three types of MWCNTs membranes, TFN MWCNT-OG membrane has revealed that the highest water flux and Na_2SO_4 retention equal to $41.4 \text{ L/m}^2 \text{ h}$ and 97.6%, respectively, at process pressure equal 6 bar. The authors have related this capacity to the synergy of $-OH$ groups in MWCNTs and $-NH_2$ groups in PIP. Additionally, membranes with MWCNTs- NH_2 have revealed better salt retention and stability than MWCNT-COOH due to adhesion between $-NH_2$ and $-COOH$ in PA matrix. Amini et al. [123] have modified TFC PA membrane surface with MWCNTs functionalized with amine

(0.01%, 0.05% and 0.1%) using IP technique. The increase of hydrophilicity of modified membrane surface observed for increasing dose of MWCNTs has been found. The high retention of salt and water permeability have been observed during testing of modified membranes in forward osmosis (FO) process with 10 mM NaCl solution as a feed and 2 M NaCl solution as a draw solution. It has been found that permeate flux of modified membrane is 160% higher than the one of conventional TFC membrane and reaches in average 95.7 L/m² h.

Tiraferri et al. [124] have presented the new strategy for immobilization of CNT functionalized with carboxylic group on skin layer of polyamide membrane, which involve strong covalent bonding (Fig. 5). Before modification, CNTs had been functionalized with carboxylic groups and next 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC/NHS) solution have been used to transform carboxylic groups of polyamide thin layer to semi-stable amino-reactive in order to enable reaction with ethylene diamine (ED). The capacity of separation of modified TFC membrane has not been significantly different, what means, that the method does not affect the integrity of polyamide. During antibacterial test, modified TFC membranes have revealed 44% higher inactivation of bacterial cells on membrane surface in regard to reference TFC membrane.

4.3.2. Modification by introduction of nano-material to polymeric membrane matrices

Membranes made of polymeric materials, especially aromatic polyamides, cellulose acetate, nylon, PVDF, polysulfone, sulfonated polyether and non-polymeric materials (ceramic, metals) and their composites are used for filtration of different solutions [1,2]. The introduction of

carbon nano-materials to polymeric membrane matrix influences on its structure and antibacterial properties as well as hydrophilicity, retention and mechanical strength [116,125–132]. In comparison with conventional membranes (without nano-material), surface of modified membrane is characterized with dense pore structure, what is the result of nano-material precipitation during phase inversion process. The significant increase of membrane hydrophilicity results in increased water permeation of modified membrane. Hence, the introduction of carbon nano-materials creates the opportunity of membranes exploitation in dry state without permeability affection, what is especially important in regard to membrane resistance to microorganisms and enhances transport.

Lee et al. [129] have explained the role of nano-materials in membrane casting process by means of phase inversion. When GO is absent, polymer solution quickly solidifies at phase boundary between polymer and non-solvent during phase separation due to concentration gradient and fast interaction of all components. In non-stable spots of forming polymeric surface damages and scratches can appear due to constant shrinking caused by desolvation. The introduction of hydrophilic substances (nano-materials) to casting solution increases its hydrophilicity and influences on the exchange rate between solvent and non-solvent during phase separation, and thus more porous membrane structure is formed. As a result, number of damages and macro-holes are minimized.

Due to Xu et al. [131] and Zhao et al. [132], the use of small amounts of functionalized nano-materials leads to increase of porosity and pore size of a membrane, but only to some critical point. It has been found that if the amount of nano-material exceeds 0.5%, the porosity of membrane noticeably decreases [133]. This trend corresponds to

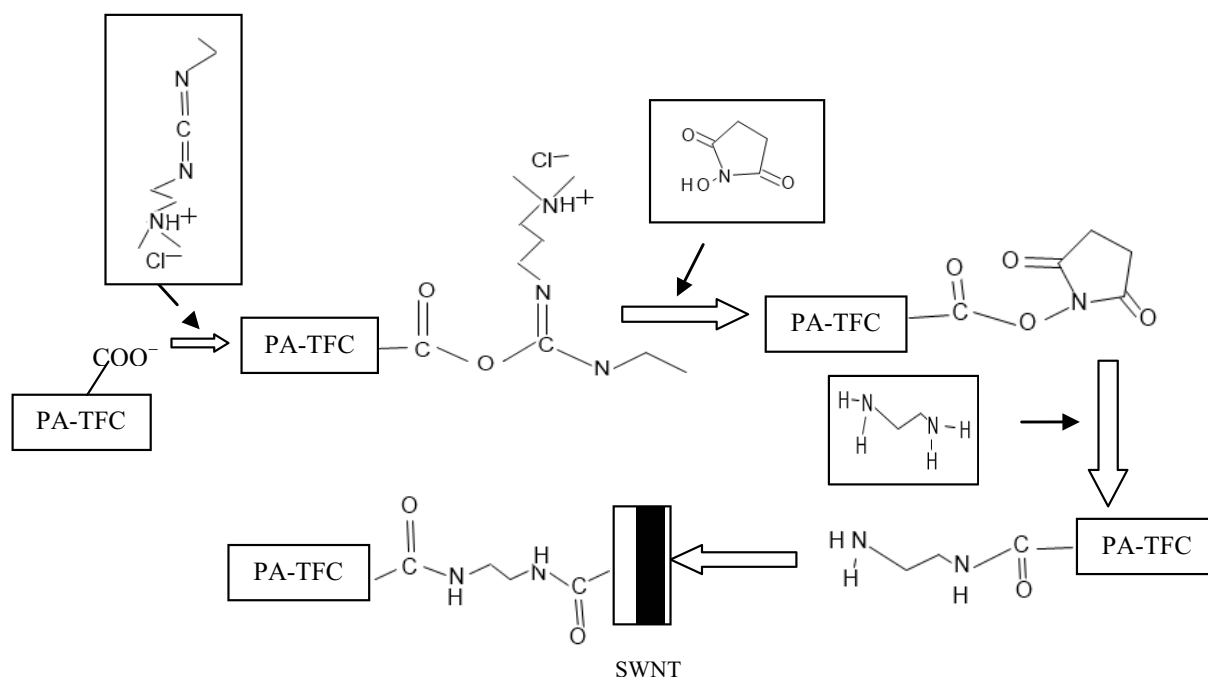


Fig. 5. Scheme of CNT immobilization on PA TFC membrane.

permeability test results, which also increases with nano-material addition up to critical point, after exceedance of which it starts to decrease. This decrease is related with pores blocking and decrease of their size caused by high concentration of nanomaterial in membrane matrix. The high content of nano-material increases solution viscosity, slows down precipitation and leads to formation of dense skin layer on a surface accompanied with formation of wider pores, size of which increase with distance from skin layer [134].

It has been stated that functionalized nano-material, due to the presence of acidic groups, may yield negative charge on membrane surface in the whole pH range [135], what enhances separation of positive ions due to repulsion of negative ions by negatively charged membrane surface. Nano-materials cause the increase of the membrane hydrophilicity, what increases permeate and pure water flux during filtration, as more hydrophilic membrane reveals higher affinity to water particles in membrane matrix and enables their permeation through the membrane [136].

The research carried out by Lai et al. [137] has shown the increase of permeate flux and retention of salt caused by non-functionalized GO to PSF support covered with polyamide layer. Membranes prepared with casting solution containing 0.3 wt.% GO have been characterized with retention of Na_2SO_4 , Mg_2SO_4 , MgCl_2 and NaCl equal 95.2%, 91.1%, 62.1% and 59.5%, respectively.

Zinadini et al. [101] have prepared NF GO/PES membranes of different GO doses. The research on membrane resistance to fouling during filtration of powdered milk solution (8,000 mg/L) has shown that the membrane containing 0.5 wt.% GO possesses the best resistance to biofouling. Additionally, this membrane is characterized with high permeate flux (ca. 65.2 kg/m² h) and high dye retention (99%). The authors relate separation efficiency improvement to the presence of hydrophilic groups responsible for overall higher hydrophilicity of prepared membranes.

Zhao et al. [126] have produced modified UF membranes of GO/PVDF type, which are characterized with increased permeate flux and BSA retention equal to 26.5 L/m² h and 44.3%, respectively. Membranes are also less vulnerable to fouling due to high hydrophilicity (the contact angle of modified membrane is 61° lower than one of reference PVDF membrane 73°) and characterize with proper surface morphology.

By using phase inversion technique, Lee et al. [129] have prepared GO/PSF membrane to treat wastewater in membrane bioreactor (MBR). The authors have found that introduction of 1 wt.% of GO nanoparticles to polymeric matrix decreases membrane fouling and decreases chemical membrane cleaning frequency five times. GO increases hydrophilicity of membrane matrix and limits biofouling, due to low energy interaction between feed and membrane surface. Additionally, negative charge of membrane surface decreases adhesion forces and accumulation of substances responsible for biofouling. It may allow for production of GO based membranes of high fouling resistance, which can be used to treat wastewater in MBR.

Fryczkowska [138] has presented results of research on the use of ultrafiltration composite GO-PAN membranes containing 0.8, 4.0 and 7.7 wt.% of GO in PAN matrix to remove dyes (Indigo – IS; methylene blue – MB and anionic

dyes thymol blue – TB; Congo red – CR) from industrial wastewater. It has been shown that anionic dyes do not worsen the transport properties of GO-PAN membrane and permeate fluxes for particular membranes were equal to 24, 35 and 58 L/m² h bar. On the other hand, cationic dyes, that is, IS and MB affect permeate flux measured during synthetic wastewater filtration. The research with real wastewater has indicated on the decrease of permeate flux of particular GO-PAN membrane by 35%, 61% and 50%. Composite GO/PAN membranes can be used for the complete removal of anionic TB and CR dyes, while cationic dyes (IS and MB) are removed in 60%–95%.

Several recent papers have also discussed further functionalization of nano-materials before their introduction to a casting solution. Functionalized, hydrophilic nanoparticles mixed with polymeric matrix improve amorphous membrane properties [139]. For membrane made of functionalized GO (f-GO), the porosity improves due to formation of more dense pores, but only if small amount of f-GO is added, while if the critical amount is exceeded, the porosity of a membrane decreases [131,132]. f-GO introduction also increases thermodynamic instability during gelling process, what stimulates phase separation stage, that is, fast exchange of solvent with non-solvent, resulting in formation of large number of pores with small amount of f-GO on the membrane surface [131]. When f-GO amount is higher than 0.5 wt.%, its coagulation during phase inversion increases viscosity of the casting solution and membrane porosity is significantly decreased [132]. Additionally, it has been observed that the increase of f-GO layers number affects retention of some metal ions, for example, Na^+ and Mg^{2+} , while water permeability is simultaneously decreased.

Various modifiers can be used as GO functionalizing agents and among them hyperbranched polyethylene imine (HPEI) [130], 3-aminopropyl-trimethoxy silane (APTS) [131] and isocyanate [132] are the most often mentioned. For example, GO functionalized with HPEI have been mixed with PSF [130] and PVDF [131] solutions and membranes produced by means of phase inversion method have revealed polyvinyl alcohol (PVA – 30 to 70 kDa) and polyethylene glycol (20 kDa) retention equal to 90% and 85%, respectively. It has also been shown that hydrophilicity of prepared membrane increases with HPEI-fGO dose increase. It has been stated that modified membranes: isocyanate-GO/PS [136] and APTS f-GO/PVDF [131] reveal BSA retention equal to 95% and 57%, respectively. TEM images of *E. coli* cells have indicated on the loss of integrity and cytoplasm leakage during contact with modified HPEI-GO membrane [130]. PSF nano-composite membrane modified with graphene grafted with diallyldimethylammonium chloride reveals increased water flux equal ca. 450 L/m² h, improved antifouling features and high retention of heavy metal ions [140].

In order to limit membranes biofouling, GO-Ag composites are introduced to membrane casting solution further processed in phase inversion method. GO composites containing silver are synthesized by mixing with silver nitrate at presence of aqueous sodium borohydride. Modified membranes reveal higher permeability and improved hydrophilic and mechanical properties in reference to non-modified membranes. Improved antibacterial features and prevention of biofilm formation are especially observed and confirmed

by conventional inhibition and anti-adhesive bacterial tests. Modified membranes also reveal elongated antibacterial features and negligible release of Ag^+ ions in regard to membranes, which do not contain GO-Ag composite.

Li et al. [141] and Mahmoudi et al. [142] have prepared PVDF membranes with different amounts of composites (0.00–0.15 wt.%). Wu et al. [143] have bonded silver nanoparticles with GO nano-sheets forming PSF membranes of different silver content (0.00–1.00 wt.%) by means of phase inversion method. The optimum amount of silver in GO, for which the best membrane performance has been observed, has been equal to 0.5 wt.%, what has been confirmed by lower contact angle, higher capacity and porosity. Additionally, surface of modified membrane has been characterized with higher NOM and bacterial fouling resistance in comparison with reference membrane, what indicates a potential use in treatment of wastewater contaminated with NOM. Hybrid membranes reveal excellent antibacterial features, which may limit or completely prevent biofouling on membrane surface.

In another research, ZnO nanoparticles have been applied as a material of good antifouling and antibacterial properties, the use of which can be advantageous in membrane-based desalination processes. Chung et al. [128] have functionalized PSF membranes using ZnO (1, 2, 3 wt.%) and graphene oxide with ZnO, that is, ZnO-GO (0.1, 0.3, 0.6 wt.%). The best efficiency has been obtained for membranes containing 2 wt.% of ZnO and 0.6 wt.% of ZnO-GO. Both membranes have been characterized with much improved hydrophilicity, higher permeability and porosity, improved retention of humic acid and significantly better antifouling features in comparison with PSF membranes. The use of GO nano-sheets has allowed for fivefold decrease of ZnO amount, while the similar antibacterial effect has been maintained.

5. Summary and development opportunities

Novel composite membranes containing NPG/GO and CNT can be divided into two categories: (i) membranes made of only FO or only NPG also known as freestanding membranes and (ii) polymeric/ceramic membranes modified with these carbon-based nanomaterials. Modification of polymeric membranes can be made either by introduction of nanomaterial on a membrane surface or its addition to a membrane casting solution followed by membrane formation from a mixture of a polymer and a nanomaterial.

Polymeric or ceramic membranes containing NPG/GO and CNT used in pressure-driven processes are characterized with very high water/permeate flux and possess unique antifouling and antibacterial properties as well as high mechanical and thermal stability. The capacity of nano-membranes is higher than one of the conventional RO or NF membranes, while retention of low molecular weight compounds is similar. The efficiency of membranes containing NPG/GO and CNT is beneficial in regard to removal of dyes, separation of monovalent ions from bivalent ones and dewatering of water–solvent mixtures. Additionally, membranes containing carbon-based nanomaterials have been successfully applied to pervaporation, forward osmosis, capacitive deionization, electro-dialysis or in photocatalytic membrane formation due to their stability and high efficiency.

The future development of membranes containing NPG/GO and CNT should be focused on separation efficiency improvement using different production strategies. A lot of effort should be also dedicated to proper recognition of role and interaction mechanism between graphene or CNT-based nanomaterial with a membrane. GO and CNT nano-membranes are promising materials to preparation of membranes for water and wastewater treatment, but more attention should be given to their potential disadvantages such as mechanical instability, aggregation, non-uniform distribution and surface damages. Additionally, scaling up related with industrial production of commercial ultrathin membranes of high capacity made of graphene is one of the greatest scientific and technical challenges. If successful, the use of such membranes at industrial scale will lead to significant energy saving in RO installation as well as in other processes. The key to success is to find the balance between production costs and manufacture simplicity. Additionally, such membranes should be resistant to fouling and scaling, what assures high flux long-term operation and savings in operational and capital costs. Moreover, the release of nanomaterials from membrane and their eventual toxicity should be carefully investigated, especially in regard to their practical use in desalination processes.

6. Photocatalysis and disinfection

Catalytic or photocatalytic oxidation belongs to advanced oxidation processes and is used to remove trace amounts of contaminants and pathogenic microorganisms from water. They are useful in preliminary treatment methods enabling increase of biodegradation rate of harmful and/or hardly biodegradable compounds [144].

Nano-catalysts characterized with high surface to volume ratio, thus they reveal much higher efficiency than conventional materials. Additionally, the energy of forbidden band (energy gap) and crystalline structure of semiconductors of nanosize depend on their size. Their electron gap redox potential and distribution of photo-generated charges vary with the size of nano-particle [145]. Moreover, immobilization of nanoparticles on different supports improves stability of a nano-catalyst, while resulting nanocomposites are compatible with existing photo-reactors [146].

Photocatalytic nanoparticles introduce to a membrane (reactive membranes) combine functions of physical separation and catalyst reactivity toward contaminants degradation. A lot of effort has been given to the development of inorganic photocatalytic membranes comprised of nano-catalysts (nano- TiO_2 or modified nano- TiO_2) [147]. Metallic/bimetallic nanoparticles/catalysts such as nano-zero valent iron (nZVI) and noble metals placed on nZVI support have been introduced to polymeric membranes to degrade contaminants, especially chlorinated derivatives of organic compound [148]. In such materials, nZVI acts as electron donor, while noble metals catalyze the reaction.

TiO_2 is a photocatalytic semiconductor, which is the most often used in water/wastewater treatment due to its low toxicity, chemical stability and wide availability. Photo-activity of nano- TiO_2 can be increased by optimization of size and shape of nanoparticles, decrease of recombination of e^-/h^+ by noble metal addition and processing of surface aiming

at contaminants adsorption increase. Among crystalline TiO₂ structure, rutile particles are the most stable at size range above 35 nm, while for particles smaller than 11 nm anatase is preferable [149]. If the size of particles is reduced to several nanometers, surface recombination is dominant and photocatalytic activity is reduced. The addition of noble metals may decrease e⁻/h⁺ recombination; as electrons excited by radiation migrate to noble metals of lower Fermi level, gaps are maintained in TiO₂ [150]. Another area of research is dedicated to widening of TiO₂ excitation spectrum by visible light. The general strategy relies on introduction of metals, dyes, semiconductors of narrow forbidden band or anions into nano-TiO₂, what results in formation of hybrid nanoparticles or nano-composites [150]. Among these methods, introduction of anions (especially nitrogen) has been found to be the most beneficial solution in regard to industrial application [149].

Nano-oxides different than TiO₂ may also be used in photocatalytic water treatment. Among them one may find CeO₂, WO₃ or ZnO, which possess narrower forbidden band than TiO₂, and due to this they can be activated by visible light (<450 nm) [151], while addition of Pt increases WO₃ reactivity by enhancing multi-electron O₂ reduction and e⁻/h⁺ separation improvement [152]. CNTs have also been investigated as catalysts in heterogenic processes of catalytic ozonation, which allow for fast and relatively complete decomposition of organic contaminants. Another nano-structural semiconductor, which interests scientist as a stable photo-catalyst is ZnSnO₃ [153]. Rahman and Mohd [154] have investigated kinetics of degradation of two pesticides, that is, dichlorvos and phosphamidon using Degussa 25 (commercially available TiO₂ nanoparticles) and they have found that addition of acceptors such as hydrogen peroxide (H₂O₂) increases contaminants degradation rate. Solar photocatalysis has been also successfully applied to degradation of aldrine and its three derivatives, that is, dieldrine, chlordane and 1,2-hydroxydieldrine [155]. Dichlorvos, which is classified as restricted use pesticide (RUP) due to its toxicity, is efficiently degraded by photo-catalysts such as TiO₂ and ZnO [156]. It has been found that addition of acceptors such as hydrogen peroxide (H₂O₂) or potassium persulfate (K₂S₂O₈) increases degradation at TiO₂ presence, while it limits the decomposition at ZnO presence. Water soluble pesticides have been also mineralized during pilot-scale research using two well-defined systems with solar UV radiation and operated in heterogenic photo-catalysis with TiO₂ nanoparticles [157]. Almost 100% mineralization accompanied with complete decomposition of pesticides such as cymoxanil, dimethoate, methomyl, oxamyl, pyrimethanil and telone have been obtained.

Photocatalytic inactivation of microorganisms is a complex process and its efficiency depends on type, concentration of physiological condition of microorganisms [158,159]. TiO₂ nanoparticles (Degussa P25) have been used in successful deactivation of different bacteria such as *E. coli*, *Pseudomonas aeruginosa*, *Salmonella typhimurium* and *Enterobacter cloacae* [160]. The use of TiO₂ nanoparticles (Degussa P25) to inactivate bacteria (*E. coli*, *P. aeruginosa*), fungi (*Candida albicans*, *Fusarium solani*), protozoa (stadium trophozoite stage of *Acanthamoeba*), spores (*Bacillus subtilis*) and cysts at sun radiation is also discussed in literature [159].

Properties and uses of nano-TiO₂ and ZnO as nano-catalysts and their application to contaminants degradation have been also discussed in the study by Bodzek et al. [161] (chapters 3 and 4).

In order to prevent spreading of diseases caused by contaminated water, disinfection is used as final and critical treatment stage [162]. The ideal disinfection agent should be characterized with: (1) wide antibacterial spectrum and short response; (2) no formation of any harmful side products; (3) low toxicity to living organisms and ecosystems; (4) low production energy costs and simple use; (5) easy storage and non-corrosive character; (6) safety utilization and deposition [163].

A number of nanomaterials are characterized with antibacterial features, for example, nano-silver (nAg) [164], nano-TiO₂ [165], nano-ZnO and nano-Ce₂O₄ [166] as well as nano-carbon materials (CNT and fullerenes) [167]. Disinfection is based on release of toxic metal ions (e.g., Ag⁺), damaging of membrane cells in direct contact (e.g., chitosan NPs) or generation of reactive oxygen species (ROS, for example, TiO₂). In contrast to conventional chemical disinfection agents, antibacterial agents based on nanomaterial deactivate microorganisms in more sustainable way, that is, they limit the formation of harmful disinfection byproducts as no strong oxidation is required [168]. Additionally, when integrated with proper separation method, several nano-agents may be used in continuous mode with high efficiency and low energy consumption, what is especially attractive for decentralized water and wastewater treatment systems.

Nano-Ag is currently the most commonly used disinfective nano-material due to strong antibacterial features, wide spectrum, low toxicity to humans and simple use. The antibacterial effect of nano-Ag mostly results from release of silver ions, which bond with thiol groups of proteins and destroy enzymes [169]. It has also been found that silver ions may prevent DNA replication and lead to structural deformations in a cell [169]. Due to this fact, the rate of release and bioavailability of silver ions is crucial for nano-Ag toxic effect. Some research suggests that physicochemical properties of nano-Ag play an important role in its antibacterial activity.

CNT destroys bacteria by causing physical and oxidative stress to a cell membrane or by interrupting specific growth of microorganisms [170] due to direct contact with bacteria cells. Graphene and graphite act as antibacterial agents basing on similar mechanism [171]. Cytotoxicity of CNT mostly depends on their physicochemical properties. Short, dispersed and metallic CNTs of small diameter are more toxic [172].

Nanomaterials containing antibacterial components, for example, nano-Ag or CNT may limit biofouling of semipermeable membranes. Nano-Ag has been introduced to or on a surface of polymeric membranes preventing bacterial cells adhesion and biofilm formation on a membrane surface [47] and inactivating viruses [173]. High bacteria inactivation rate (>90%) has been reached using polyvinyl N-carbazole SWCNT nanocomposite containing 3 wt.% of SWCNT [174]. Antibacterial features, fiber-like shape and high conductance of CNT make CNT-based filter very useful in the removal of bacteria and viruses. Thin CNT layer efficiently rejects bacteria due to sieving mechanisms, while viruses are eliminated

by depth filtration [175]. Nano-Ag has high potential in water treatment of point-of-use (POU) type due to the fact, that it can be an additional barrier for pathogens, which appear in drinking water. There are nano-Ag based commercially devices, for example, MARATHON™ and Aquapure™. Nano-Ag has been also introduced as a barrier to pathogens to ceramic micro-filters, which can be used in developing countries [176].

References

- [1] L. Madhura, S. Kanchi, M.I. Sabela, S. Singh, K. Bisetty, Inamuddin, Membrane technology for water purification, *Environ. Chem. Lett.*, 16 (2018) 343–365.
- [2] M. Bodzek, Membrane separation techniques – removal of inorganic and organic admixtures and impurities from water environment – review, *Arch. Environ. Prot.*, 45 (2019) 4–19.
- [3] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science*, 333 (2011) 712–717.
- [4] S. Miller, H. Shemer, R. Semiat, Energy and environmental issues in desalination, *Desalination*, 366 (2014) 2–8.
- [5] X. Qu, P.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, *Water Res.*, 47 (2013) 3931–3946.
- [6] D. Cohen-Tanugi, R.K. McGovern, S.H. Dave, J.H. Lienhard, J.C. Grossman, Quantifying the potential of ultra-permeable membranes for water desalination, *Energy Environ. Sci.*, 7 (2014) 1134–1141.
- [7] Z. Altintas, I. Chianella, G. Da Ponte, S. Paulussen, S. Gaeta, I.E. Tothill, Development of functionalized nanostructured polymeric membranes for water purification, *Chem. Eng. J.*, 300 (2016) 358–366.
- [8] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, *Nat. Rev. Mater.*, 1 (2016) 16018.
- [9] N. Songa, X. Gao, Z. Mac, X. Wanga, Y. Weia, C. Gao, A review of graphene-based separation membrane: materials, characteristics, preparation and applications, *Desalination*, 437 (2018) 59–72.
- [10] A. Anand, B. Unnikrishnan, J.-Y. Mao, H.-J. Lin, C.-C. Huang, Graphene-based nanofiltration membranes for improving salt rejection, water flux and antifouling – a review, *Desalination*, 429 (2018) 119–133.
- [11] Y.-X. Shen, P.O. Saboe, I.T. Sines, M. Erbakan, M. Kumar, Biomimetic membranes: a review, *J. Membr. Sci.*, 454 (2014) 359–381.
- [12] B.J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas, L.G. Bachas, Aligned multiwalled carbon nanotube membranes, *Science*, 303 (2004) 62–65.
- [13] Y. Manawi, V. Kochkodan, M. Ali Hussein, M.A. Khaleel, M. Khraisheh, N. Hilal, Can carbon-based nanomaterials revolutionize membrane fabrication for water treatment and desalination?, *Desalination*, 391 (2016) 69–88.
- [14] P.S. Goh, A.F. Ismail, N. Hilal, Nano-enabled membranes technology: sustainable and revolutionary solutions for membrane desalination?, *Desalination*, 380 (2016) 100–104.
- [15] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, 83 (1993) 81–150.
- [16] C. Feng, X. Ju, M. Li, T. Yang, C. Gao, Studies on a novel nanofiltration membrane prepared by cross-linking of polyethyleneimine on polyacrylonitrile substrate, *J. Membr. Sci.*, 451 (2014) 103–110.
- [17] J.T. Arena, B. McCloskey, B.D. Freeman, J.R. McCutcheon, Surface modification of thin film composite membrane support layers with polydopamine: enabling use of reverse osmosis membranes in pressure retarded osmosis, *J. Membr. Sci.*, 375 (2011) 55–62.
- [18] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention, *Desalination*, 281 (2011) 1–16.
- [19] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—development to date and future potential, *J. Membr. Sci.*, 370 (2011) 1–22.
- [20] L.-X. Dong, X.-C. Huang, Z. Wang, Z. Yang, X.-M. Wang, C.Y. Tang, A thin-film nanocomposite nanofiltration membrane prepared on a support with in situ embedded zeolite nanoparticles, *Sep. Purif. Technol.*, 166 (2016) 230–239.
- [21] A. Mollahosseini, A. Rahimpour, Interfacially polymerized thin film nanofiltration membranes on TiO₂ coated polysulfone substrate, *J. Ind. Eng. Chem.*, 20 (2014) 1261–1268.
- [22] A.S. AL-Hobaib, J.E. Ghoul, L.E. Mir, Fabrication of polyamide membrane reached by MgTiO₃ nanoparticles for ground water purification, *Desal. Wat. Treat.*, 57 (2016) 8639–8648.
- [23] G.L. Jadav, P.S. Singh, Synthesis of novel silica-polyamide nanocomposite membrane with enhanced properties, *J. Membr. Sci.*, 328 (2009) 257–267.
- [24] P.F. Andrade, A.F. de Faria, S.R. Oliveira, M.A.Z. Arruda, M.D.C. Gonçalves, Improved antibacterial activity of nanofiltration polysulfone membranes modified with silver nanoparticles, *Water Res.*, 81 (2015) 333–342.
- [25] Y. Lv, H.-C. Yang, H.-Q. Liang, L.-S. Wan, Z.-K. Xu, Novel nanofiltration membrane with ultrathin zirconia film as selective layer, *J. Membr. Sci.*, 500 (2016) 265–271.
- [26] M.L. Lind, A.K. Ghosh, A. Jawor, X.F. Huang, W. Hou, Y. Yang, E.M.V. Hoek, Influence of zeolite crystal size on zeolite-polyamide thin film nanocomposite membranes, *Langmuir*, 25 (2009) 10139–10145.
- [27] F. Dorosti, M.R. Omidkhan, M.Z. Pedram, F. Moghadam, Fabrication and characterization of polysulfone/polyimide-zeolite mixed matrix membrane for gas separation, *Chem. Eng. J.*, 171 (2011) 1469–1476.
- [28] M.R.S. Kebria, M. Jahanshahi, A. Rahimpour, SiO₂ modified polyethyleneimine-based nanofiltration membranes for dye removal from aqueous and organic solutions, *Desalination*, 367 (2015) 255–264.
- [29] J. Yin, E.-S. Kim, J. Yang, B. Deng, Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification, *J. Membr. Sci.*, 423 (2012) 238–246.
- [30] S. Yu, X. Zuo, R. Bao, X. Xu, J. Wang, J. Xu, Effect of SiO₂ nanoparticle addition on the characteristics of a new organic-inorganic hybrid membrane, *Polymer*, 50 (2009) 553–559.
- [31] J. Ahn, W.-J. Chung, I. Pinnau, M.D. Guiver, Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation, *J. Membr. Sci.*, 314 (2008) 123–133.
- [32] M. Sadeghi, M.A. Semsarzadeh, H. Moadel, Enhancement of the gas separation properties of polybenzimidazole (PBI) membrane by incorporation of silica nano particles, *J. Membr. Sci.*, 331 (2009) 21–30.
- [33] H. Zhang, H. Mao, J. Wang, R. Ding, Z. Du, J. Liu, S. Cao, Mineralization-inspired preparation of composite membranes with polyethyleneimine–nanoparticle hybrid active layer for solvent resistant nanofiltration, *J. Membr. Sci.*, 470 (2014) 70–79.
- [34] S.N. Hoseini, A.K. Pirzaman, M.A. Aroon, A.E. Pirbazari, Photocatalytic degradation of 2, 4-dichlorophenol by Co-doped TiO₂ (Co/TiO₂) nanoparticles and Co/TiO₂ containing mixed matrix membranes, *J. Water Process Eng.*, 17 (2017) 124–134.
- [35] A. Kowalik-Klimczak, E. Stanisławek, J. Kacprzyńska-Gołacka, A. Bednarska, E. Osuch-Słomka, J. Skowroński, The polyamide membranes functionalized by nanoparticles for biofouling control, *Desal. Wat. Treat.*, 128 (2018) 243–252.
- [36] M.R. Esfahani, T.J. Lyler, H.A. Stretz, M.J.M. Wells, Effects of a dual nanofiller, nano-TiO₂ and MWCNT, for polysulfone-based nanocomposite membranes for water purification, *Desalination*, 372 (2015) 47–56.
- [37] K. Szymański, P. Sienkiewicz, D. Darowna, M. Jose, K. Szymańska, S. Mozia, Investigation on polyethersulfone membranes modified with Fe₃O₄ – trisodium citrate nanoparticles, *Desal. Wat. Treat.*, 128 (2018) 265–271.
- [38] H. Rabiee, V. Vatanpour, M.H.D.A. Farahani, H. Zarrabi, Improvement in flux and antifouling properties of PVC ultrafiltration membranes by incorporation of zinc oxide (ZnO) nanoparticles, *Sep. Purif. Technol.*, 156 (2015) 299–310.

- [39] H. Li, W. Shi, H. Zhu, Y. Zhang, Q. Du, X. Qin, Effects of zinc oxide nanospheres on the separation performance of hollow fiber poly(piperazine-amide) composite nanofiltration membranes, *Fibers Polym.*, 17 (2016) 836–846.
- [40] L.-H. Li, J.-C. Deng, H.-R. Deng, Z.-L. Liu, L. Xin, Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes, *Carbohydr. Res.*, 345 (2010) 994–998.
- [41] L. Yan, Y.-S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al_2O_3 -particle addition on PVDF ultrafiltration membrane performance, *J. Membr. Sci.*, 276 (2006) 162–167.
- [42] N. Maximous, G. Nakhla, W. Wan, K. Wong, Preparation, characterization and performance of Al_2O_3 /PES membrane for wastewater filtration, *J. Membr. Sci.*, 341 (2009) 67–75.
- [43] P. Maheswari, D. Prasannadevi, D. Mohan, Preparation and performance of silver nanoparticle incorporated poly-etherethersulfone nanofiltration membranes, *High Perform. Polym.*, 25 (2012) 174–187.
- [44] C. Zhang, Z. Hu, B. Deng, Silver nanoparticles in aquatic environments: physicochemical behavior and antimicrobial mechanisms, *Water Res.*, 88 (2016) 403–427.
- [45] M. Ben-Sasson, X. Lu, E. Bar-Zeev, K.R. Zodrow, S. Nejati, G. Qi, E.P. Giannelis, M. Elimelech, In situ formation of silver nanoparticles on thin-film composite reverse osmosis membranes for biofouling mitigation, *Water Res.*, 62 (2014) 260–270.
- [46] H.-L. Yang, J. Chun-Te Lin, C. Huang, Application of nanosilver surface modification to RO membrane and spacer for mitigating biofouling in seawater desalination, *Water Res.*, 43 (2009) 3777–3786.
- [47] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P.J.J. Alvarez, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, *Water Res.*, 43 (2009) 715–723.
- [48] A. Mollahosseini, A. Rahimpour, M. Jahamshahi, M. Peyravi, M. Khavarpour, The effect of silver nanoparticle size on performance and antibacteriality of polysulfone ultrafiltration membrane, *Desalination*, 306 (2012) 41–50.
- [49] S. Mozia, M. Jose, P. Sienkiewicz, K. Szymański, D. Darowna, M. Zgrzebnicki, A. Markowska-Szczupak, Polyethersulfone ultrafiltration membranes modified with hybrid Ag/titanate nanotubes: physicochemical characteristics, antimicrobial properties and fouling resistance, *Desal. Wat. Treat.*, 128 (2018) 106–118.
- [50] A.M. Ferreira, É.B. Roque, F.V.D. Fonseca, C.P. Borges, High flux microfiltration membranes with silver nanoparticles for water disinfection, *Desal. Wat. Treat.*, 56 (2015) 3590–3598.
- [51] N.C. Mueller, B. van der Bruggen, V. Keuter, P. Luis, T. Melin, W. Pronk, W. Reisewitz, D. Rickerby, G.M. Rios, W. Wenekes, B. Nowack, Nanofiltration and nanostructured membranes—should they be considered nanotechnology or not?, *J. Hazard. Mater.*, 211–212 (2012) 275–280.
- [52] V. Srivastava, D. Gusain, Y.C. Sharma, Critical review on the toxicity of some widely used engineered nanoparticles, *Ind. Eng. Chem. Res.*, 54 (2015) 6209–6233.
- [53] C. Dong, G. He, H. Li, R. Zhao, Y. Han, Y. Deng, Antifouling enhancement of poly(vinylidene fluoride) microfiltration membrane by adding $Mg(OH)_2$ nanoparticles, *J. Membr. Sci.*, 387–388 (2012) 40–47.
- [54] A.K. Nair, A.M. Isloor, R. Kumar, A.F. Ismail, Antifouling and performance enhancement of poly-sulfone ultrafiltration membranes using $CaCO_3$ nanoparticles, *Desalination*, 322 (2013) 69–75.
- [55] R.J. Gohari, E. Halakoo, W.J. Lau, M.A. Kassim, T. Matsuura, A.F. Ismail, Novel polyethersulfone (PES)/hydrous manganese dioxide (HMO) mixed matrix membranes with improved antifouling properties for oily wastewater treatment process, *RSC Adv.*, 4 (2014) 17587–17596.
- [56] R. Das, M.E. Ali, S.B. Abd Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: a bright future in water desalination, *Desalination*, 336 (2014) 97–109.
- [57] P.S. Goh, A.F. Ismail, B.C. Ng, Carbon nanotubes for desalination: performance evaluation and current hurdles, *Desalination*, 308 (2013) 2–14.
- [58] R. Das, S.B. Abd Hamid, M.E. Ali, A.F. Ismail, M.S.M. Annuar, S. Ramakrishna, Multifunctional carbon nanotubes in water treatment: the present, past and future, *Desalination*, 354 (2014) 160–179.
- [59] M. Tian, Y.N. Wang, R. Wang, Synthesis and characterization of novel high-performance thin film nanocomposite (TFN) FO membranes with nanofibrous substrate reinforced by functionalized carbon nanotubes, *Desalination*, 370 (2015) 79–86.
- [60] P.S. Goh, A.F. Ismail, Graphene-based nanomaterial: the state-of-the-art material for cutting edge desalination technology, *Desalination*, 356 (2015) 115–128.
- [61] I. Akin, E. Zor, H. Bingol, M. Ersoz, Green synthesis of reduced graphene oxide/ polyaniline composite and its application for salt rejection by polysulfonebased composite membranes, *J. Phys. Chem. B*, 118 (2014) 5707–5716.
- [62] S.P. Surwade, S.N. Smirnov, I.V. Vlassioux, R.R. Unocic, G.M. Veith, S. Dai, S.M. Mahurin, Water desalination using nanoporous single-layer graphene, *Nat. Nanotechnol.*, 10 (2015) 459–464.
- [63] D. Cohen-Tanugi, J.C. Grossman, Nanoporous graphene as a reverse osmosis membrane: recent insights from theory and simulation, *Desalination*, 366 (2015) 59–70.
- [64] J. Wang, P. Zhang, B. Liang, Y. Liu, T. Xu, L. Wang, B. Cao, K. Pan, Graphene oxide as an effective barrier on a porous nanofibrous membrane for water treatment, *ACS Appl. Mater. Interfaces*, 8 (2016) 6211–6218.
- [65] M. Hu, B. Mi, Enabling graphene oxide nanosheets as water separation membranes, *Environ. Sci. Technol.*, 47 (2013) 3715–3723.
- [66] M. Bodzek, K. Konieczny, A. Kwiecińska-Mydlak, Nanotechnology in water and wastewater treatment. Graphene – the nanomaterial for next generation semipermeable membranes, *Crit. Rev. Environ. Sci. Technol.*, (2019), DOI:10.1080/10643389.2019.1664258.
- [67] J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes, *Science*, 312 (2006) 1034–1037.
- [68] J. Abraham, K.S. Vasu, C.D. Williams, K. Gopinadhan, Y. Su, C.T. Cherian, J. Dix, E. Prestat, S.J. Haigh, I.V. Grigorieva, P. Carbone, A.K. Geim, R.R. Nair, Tunable sieving of ions using graphene oxide membranes, *Nat. Nanotechnol.*, 12 (2017) 546–545.
- [69] A.T. Smith, A.M. LaChance, S. Zeng, B. Liu, L. Sun, Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites, *Nano Mat. Sci.*, 1 (2019) 31–47.
- [70] Y. You, V. Sahajwalla, M. Yoshimura, R.K. Joshi, Graphene and graphene oxide for desalination, *Nano*, 8 (2016) 117–119.
- [71] S. Homaeigohar, M. Elbahri, Graphene membranes for water desalination, *NPG Asia Mater.*, 9 (2017) e427.
- [72] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45 (2007) 1558–1565.
- [73] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials, *Nature*, 442 (2006) 282–286.
- [74] M. Hu, B. Mi, Layer-by-layer assembly of graphene oxide membranes via electrostatic interaction, *J. Membr. Sci.*, 469 (2014) 80–87.
- [75] X. Wang, Z. Xiong, Z. Liu, T. Zhang, Exfoliation at the liquid/air interface to assemble reduced graphene oxide ultrathin films for a flexible noncontact sensing device, *Adv. Mater.*, 27 (2015) 1370–1375.
- [76] X. Chen, G. Liu, H. Zhang, Y. Fan, Fabrication of graphene oxide composite membranes and their application for pervaporation dehydration of butanol, *Chin. J. Chem. Eng.*, 23 (2015) 1102–1109.
- [77] G. Decher, M. Eckle, J. Schmitt, B. Strut, Layer-by-layer assembled multicomposite films, *Curr. Opin. Colloid Interface Sci.*, 3 (1998) 32–39.

- [78] H. Li, Z. Song, X. Zhang, Y. Huang, S. Li, Y. Mao, H.J. Ploehn, Y. Bao, M. Yu, Ultrathin, molecular-sieving graphene oxide membranes for selective hydrogen separation, *Science*, 342 (2013) 95–98.
- [79] R. Nair, H. Wu, P. Jayaram, I. Grigorieva, A. Geim, Unimpeded permeation of water through helium-leak-tight graphene-based membranes, *Science*, 335 (2012) 442–444.
- [80] M.J. McAllister, J.L. Li, D.H. Adamson, H.C. Schniepp, A.A. Abdala, J. Liu, M. Herrera-Alonso, D.L. Milius, R. Car, R.K. Prud'homme, Single sheet functionalized graphene by oxidation and thermal expansion of graphite, *Chem. Mater.*, 19 (2007) 4396–4404.
- [81] H. Boehm, A. Clauss, G. Fischer, U. Hoffman, The adsorption behavior of very thin carbon films, *Z. Anorg. Allg. Chem.*, 316 (1962) 119–127.
- [82] W.L. Xu, C. Fang, F. Zhou, Z. Song, Q. Liu, R. Qiao, M. Yu, Self-assembly: a facile way of forming ultrathin, high-performance graphene oxide membranes for water purification, *Nano Lett.*, 17 (2017) 2928–2933.
- [83] C. Yu, B. Zhang, F. Yana, J. Zhao, J. Li, L. Li, J. Li, Engineering nano-porous graphene oxide by hydroxyl radicals, *Carbon*, 105 (2016) 291–296.
- [84] B. Mi, Graphene oxide membranes for ionic and molecular sieving, *Science*, 343 (2014) 740–742.
- [85] Y. Yuan, X. Gao, Y. Wei, X. Wang, J. Wang, Y. Zhang, C. Gao, Enhanced desalination performance of carboxyl functionalized graphene oxide nanofiltration membranes, *Desalination*, 405 (2017) 29–39.
- [86] A. Nicolai, B.G. Sumpter, V. Meunier, Tunable water desalination across Graphene oxide framework membranes, *Phys. Chem. Chem. Phys.*, 16 (2014) 8646–8654.
- [87] D. Cohen-Tanugi, J.C. Grossman, Water desalination across nanoporous graphene, *Nano Lett.*, 12 (2012) 3602–3608.
- [88] Y. Han, Z. Xu, C. Gao, Ultrathin Graphene Nanofiltration Membrane for Water Purification, *Adv. Funct. Mater.*, 23 (2013) 3693–3700.
- [89] R.K. Joshi, P. Carbone, F.C. Wang, V.G. Kravets, Y. Su, I.V. Grigorieva, H.A. Wu, A.K. Geim, R.R. Nair, Precise and ultrafast molecular sieving through graphene oxide membranes, *Science*, 343 (2014) 752–754.
- [90] C. Xu, A. Cui, Y. Xu, X. Fu, Grapheneoxide–TiO₂ composite filtration membranes and their potential application for water purification, *Carbon*, 62 (2013) 465–471.
- [91] K. Sears, L. Dumée, J. Schütz, M. She, C. Huynh, S. Hawkins, M. Duke, S. Gray, Recent developments in carbon nanotube membranes for water purification and gas separation, *Materials*, 3 (2010) 127.
- [92] G. Hummer, J.C. Rasaiah, J.P. Noworyta, Water conduction through the hydrophobic channel of a carbon nanotube, *Nature*, 414 (2001) 188–190.
- [93] J.A. Thomas, A.J.H. McGaughey, Water flow in carbon nanotubes: transition to subcontinuum transport, *Phys. Rev. Lett.*, 102 (2009) 184502.
- [94] Y. Chan, J.M. Hill, Ion selectivity using membranes comprising functionalized carbon nanotubes, *J. Math. Chem.*, 51 (2013) 1258–1273.
- [95] X. Peng, J. Jin, E.M. Ericsson, I. Ichinose, General method for ultrathin free-standing films of nanofibrous composite materials, *J. Am. Chem. Soc.*, 129 (2007) 8625–8633.
- [96] L. Zhang, G.-Z. Shi, S. Qiu, L.-H. Cheng, H.-L. Chen, Preparation of high-flux thin film nanocomposite reverse osmosis membranes by incorporating functionalized multi-walled carbon nanotubes, *Desal. Wat. Treat.*, 34 (2011) 19–24.
- [97] S. Kar, R.C. Bindal, P.K. Tewari, Carbon nanotube membranes for desalination and water purification: challenges and opportunities, *Nano Today*, 7 (2012) 385–389.
- [98] L.F. Dumée, K. Sears, J. Schütz, N. Finn, C. Huynh, S. Hawkins, M. Duke, S. Gray, Characterization and evaluation of carbon nanotube Bucky-Paper membranes for direct contact membrane distillation, *J. Membr. Sci.*, 351 (2010) 36–43.
- [99] M. Bhadra, S. Roy, S. Mitra, Enhanced desalination using carboxylated carbon nanotube immobilized membranes, *Sep. Purif. Technol.*, 120 (2013) 373–377.
- [100] J. Yin, G. Zhu, B. Deng, Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification, *Desalination*, 379 (2016) 93–101.
- [101] S. Zinadini, A.A. Zinatizadeh, M. Rahimi, V. Vatanpour, H. Zangeneh, Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates, *J. Membr. Sci.*, 453 (2014) 292–301.
- [102] B. Fryczkowska, M. Sieradzka, E. Sarna, R. Fryczkowski, J. Janicki, Influence of a graphene oxide additive and the conditions of membrane formation on the morphology and separative properties of poly(vinylidene fluoride) membranes, *J. Appl. Polym. Sci.*, 132 (2015) 1–18.
- [103] J. Xu, L. Zhang, X. Gao, H. Bie, Y. Fu, C. Gao, Constructing antimicrobial membrane surfaces with polycation-copper(II) complex assembly for efficient seawater softening treatment, *J. Membr. Sci.*, 491 (2015) 28–36.
- [104] Z. Yang, X.H. Ma, C.Y. Tang, Recent development of novel membranes for desalination, *Desalination*, 434 (2018) 37–59.
- [105] F. Perreault, M.E. Tousley, M. Elimelech, Thin-film composite polyamide membranes functionalized with biocidal graphene oxide nanosheets, *Environ. Sci. Technol. Lett.*, 1 (2014) 71–76.
- [106] W. Choi, J. Choi, J. Bang, J.H. Lee, Layer-by-layer assembly of graphene oxide nanosheets on polyamide membranes for durable reverse-osmosis applications, *ACS Appl. Mater. Interfaces*, 5 (2013) 12510–12519.
- [107] S. Liu, T.H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R. Jiang, J. Kong, Y. Chen, Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress, *ACS Nano*, 5 (2011) 6971–6980.
- [108] K. Xu, B. Feng, C. Zhou, A. Huang, Synthesis of highly stable graphene oxide membranes on polydopamine functionalized supports for seawater desalination, *Chem. Eng. Sci.*, 146 (2016) 159–165.
- [109] S.G. Kim, D.H. Hyeon, J.H. Chun, B.H. Chun, S.H. Kim, Novel thin nanocomposite RO membranes for chlorine resistance, *Desal. Wat. Treat.*, 51 (2013) 6338–6345.
- [110] V. Kochkodan, D.J. Johnson, N. Hilal, Polymeric membranes: surface modification for minimizing (bio)colloidal fouling, *Adv. Colloid Interface Sci.*, 206 (2014) 116–140.
- [111] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science*, 321 (2008) 385–388.
- [112] J. Liang, Y. Huang, L. Zhang, Y. Wang, Y. Ma, T. Guo, Y. Chen, Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites, *Adv. Funct. Mater.*, 19 (2009) 2297–2302.
- [113] Y. Tu, M. Lv, P. Xiu, T. Huynh, M. Zhang, M. Castelli, Z. Liu, Q. Huang, C. Fan, H. Fang, R. Zhou, Destructive extraction of phospholipids from *Escherichia coli* membranes by graphene nanosheets, *Nat. Nanotechnol.*, 8 (2013) 594–601.
- [114] X.F. Sun, J. Qin, P.F. Xia, B.B. Guo, C.M. Yang, C. Song, S.G. Wang, Graphene oxide-silver nanoparticle membrane for biofouling control and water purification, *Chem. Eng. J.*, 281 (2015) 53–59.
- [115] W. Ma, A. Soroush, T. Van Anh Luong, S. Rahaman, Cysteamine- and graphene oxide-mediated copper nanoparticle decoration on reverse osmosis membrane for enhanced anti-microbial performance, *J. Colloid Interface Sci.*, 501 (2017) 330–340.
- [116] J. Zhang, Z. Xu, M. Shan, B. Zhou, Y. Li, B. Li, J. Niu, X. Qian, Synergistic effects of oxidized carbon nanotubes and graphene oxide on fouling control and anti-fouling mechanism of polyvinylidene fluoride ultrafiltration membranes, *J. Membr. Sci.*, 448 (2013) 81–92.
- [117] S.-M. Xue, Z.-L. Xu, Y.-J. Tang, C.-H. Ji, Polypiperazine-amide nanofiltration membrane modified by different functionalized multiwalled carbon nanotubes (MWCNTs), *ACS Appl. Mater. Interfaces*, 8 (2016) 19135–19144.
- [118] W.-F. Chan, E. Marand, S.M. Martin, Novel zwitterion functionalized carbon nanotube nanocomposite membranes for improved RO performance and surface anti-biofouling resistance, *J. Membr. Sci.*, 509 (2016) 125–137.

- [119] O.-K. Park, N.H. Kim, K.-t. Lau, J.H. Lee, Effect of surface treatment with potassium persulfate on dispersion stability of multi-walled carbon nanotubes, *Mater. Lett.*, 64 (2010) 718–721.
- [120] K. Balasubramanian, M. Burghard, Chemically functionalized carbon nanotubes, *Small*, 1 (2005) 180–192.
- [121] J. Yin, B. Deng, Polymer-matrix nanocomposite membranes for water treatment, *J. Membr. Sci.*, 479 (2015) 256–275.
- [122] W.-F. Chan, H.-y. Chen, A. Surapathi, M.G. Taylor, X. Shao, E. Marand, J.K. Johnson, Zwitterion functionalized carbon nanotube/polyamide nanocomposite membranes for water desalination, *ACS Nano*, 7 (2013) 5308–5319.
- [123] M. Amini, M. Jahanshahi, A. Rahimpour, Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes, *J. Membr. Sci.*, 435 (2013) 233–241.
- [124] A. Tiraferri, C.D. Vecitis, M. Elimelech, Covalent binding of single-walled carbon nanotubes to polyamide membranes for antimicrobial surface properties, *ACS Appl. Mater. Interfaces*, 3 (2011) 2869–2877.
- [125] B.M. Ganesh, A.M. Isloor, A.F. Ismail, Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane, *Desalination*, 313 (2013) 199–207.
- [126] C. Zhao, X. Xu, J. Chen, F. Yang, Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes, *J. Environ. Chem. Eng.*, 1 (2013) 349–354.
- [127] N.F.D. Aba, J.Y. Chong, B. Wang, C. Mattevi, K. Li, Graphene oxide membranes on ceramic hollow fibers – Microstructural stability and nanofiltration performance, *J. Membr. Sci.*, 484 (2015) 87–94.
- [128] Y.T. Chung, E. Mahmoudi, A.W. Mohammad, A. Benamor, D. Johnson, N. Hilal, Development of polysulfone-nanohybrid membranes using ZnO-GO composite for enhanced antifouling and antibacterial control, *Desalination*, 402 (2017) 123–132.
- [129] J. Lee, H.R. Chae, Y.J. Won, K. Lee, C.H. Lee, H.H. Lee, I.C. Kim, J.M. Lee, Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment, *J. Membr. Sci.*, 448 (2013) 223–230.
- [130] L. Yu, Y. Zhang, B. Zhang, J. Liu, H. Zhang, C. Song, Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties, *J. Membr. Sci.*, 447 (2013) 452–462.
- [131] Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, J. Niu, B. Zhou, X. Qian, Organosilane functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes, *J. Membr. Sci.*, 458 (2014) 1–13.
- [132] H. Zhao, L. Wu, Z. Zhou, L. Zhang, H. Chen, Improving the antifouling property of polysulfone ultrafiltration membrane by incorporation of isocyanate-treated Graphene oxide, *Phys. Chem. Chem. Phys.*, 15 (2013) 9084–9092.
- [133] J. Yin, G. Zhu, B. Deng, Multi-walled carbon nanotubes (MWNTs)/polysulfone (PSU) mixed matrix hollow fiber membranes for enhanced water treatment, *J. Membr. Sci.*, 437 (2013) 237–248.
- [134] F. Liu, M.R.M. Abed, K. Li, Preparation and characterization of poly(vinylidene fluoride) (PVDF) based ultrafiltration membranes using nano γ - Al_2O_3 , *J. Membr. Sci.*, 366 (2011) 97–103.
- [135] A.M. Dimiev, L.B. Alemany, J.M. Tour, Graphene oxide. Origin of acidity, its instability in water, and a new dynamic structural model, *ACS Nano*, 7 (2013) 576–588.
- [136] N. Pezeshk, D. Rana, R.M. Narbaitz, T. Matsuura, Novel modified PVDF ultrafiltration flat-sheet membranes, *J. Membr. Sci.*, 389 (2012) 280–286.
- [137] G.S. Lai, W.J. Lau, P.S. Goh, A.F. Ismail, N. Yusof, Y.H. Tan, Graphene oxide incorporated thin film nanocomposite nanofiltration membrane for enhanced salt removal performance, *Desalination*, 387 (2016) 14–24.
- [138] B. Fryczkowska, The application of ultrafiltration composite GO/PAN membranes for removing dyes from textile wastewater, *Desal. Wat. Treat.*, 128 (2018) 79–88.
- [139] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO_2 coated multiwalled carbon nanotubes, *Sep. Purif. Technol.*, 90 (2012) 69–82.
- [140] M.G. Kochameshki, A. Marjani, M. Mahmoudian, K. Farhadi, Grafting of diallyldimethylammonium chloride on graphene oxide by RAFT polymerization for modification of nanocomposite polysulfone membranes using in water treatment, *Chem. Eng. J.*, 309 (2017) 206–221.
- [141] J. Li, X. Liu, J. Lu, Y. Wang, G. Li, F. Zhao, Anti-bacterial properties of ultrafiltration membrane modified by graphene oxide with nano-silver particles, *J. Colloid Interface Sci.*, 484 (2016) 107–115.
- [142] E. Mahmoudi, L.Y. Ng, M.M. Ba-Abbad, A.W. Mohammad, Novel nanohybrid polysulfone membrane embedded with silver nanoparticles on graphene oxide nanoplates, *Chem. Eng. J.*, 277 (2015) 1–10.
- [143] Q. Wu, G.E. Chen, W.G. Sun, Z.L. Xu, Y.P. Kong, X.P. Zheng, S.J. Xu, Bio-inspired GO-Ag/PVDF/F127 membrane with improved anti-fouling for natural organic matter (NOM) resistance, *Chem. Eng. J.*, 313 (2017) 450–460.
- [144] P.A.K. Reddy, P.V.L. Reddy, E. Kwon, K.H. Kim, T. Akter, S. Kalagara, Recent advances in photocatalytic treatment of pollutants in aqueous media, *Environ. Int.*, 91 (2016) 94–103.
- [145] A. Turki, C. Guillard, F. Dapozze, Z. Ksibi, G. Berhault, H. Kochkar, Phenol photocatalytic degradation over anisotropic TiO_2 nanomaterials: kinetic study, adsorption isotherms and formal mechanisms, *Appl. Catal., B*, 163 (2015) 404–414.
- [146] F. Petronella, A. Truppi, C. Ingrosso, T. Placido, M. Striccoli, M.L. Curri, A. Agostiano, R. Comparelli, Nanocomposite materials for photocatalytic degradation of pollutants, *Catal. Today*, 281 (2016) 85–100.
- [147] H. Choi, E. Stathatos, D.D. Dionysiou, Sol-gel preparation of mesoporous photocatalytic TiO_2 films and $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite membranes for environmental applications, *Appl. Catal., B*, 63 (2006) 60–67.
- [148] L.F. Wu, S.M.C. Ritchie, Enhanced dechlorination of trichloroethylene by membrane-supported Pd-coated iron nanoparticles, *Environ. Progress*, 27 (2008) 218–224.
- [149] H.Z. Zhang, J.F. Banfield, Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO_2 , *J. Phys. Chem. B*, 104 (2000) 3481–3487.
- [150] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production, *Renew. Sustain. Energy Rev.*, 11 (2007) 401–425.
- [151] H. Kominami, K. Yabutani, T. Yamamoto, Y. Kara, B. Ohtani, Synthesis of highly active tungsten(VI) oxide photocatalysts for oxygen evolution by hydrothermal treatment of aqueous tungstic acid solutions, *J. Mater. Chem.*, 11 (2001) 3222–3227.
- [152] J. Kim, C.W. Lee, W. Choi, Platinized WO_3 as an environmental photocatalyst that generates OH radicals under visible light, *Environ. Sci. Technol.*, 44 (2010) 6849–6854.
- [153] J. Huang, X. Xu, C. Gu, W. Wang, Size-controlled synthesis of porous ZnSnO_3 cubes and their gas-sensing and photocatalysis properties, *Sens. Actuators B Chem.*, 171–172 (2012) 572–579.
- [154] M.A. Rahman, M. Mohd, Photocatalysed degradation of two selected pesticide derivatives, dichlorvos and phosphamidon, in aqueous suspensions of titanium dioxide, *Desalination*, 181(2005) 161–172.
- [155] E.R. Bandala, S. Gelover, T. Leal, C. Arancibia, A. Jiménez, C. Estrada, Solar photocatalytic degradation of Aldrin, *Catal. Today*, 76 (2002) 189–199.
- [156] E. Evgenidou, J. Poullos, F. Fytianos, Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalysts, *Appl. Catal., B*, 59 (2005) 81–89.
- [157] I. Oller, W. Gernjak, M.I. Maldonado, L.A. Pérez-Estrada, S. Malato, Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale, *J. Hazard. Mater.*, 138 (2006) 507–517.

- [158] A.G. Rincon, C. Pulgarin, Bactericidal action of illuminated TiO₂ on pure *Escherichia coli* and natural bacterial consortia: postirradiation events in the dark and assessment of the effective disinfection time, *Appl. Catal., B*, 49 (2004) 99–112.
- [159] J. Lonnen, S. Kilvington, S.C. Kehoe, F. Al-Touati, K.G. McGuigan, Solar and photocatalytic disinfection of protozoan, fungal and bacterial microbes in drinking water, *Water Res.*, 39 (2005) 877–883.
- [160] J.A. Ibanez, M.I. Litter, R.A. Pizarro, Photocatalytic bactericidal effect of TiO₂ on *Enterobacter cloacae*: comparative study with other Gram (-) bacteria, *J. Photochem. Photobiol. A Chem.*, 157 (2003) 81–85.
- [161] M. Bodzek, K. Konieczny, A. Kwiecińska-Mydlak, The application of nanomaterial adsorbents for the removal of impurities from water and wastewaters: a review, *Desal. Wat. Treat.*, (2020).
- [162] M. Bodzek, K. Konieczny, M. Rajca, Membranes in water and wastewater disinfection– review, *Arch. Environ. Prot.*, 45 (2019) 3–18.
- [163] Y. Zhang, B. Wu, H. Liu, M. Wang, Y. He, B. Pan, Nanomaterials-enabled water and wastewater treatment, *NanoImpact*, 3–4 (2016) 22–39.
- [164] M. Rai, A. Yadav, A. Gade, Silver nanoparticles as a new generation of antimicrobials, *Biotechnol. Adv.*, 27 (2009) 76–83.
- [165] A.A. Hebeish, M.M. Abdelhady, A.M. Youssef, TiO₂ nanowire and TiO₂ nanowire doped Ag-PVP nanocomposite for antimicrobial and self-cleaning cotton textile, *Carbohydr. Polym.*, 91 (2013) 549–559.
- [166] Q.L. Li, S. Mahendra, D.Y. Lyon, L. Brunet, M.V. Liga, D. Li, P.J.J. Alvarez, Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications, *Water Res.*, 42 (2008) 4591–4602.
- [167] G.S. Martynkova, M. Valaskova, Antimicrobial nanocomposites based on natural modified materials: a review of carbons and clays, *J. Nanosci. Nanotechnol.*, 14 (2014) 673–693.
- [168] Z.M. Xiu, J. Ma, P.J.J. Alvarez, Differential effect of common ligands and molecular oxygen on antimicrobial activity of silver nanoparticles versus silver ions, *Environ. Sci. Technol.*, 45 (2011) 9003–9008.
- [169] Q.L. Feng, J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim, J.O. Kim, A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*, *J. Biomed. Mater. Res.*, 52 (2000) 662–668.
- [170] C.D. Vecitis, K.R. Zdrov, S. Kang, M. Elimelech, Electronic-structure-dependent bacterial cytotoxicity of single-walled carbon nanotubes, *ACS Nano*, 4 (2010) 5471–5479.
- [171] J. Tang, Q. Chen, L. Xu, S. Zhang, L. Feng, L. Cheng, H. Xu, Z. Liu, R. Peng, Graphene oxide–silver nanocomposite as a highly effective antibacterial agent with species-specific mechanisms, *ACS Appl. Mater. Interfaces*, 5 (2013) 3867–3874.
- [172] S. Kang, M.S. Mauter, M. Elimelech, Physicochemical determinants of multiwalled carbon nanotube bacterial cytotoxicity, *Environ. Sci. Technol.*, 42 (2008) 7528–7534.
- [173] B. De Gussemme, T. Hennebel, E. Christiaens, H. Saveyn, K. Verbeken, J.P. Fitts, N. Boon, W. Verstraete, Virus disinfection in water by biogenic silver immobilized in polyvinylidene fluoride membranes, *Water Res.*, 45 (2011) 1856–1864.
- [174] F. Ahmed, C.M. Santos, R. Vergara, M.C.R. Tria, R. Advincula, D.F. Rodrigues, Antimicrobial applications of electroactive PVK-SWNT nanocomposites, *Environ. Sci. Technol.*, 46 (2012) 1804–1810.
- [175] A.S. Brady-Estevez, M.H. Schnoor, S. Kang, M. Elimelech, SWNT-MWNT hybrid filter attains high viral removal and bacterial inactivation, *Langmuir*, 26 (2010) 19153–19158.
- [176] M. Peter-Varbanets, C. Zurbrugg, C. Swartz, W. Pronk, Decentralized systems for potable water and the potential of membrane technology, *Water Res.*, 43 (2009) 245–265.