Application of Nanotechnology in Membranes for Water Treatment

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Publication details
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Published online on: 30 May 2017

How to cite: Derya Y. Koseoglu-Imer, Ismail Koyuncu. 30 May 2017, Fabrication and application areas of mixed matrix flat-sheet membranes from: Application of Nanotechnology in Membranes for Water Treatment CRC Press
Accessed on: 11 Oct 2020
CHAPTER 3

Fabrication and application areas of mixed matrix flat-sheet membranes

Derya Y. Koseoglu-Imer & Ismail Koyuncu

3.1 INTRODUCTION

Polymer-nanoparticle composite materials have unique characteristics, such as high mechanical strength, good electrical conductivity, optical and thermal properties. Nanoparticles can gain high functionality and therefore they increase the overall performance of conventional materials, such as membranes, used in environmental applications. Membrane separation properties can be controlled for each specific application by the proper choice of fabrication components (main polymer, solvent, additives like nanoparticles, pore forming agents, etc.) and parameters (evaporation time and temperature, coagulation bath temperature, etc.). Moreover, especially in recent years, the membrane fouling problem can be avoided with different membrane fabrication components. Membrane fouling can be defined as the uncontrolled deposition of particles, colloids, macromolecules or salt ions from feed solution at the membrane surface or inside the membrane pores. It is a severe problem for membrane materials used in pressure-driven processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) and also for other membrane processes. Different polymers (Polyethersulfone (PES), polysulfone (PS), cellulose acetate (CA), polyvinylidene fluoride (PVDF), etc.) could be selected as membrane materials for these membrane systems according to their physical and chemical characteristics, such as good chemical, heat, mechanical and cleaning resistance and environmental endurance, as well as easy processing and manufacturing. For instance, the intrinsic hydrophobicities of some polymers are high and so this results in hydrophobic membrane materials and leads to a low membrane flux, poor anti-fouling properties and low application and useful life. The fouling causes a decrease in membrane performance, either temporarily or permanently. The fouling mechanism includes the interaction between the membrane surface and the foulants (inorganic, organic, and biological substances in many different forms). The foulant molecules not only physically interact with the membrane surface but also chemically degrade the membrane material. Most of the latest membrane fouling studies focused on the physical or chemical modification of membrane material for low fouling properties. These studies can be summarized in three main areas; (i) the modification of the membrane surface with in-situ physical and chemical treatments, (ii) the coating of the membrane with special materials that have low fouling properties and (iii) the preparation of the membrane by adding nanomaterials (mixed matrix membranes, MMMs). MMMs are formed by the addition of inorganic or metal oxide particles, having micrometer or nanometer sizes, to the polymeric casting solution or by in-situ generation. Over the past few years, the rapid growth in nanotechnology has aroused significant interest in the use of nanomaterials in membrane applications. So far, the membrane modification studies using nanotechnological methods in particular have achieved useful results. Nanoparticles (NPs) are defined as particles having the size of 1–100 nm and they have unique magnetic, electrical, optical, mechanical and structural properties. More recently, several natural and engineered nanomaterials have also proved to have exceptional properties, including chitosan, silver nanoparticles (nAg), photocatalytic TiO₂, fullerol, aqueous fullerene nanoparticles (nC60), and carbon nanotubes (CNT). Moreover, some nanoparticles, such as silver (Ag), copper (Cu), zinc oxide (ZnO), titanium oxide (TiO₂), etc.,
have antibacterial properties and thus show high toxicity to a broad spectrum of microorganisms, including bacteria, fungi, viruses and yeasts, and have been studied as antibacterial agents in different areas. The combination of membrane chemistry and the antibacterial properties of NPs may particularly solve the biofouling problem in membrane systems. To prevent fouling problems, NPs can be applied by directly coating on to the membrane surface or by blending in the polymer matrix of the membrane during the membrane fabrication process.

This chapter is focused on identifying the fabrication and application areas of mixed matrix flat-sheet membranes.

### 3.2 FABRICATION OF MIXED MATRIX FLAT-SHEET MEMBRANES

#### 3.2.1 Self-assembled mixed matrix membranes (MMMs)

Self-assembly provides a feasible and low-cost method for preparing the membranes including nanoparticles (Yang et al., 2014). This method is a bottom-up approach but it is limited to the fabrication of single-sided coatings on planar substrates. This technique does not require complicated equipment and can be easily applied to a large variety of materials (Askar et al., 2013). A solution-based bottom-up assembly process represents the layer-by-layer (LbL) self-assembly, it provides the sequential adsorption of nanometer-thick monolayers of oppositely charged polyelectrolytes and nanoparticles to form a molecular-level controlled membrane. It is a very successful process with which to form cross-linked films with interfacial interactions between the carbon nanotube and polymers through dense covalent bonding and the stiffening of polymer chains (Zhang and Cui, 2012). Kim et al. (2003) designed self-assembled TiO$_2$ membranes to create membrane surfaces that have a low biofouling performance. They assembled the anatase TiO$_2$ nanoparticles on thin film composite membranes through bonding between hydroxyl groups of TiO$_2$ nanoparticles and carboxyl functional groups of aromatic polyamide thin film layer (Kim et al., 2003). Since TiO$_2$ nanoparticles have a high affinity to water molecules and generate hydrogen bonding with groups in the polymer segment, it is also a good hydrophilic agent for modification of the membrane surface by self-assembly (Li X. et al., 2014).

Bae et al. (2006) used the self-assembly procedure for membranes with TiO$_2$ nanoparticles. They modified the sulfonated PES membranes as fouling-resistant mixed matrix membranes and used the electrostatic self-assembly method between TiO$_2$ nanoparticles and sulfonic acid groups on the membrane surface. In this study, the sulfonated polyethersulfone (SPES) ultrafiltration membranes were fabricated with the phase inversion method and then the fabricated membranes were dipped into the TiO$_2$ nanoparticle solution including the controlled hydrolysis of titanium tetraisopropoxide. The fouling mitigation property of the mixed matrix membrane was examined using membrane bioreactor (MBR) sludge, which contains a great number of various foulants. The fouling mitigation ratios were evaluated quantitatively; the filtration resistances were calculated according to the resistance in a series model. The results showed that both the amount and rate of membrane fouling decreased in the mixed matrix membrane compared to the pristine polymeric membrane. The mixed matrix membrane had a higher stabilized relative flux (36% of the initial flux) than the pristine membrane (20% of the initial flux). The cake layer resistance of the mixed matrix membrane was decreased when compared to the pristine PES membrane (from $58.70 \times 10^{11}$ to $33.27 \times 10^{11}$ m$^{-1}$) and also the pore resistance of the mixed matrix membrane decreased from $4.31 \times 10^{11}$ to $2.23 \times 10^{11}$ (Bae et al., 2006).

Mansourpanah et al. (2009) assembled TiO$_2$ nanoparticles on the surface of polyethersulfone (PES)/polyimide (PI) and –OH functionalized PES/PI blend membranes. They exposed the membranes to UV light after membrane fabrication using different concentrations of TiO$_2$. UV light gained a photocatalytic property to the membrane surface and this property increased the membrane hydrophilicity. With UV irradiated TiO$_2$ deposited blend membranes, –OH groups provided excellent adhesion of TiO$_2$ nanoparticles on the membrane surface and this increased the reversible deposition onto the membrane surface and diminished irreversible fouling into the
membrane pores. Li X. et al. (2014) prepared a polyethersulfone (PES) hybrid ultrafiltration (UF) membrane with TiO2 nanoparticles using a novel method. This method was to combine the self-assembly of TiO2 nanoparticles with the formation of PES membranes via the non-solvent induced phase separation (NIPS) process. TiO2 nanoparticles were self-assembled around the membrane pores during the NIPS process by controlling the hydrolysis and condensation of precursor (tetrabutyltitanate-TBT) confirmed by TEM and SEM-EDX mapping. The water permeability of the hybrid PES membranes was four times higher than that of the pristine PES membranes, 50.8 L m\(^{-2}\) h\(^{-1}\) for pristine PES and 235.9 L m\(^{-2}\) h\(^{-1}\) for hybrid membranes. An anti-fouling experiment, using BSA and humic acid (HA) as model foulants, showed that the PES hybrid membrane had good organic anti-fouling properties. Importantly, the leaching of self-assembly TiO2 nanoparticles was moderate and this provided a stable and sustainable anti-fouling activity for the hybrid membranes (Li X. et al., 2014).

3.2.2 Surface modified mixed matrix membranes (MMMs)

Surface treatment is one of the modification methods used for fabricated pristine membranes to increase the surface hydrophilicity and to reduce the membrane fouling. The surface modification of the membranes may be performed by coating, grafting, covalent bond, cold plasma treatment and incorporating hydrophilic fillers, including inorganic nanoparticles (Moghimifar et al., 2014).

Coating is a physical modification method and includes the coating material(s) forming a thin layer that non-covalently adheres to the membrane surface. Coating methods can be divided into five techniques: coating by physical adsorption, heat curing, coating with a monolayer using Langmuir-Blodgett or analogous techniques, deposition from a glow discharge plasma, and casting or extrusion of two solutions by simultaneous spinning (Nady et al., 2011). With these methods, nanoparticles can be coated as a layer on the membrane surface by physical or chemical bonds. It might provide a simple way to place nanoparticles onto the membrane surface. Although locating nanoparticles in a direct position with contact to the filtering solution improves the efficiency of nanoparticles, this procedure could lead to early detachment of the nanoparticles from the membrane surface with time. Nevertheless, with the physical coating method, a release of nanoparticles from the membrane material could be observed due to the difficulty of immobilizing them on the membranes without using binding mediums to form covalent bonds between the nanoparticles and the membrane. Despite many attempts being made to find appropriate organic binders for nanoparticles, the release of nanoparticles from the membrane still creates important operational problems over a long filtration period (Mericq et al., 2015).

3.2.3 Thin film nanocomposite (TFN) membranes

Thin film nanocomposite membranes (TFN) were recently introduced as a new field in membrane technology. It is believed that the concept of dispersing nanophase materials into a polymeric matrix has brought a new perspective to advanced membrane materials. TFN membranes are fabricated by embedding porous nanoparticle materials, such as pure metals, metal oxides, silicon nanoparticles and carbon nanomaterials, into a polyamide matrix layer (Shen et al., 2013). Nanomaterials give benefits to membranes, such as unique optical, thermal and physiochemical activities, so organic-inorganic membranes with nanoparticles have a high separation efficiency, low cost and easy operation. However, these membranes acquire some specific properties, like high permeability and selectivity, good chemical, thermal and mechanical stability, crystallinity, catalytic activity and antibacterial characteristics (Mollahosseini and Rahimpour, 2014).

Thin film membranes used for nanofiltration or reverse osmosis are polyamide thin film composites (TFC), which are prepared by an interfacial polymerization technique. Polyamide membranes have several disadvantages, such as relatively low water flux, low chlorine resistance and poor anti-fouling properties. Therefore, the fabrication of polyamide membranes that have a high water permeability and simultaneously high salt rejection is still a challenge and a strong research topic for the development of new and improved polyamide membranes. One effective
strategy is to introduce inorganic nanoparticles into the polyamide skin layer to produce inorganic-polyamide membranes. Incorporation of inorganic materials into the polymer matrix generally increases hydrophilicity and typically contributes to fouling reduction (Xu et al., 2013).

Different nanoparticles have been used to modify polyamide (PA) TFC membranes, such as zeolite, TiO₂, silver, silicate or alumina. Zeolite nanoparticles are particularly used as inorganic materials to be embedded into the active layer to modify the PA-TFC RO membranes. Incorporation of zeolite nanoparticles into the PA active layer of TFC membranes can significantly improve the water flux without a large loss of salt rejection under high pressure in the RO process. Dong et al. (2016) found that TFN membranes with zeolite nanoparticles had a much higher water permeability than the TFC membranes (15.7 vs. 6.4 × 10⁻⁶ m s⁻¹ MPa⁻¹). These authors explained that this trend was due to the internal pores of zeolite nanoparticles increasing the membrane surface roughness. Jeong et al. (2007) fabricated a TFN polyamide RO membrane including 0.004–0.4% (w/v) of NaA zeolite nanoparticles dispersed within 50–200 nm thick polyamide films (Fig. 3.1). Pure polyamide membranes exhibited surface morphologies characteristic of commercial polyamide RO membranes, whereas TFN membranes had measurably smoother and more hydrophilic, negatively charged surfaces. At the highest nanoparticle ratio, TFN morphology was visibly different and pure water permeability (3.8×10⁻¹² m Pa⁻¹ s⁻¹) was nearly double that of the polyamide membrane (2.1×10⁻¹² m Pa⁻¹ s⁻¹) with equivalent solute rejections. It was suggested that the zeolite nanoparticle pores played an active role in water permeation and
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Figure 3.2. Fluxes of polyamide TFC-RO membranes by using silica (SiO₂) nanoparticles at RO tests with aqueous NaCl salt solutions (11,000 mg L⁻¹) (Peyki et al., 2015).

salt rejection. As a concept, TFN membrane technology may offer new options in tailoring RO membrane separation performance and material properties (Jeong et al., 2007).

Kim et al. (2012) synthesized a new type of TFN membrane having antibacterial properties by interfacial polymerization. They used two different nanomaterials, which were acid modified multi-walled carbon nanotubes (MW-NTs) for a support layer and nanosilver (nAg) particles for a thin film layer. MW-NTs at 5.0 wt% in the support layer and nAg particles at 10 wt% in the thin film layer enhanced the pure water permeability of the TFN membrane by 23 and 20%, respectively, compared to 0 wt% of these components in their respective layers. The water permeability and hydrophilicity was enhanced in the TFN membrane that had a CNT support layer compared to a non-CNT matrix through the diffusive tunnel effects of nanopores in MW-NTs. nAg particles in the thin film particularly increased the anti-biofouling properties of the TFN membranes and did not change the salt rejections of the membranes. Pseudomonas aeruginosa PA01 batch tests indicated greater anti-adhesive and antibacterial properties of the TFN membrane compared to similar membranes without nAg particles (Kim et al., 2012).

Peyki et al. (2015) modified the surface of polyamide TFC-RO membranes by using silica (SiO₂) nanoparticles. The SiO₂ nanoparticles were added to amine solution with different concentrations of 0.005 to 0.5 wt%. FT-IR spectroscopy and SEM images confirmed the incorporation of SiO₂ nanoparticles on the polyamide active layer. The surface hydrophilicity and roughness of the membranes increased with the increasing SiO₂ concentration in the amine solution. The salt rejection and flux of the membranes were tested with NaCl aqueous solution. The flux values of the membranes increased gradually at lower levels of nanoparticles (0.005–0.1 wt%) and then decreased at 0.5 wt% (as seen in Fig. 3.2). Moreover, the rejection values increased at lower concentrations of SiO₂ (0.005 and 0.01 wt%) and then decreased with an increasing content of SiO₂. Long-term experiments showed that the modified RO membranes had lower flux decline compared to neat thin film composite RO membranes. The flux decline for unmodified RO membranes was 31%, while the flux declines for 0.005, 0.01, 0.05 and 0.1 wt% SiO₂ modified membranes were about 10%, 16%, 13% and 15%, respectively (Peyki et al., 2015).

3.2.4 Blending method

The most conventional and simple method for the synthesis of polymer/inorganic mixed matrix membrane (MMM) is direct mixing of the nanoparticles into the polymer solution. The mixing can generally be done by melt blending or solution blending. Solution blending is a simple way to fabricate polymer-inorganic MMM (Fig. 3.3). In this method, a polymer is dissolved in a proper solvent to form an homogenous polymer solution, and then inorganic nanoparticles are added.
into the solution and dispersed by mixing. The polymer solution is cast by removing the solvent and the membrane is obtained (Cong et al., 2007). The main difficulty in the mixing process is to achieve an effective dispersion of the nanoparticles in the polymer matrix because they have a strong tendency to form agglomerates (Kango et al., 2013). Firstly, the nanoparticles should be added to solvent and stirred with sonication for preventing their agglomeration in polymer solution when the solubility of nanoparticle is low in solvent. The aggregation of nanoparticles in the membranes and the easy leaching of nanoparticles from the membranes are the main concerns of the solution blending method. However, commercial polymeric membranes can be modified by blending with hydrophilic materials during the industrial membrane production. It is a common practical technique and no additional processing steps are needed during or after the phase inversion process (Wu et al., 2013).

Wang et al. (2012) fabricated the mixed matrix (polyvinylidene fluoride (PVDF) and graphene oxide (GO)) blended ultrafiltration membranes using the immersion phase inversion process. GO-blended PVDF membranes appeared to have a more hydrophilic surface and have a higher pure water fluxes recovery ratio than the unblended PVDF membranes due to the hydrophilic nature of GO. The permeation properties and mechanical structure of the blended membranes can obviously be improved. The permeability of the blended membrane increased by 96.4%; the tensile strength increased by 123%. Moreover, the contact angle decreased from 79.2° to 60.7°, which implies that the anti fouling ability of the membrane was improved. Similarly, Silva et al. (2015) blended polyvinylidene fluoride (PVDF) with multi-walled carbon nanotubes (MW-CNTs) for the fabrication of flat-sheet direct contact membrane distillation (DCMD) membranes by the phase inversion method. The synthesis parameters, such as MW-CNT loading, polyvinylpyrrolidone (PVP) addition and MW-CNT surface chemistry, affected markedly the membrane properties and performances. MW-CNT/PVDF membranes prepared with functionalized MW-CNTs had a smaller pore size and lower contact angles (more hydrophilic), thus the functionalization of MW-CNTs is not recommended for this application. Sponge-like pores and smaller thickness (i.e. membranes prepared without PVP) allowed complete salt rejection (i.e. 100%). In contrast with larger thickness and elongated finger-like pores (resulting from PVP addition) salt exclusion ranged from 88.8 to 98.6%. Overall, the MW-CNT/PVDF blended membrane prepared with 0.2 wt% MW-CNTs (without adding PVP) exhibited the best performance in DCMD, presenting total salt rejection and a higher permeate flux ($9.5 \times 10^{-3}$ kg m$^{-2}$ s$^{-1}$) than that obtained with a commercial PVDF membrane ($7.8 \times 10^{-3}$ kg m$^{-2}$ s$^{-1}$).

Arsuaga et al. (2013) used different metal oxides nanoparticles (TiO$_2$, Al$_2$O$_3$ and ZrO$_2$) for the fabrication of pressure-driven membranes. The nanoparticles were blended in PES polymer solution. The membranes were characterized with hydrophilicity (contact angle), morphology (SEM), porosity, and thermal analysis (TGA). Membrane fouling was studied with BSA and humic acids as model organic foulants. Entrapped metal oxides caused a more open and porous structure in membrane morphology and significantly enhanced the anti-fouling property and long-term flux

**Figure 3.3.** Polymer and inorganic phases connected by Van der Waals force or hydrogen bonds at blending method (Cong et al., 2007).
stability of the membranes. PES-Al₂O₃ membranes exhibited the highest value of 208.9 L m⁻² h⁻¹ while the permeability of pristine PES membranes was 180 L m⁻² h⁻¹. Strong correlations were observed between physico-chemical properties such as porosity, hydrophilicity and permeability of modified membranes with the spatial particle distribution in the membrane structure. The fouling resistance of modified membranes was significantly reduced. The relative fouling resistances of the membranes were found to be 7.56 × 10¹² m⁻¹ for pristine PES and 5.52 × 10¹², 4.79 × 10¹² and 5.46 × 10¹² m⁻¹ for PES-TiO₂, PES-Al₂O₃ and PES-ZrO₂, respectively.

3.3 NANOMATERIAL TYPES FOR FABRICATION OF MIXED MATRIX MEMBRANES (MMMs)

3.3.1 Polymeric mixed matrix membranes (MMMs) with silver nanoparticles (AgNPs)

In recent years, several studies have demonstrated the potential to use silver nanoparticles (AgNPs) as antibacterial agents in membrane separation processes. AgNPs have three different antibacterial mechanisms: (i) attachment to the cell membrane drastically disturbing the permeability and respiration of the membrane, (ii) penetration inside the bacteria cytoplasm and interaction with sulfur- and phosphorus-containing compounds, such as DNA, causing further damage and (iii) release of silver ions, which also have a known bactericidal effect as reported by Feng et al. (2000). The release of silver ions is also involved in mechanisms (i) and (ii) and it is the definitive molecular toxicant under aerobic conditions (Cruz et al., 2015).

AgNPs have strong antibacterial activity against a different type of bacteria, but the use of AgNPs as biocide is mainly limited by its relatively high cost. Localized loading of small amounts of silver adjacent to the membrane surface, where biofilms develop, is viable for protecting the membrane from biofouling. Therefore, the anti-biofouling potential of AgNPs is well established in the literature, but the loading method of AgNPs on the membrane material is one of the main obstacles (Ben-Sasson et al., 2014). During the fabrication of membranes with AgNP, the different pathways can be used to incorporate silver nanoparticles in the membrane structure, such as ex-situ synthesis (subsequent addition to the casting solution), or in-situ reduction of ionic silver during the phase inversion process (Taurozzi et al., 2008). Furthermore, the silver can be applied by coating AgNP directly on to the surface of the membranes or by embedment in the polymer matrix of the membrane itself (Yang et al., 2009; Zodrow et al., 2009). Zodrow et al. (2009) prepared AgNP incorporating membranes having antimicrobial properties by using the phase inversion technique, in which the dope solution containing the polymer and AgNP was casted on a support and then immersed in a water bath to provide polymer precipitation. They found that the addition of AgNP prevented the bacterial attachment and biofilm formation on the membrane surface. Moreover, the authors suggested that the release of ionic silver can be the main mechanism.

The combination of polymer and AgNPs enhanced the separation properties due to the prevention of particle deposition (Babu et al., 2010). AgNPs have a high antibacterial activity and this property may provide the long-term stability and efficient operation for mixed matrix membranes in filtration, especially for prolonged operational time periods. In the literature, there have been a number of studies to improve the distribution of AgNPs and its stability. Cellulose acetate (CA), chitosan, polyacrylonitrile (PAN) and polysulfone (PS) were the most popular polymeric materials studied with AgNPs (Basri et al., 2011). However, CA, chitosan and PAN polymers have disadvantages such as poor solubility in common organic solvent and high cost. Therefore, PES appeared to be a more promising polymer because it is an easy handling material with good solubility in most of the organic solvents and is resistant to chemical attack (Susanto and Ulbricht, 2009; Wang et al., 2005).

Liu et al. (2013) fabricated novel nanofiltration and forward osmosis membranes, including AgNP, using the layer-by-layer (LbL) assembly method. The incorporation of AgNPs in the membranes did not adversely affect the membrane separation performance in NF and forward osmosis
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The membranes with silver exhibited excellent antibacterial properties against both Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli*. They showed that the performances of the membranes, including AgNPs, are highly dependent on silver incorporation in the membranes, which could be controlled by using different membrane synthesis methods and the addition of AgNPs.

### 3.3.2 Polymeric mixed matrix membranes (MMMs) with silica nanoparticles (SiNPs)

Silica nanoparticles (SiNPs) have high surface areas, narrow pore size distributions, high porosity and low density (Zargar *et al.*, 2016). They have been studied extensively for various applications. At polymeric membrane fabrication, SiNPs have been widely used to fabricate the gas separation membranes to enhance both gas permeability and selectivity. They increased the permeability of mixed matrix membranes without changing their selectivity due to their good compatibility with the polymer matrix. Furthermore, the functional –OH group on the silica should improve the hydrophilicity of the membrane and have a positive effect on the fouling resistance of the membrane (Huang *et al.*, 2012).

The use of SiNPs in membrane fabrication has not yet been studied to a large extent, despite the wide availability of different types with a wide range of particle sizes. Jadav and Singh (2009) incorporated two types of SiNPs *in-situ* into polyamide films. One type of SiNP was commercial Ludox® HS 40 (particle size of 16 nm); the other type of SiNP was a lab-synthesized colloid prepared from controlled hydrolysis of tetraethyloortho silicate (TEOS) (0.4 wt% suspension in water). SiNPs were trapped into the polymer film with high temperature curing. It was observed that the effective pore radius of the mixed matrix membranes increased when the silica concentration in the casting solution was increased. Depending on the SiNPs content, the average pore radius of the membranes varied from a smaller radius of 0.34 nm to a larger radius of 0.73 nm. Furthermore, the number of pores in the membrane also increased. Silica has the advantage of improving the mechanical stability and, as a result of partial leaching, introduced additional pores in the membranes. Silica nanoparticles with silanol groups on the surface could act as active sites for polymer adsorption or reaction, thus providing a platform for anchoring anti-fouling ligands (Wu *et al.*, 2013).

### 3.3.3 Polymeric mixed matrix membranes (MMMs) with carbon nanotubes (CNT)

Carbon nanotube (CNT) was discovered in 1991 and classified as single-walled (SW-CNT) and multi-walled (MW-CNT). CNTs have attracted significant research areas because of their unique structure, physical, electronic, and thermal properties. MW-CNTs are more often preferred because of their relatively low cost and more advanced stage of commercial production. In recent times, CNT/polymer composites are prepared with the addition of CNTs into the intermediate and final polymer products, and these composites significantly increase the separation performance of the hybrid membranes (Wang *et al.*, 2014). MW-CNTs are naturally hydrophobic but they can be easily modified with different treatment methods and attached to different functional groups, such as hydrogen, nitrenes, fluorine, carbenes, radicals and aryl radicals. Acid treatment develops some hydrophilic part (–COOH, and –OH) on the MW-CNT substrate. Carbon part on one side of the MW-CNT makes it hydrophobic and creates sites for the attachment of hydrophobic polymer by hydrophobic-hydrophobic interaction and π–π stacking. On the other side, acid and hydroxyl groups are created after acid treatment and this brings the hydrophilic part by hydrogen bonding, dipole-dipole interaction and dispersion forces (Irfan *et al.*, 2014).

CNTs are most widely used in membrane applications in water and wastewater treatment and they are also effective adsorbents for contaminants in water and wastewater treatment processes. Membrane roughness, surface functional groups, hydrophilicity, and fouling can influence permeate fluxes of CNT composite membranes (Kim *et al.*, 2013).

Recently, carbon nanotube (CNT) membranes have been investigated by many researchers as a novel membrane technology for water treatment. When CNTs are used as pores of membranes,
they appear to allow fast fluid flow due to their strong hydrophobicity (Park et al., 2014). In polymeric membranes that have CNTs, the membrane fabrication processes may not be so easy. The size and uniformity of CNTs are very important parameters because they may cause stability problems in membranes.

3.3.4 Polymeric mixed matrix membranes (MMMs) with alumina nanoparticles (Al$_2$O$_3$NP)

Alumina nanoparticles (Al$_2$O$_3$NP) are one of the nanoparticles used in polymeric mixed matrix membranes. Al$_2$O$_3$NP can increase the mechanical resistance and hydrophilicity and also modify the membrane morphology during the membrane formation in the phase inversion process (Homayoonfal et al., 2015). Homayoonfal et al. (2015) synthesized a polysulfone (PSf)/alumina (Al$_2$O$_3$NP) mixed matrix membrane with the principal aim of reducing biofouling in the membrane bioreactors. The filtration experiments indicated that the addition of Al$_2$O$_3$NP increased the membrane hydrophilicity and so the pure water flux was enhanced from 450 L m$^{-2}$ h$^{-1}$ to 1600 L m$^{-2}$ h$^{-1}$ for 0.02 Al$_2$O$_3$/PSf and 2075 L m$^{-2}$ h$^{-1}$ for 0.03 Al$_2$O$_3$/PSf. The separation efficiency was maintained because of decreasing porosity. The presence of alumina nanoparticles up to the polymer concentration of 0.03 wt% resulted in an 83% reduction in biofouling (Homayoonfal et al., 2015). The comprehensive study concerning the fabrication of mixed matrix membranes with Al$_2$O$_3$NP was carried out by Yan et al. (2005). They fabricated PVDF membranes with incorporated Al$_2$O$_3$NP. Dimethylacetamide (DMAC) was used as the solvent and the dope solution consisted of 19 wt% PVDF polymer, 0–4 wt% Al$_2$O$_3$NP and additional additives (hexad-sodium phosphate, and polyvinylpyrrolidone (PVP)). They found a remarkable change in the contact angle values. The contact angle of the bare PVDF membrane was 84° and decreased to 57–59° for membranes with 2–4% of Al$_2$O$_3$NP. Only the membrane with the lowest concentration of Al$_2$O$_3$NP still had a higher contact angle (68°). The porosity and rejection values remained unchanged in all experiments. Interestingly, SEM images showed that the addition of Al$_2$O$_3$NP did not affect the structure of the surface and cross-section. Furthermore, the mechanical properties of the membranes had improved; the tensile strength had increased remarkably, whereas the break elongate ratio reached a maximum at 2% Al$_2$O$_3$NP added. From these studies, it can be said that Al$_2$O$_3$NP increased the membrane hydrophilicity.

3.3.5 Polymeric mixed matrix membranes (MMMs) with TiO$_2$ nanoparticles

In the membrane fabrication studies, titanium dioxide (TiO$_2$) was one of the most preferred nanoparticles. Titanium dioxide nanoparticles (TiO$_2$NP) loaded membranes have received much attention because of their high hydrothermal nature, chemical stability and photocatalytic activity (Li D. et al., 2014). Mixed matrix membranes with TiO$_2$NP can be manufactured in two ways, with assembling or blending. In the assembling method, TiO$_2$NP is coated to the surface of porous membranes with self-organization. The cross-linking degree of polymeric matrix and the types of bonds between the polymer and inorganic molecules can control the assembled membrane structure. TiO$_2$NP is directly added to the polymeric casting solution during the blending method and the homogeneity is the main problem. Some mechanical and chemical approaches (introduction of organic functional groups on the TiO$_2$ surface) have been applied for the modification of TiO$_2$NP to increase homogenous dispersivity, reduce agglomeration, improve the stability of TiO$_2$NP in polymer and enhance the nanofiller-polymer interaction (Vatanpour et al., 2012).

Mericq et al. (2015) prepared low fouling PVDF membranes with TiO$_2$NP by NIPS (Non-solvent Induced Phase Separation) wet-process. They obtained a typical asymmetric membrane structure. The membrane structure, hydrophilic properties and permeability were improved in comparison with the PVDF neat membrane when the TiO$_2$NP concentration was increased up to an optimum concentration of 25 wt%. Under UV irradiation the phenomena of super-hydrophilicity due to the presence of TiO$_2$NP in the composite membrane permits the suppression of pure water permeate flux decline and the achievement of higher fluxes. Fouled composite membranes after
BSA filtration were successfully cleaned using water and UV irradiation. Permeate flux was totally recovered after this cleaning (Mericq et al., 2015).

Under UV light TiO$_2$NPs produces some radicals such as OH$^\bullet$, O$_2$$^\bullet$, and HO$_2$ in water and these radicals are assigned as bactericidal action. The adhesion of the bacterial cells to TiO$_2$NP is controlled by hydrophobic and charge interactions and the active oxygen reaches and damages the bacterial cell wall. Due to the strong bactericidal properties as photocatalytic under UV light, the mixed matrix membranes having TiO$_2$NP inhibit the growth of microorganisms on the membrane surface, and thus membrane biofouling is reduced (Kochkodan and Hilal, 2015). This reduction in biofouling was demonstrated when TiO$_2$ modified membranes were used for water filtration, which showed that the fluxes of the modified membranes were 1.7–2.3 times higher compared with those for the control samples. The flux values of TiO$_2$ modified membranes reached to approximately 0.3 L h$^{-1}$ after 4 days, while it was 0.15 L h$^{-1}$ for the control membrane (Kochkodan et al., 2008).

3.4 APPLICATION OF MIXED MATRIX MEMBRANES (MMMs)

3.4.1 Antimicrobial activity

Microbial growth and uncontrolled biofilm formation cause the membrane biofouling and it is a serious operational issue in filtration for water and wastewater treatment. It decreases membrane permeability and permeates quality, and so increases the energy costs of the separation process. Antimicrobial chemicals can be used for the prevention of biofouling problems in membranes, especially at the membrane fabrication step. Membranes having antimicrobial chemicals inhibit bacterial growth on the membrane surface and help to provide pathogen-free clean water. Development of antimicrobial or biofouling resistant membranes has focused on membrane surface modification to reduce the adhesion of bacteria or biopolymers, or the inhibition of bacterial growth. Several studies have incorporated antimicrobial nanoparticles in membranes. A commonly used method is to disperse the nanoparticles in the polymer solution during the phase inversion process (Wu et al., 2015). Among antimicrobial nanoparticles, AgNPs are the most popular antimicrobial agent used in different areas. There are different methods to integrate AgNPs into the matrix, such as electroless plating and vacuum deposition. Immobilization of silver element or ions onto the modified polymeric surface through metal-ligand interaction was found to be the most efficient way (Zhang et al., 2013).

Zhang et al. (2014) prepared polyethersulfone membranes with biogenic AgNP synthesized from Lactobacillus fermentum. Biogenic AgNP was introduced into the membrane by blending at different concentrations. The fabricated membranes were tested for physical properties such as water permeability, MWCO (molecular weight cut-off), contact angle, SEM and AFM. Cross-section micrographs demonstrated that the biogenic silver nanoparticles dispersed well into the PES matrix without aggregation. Well dispersed biogenic AgNP contained the hydroxyl and amino groups, which are known as hydrophilic groups, and the hydrophilicity of the PES membranes slightly increased and so the protein adsorption on the membrane surface decreased significantly. Moreover, biogenic AgNP improved the water permeability and did not sacrifice the selectivity of protein. The evaluation of silver release from the mixed matrix membranes indicated the good stability of biogenic silver nanoparticles in the membrane matrix. The results of the disk diffusion test revealed the excellent antibacterial activity of the membranes, including biogenic AgNP. In addition, the sludge immersion and the bacterial suspension filtration experiments showed that the membranes with biogenic AgNP not only prevented the bacteria attachment on the membrane surface but also inhibited the reproduction and development of biofilms. As seen in Figure 3.4, the biogenic AgNP was an effective material for decreasing the biofouling in the membrane process. Similarly, carbon based nanomaterials, like single-walled carbon nanotubes (SW-NTs), significantly reduce the bacterial and viral suspension in water due to their antimicrobial properties (Kang et al., 2007). Ahmed et al. (2013) coated nitrocellulose membranes with a nanomaterial...
solution containing 97 wt% of polyvinyl-N-carbazole (PVK) and 3 wt% of single-walled carbon nanotubes (SW-NTs) (97:3 wt% ratio PVK:SW-NT). Membranes coated with the nanomaterial solution exhibited significant antimicrobial activity towards Gram-positive and Gram-negative bacteria (80–90%); and presented a virus removal efficiency of $\sim 2.5$ logs. The possible antibacterial mechanism was explained as cellular inactivation with cell membrane damage, because the higher efflux of intracellular material (deoxyribonucleic acid, DNA) was analyzed in the permeate of membranes with SW-CNTs rather than in the filtrate of control membranes.

Rahimpour et al. (2011) fabricated novel poly(vinylidene fluoride) (PVDF)/sulfonated polyethersulfone (SPES) blend membranes with the immersion precipitation technique and then modified these membranes with TiO$_2$NP for antibacterial activity. The results of this antibacterial study indicated that the membranes with TiO$_2$NP efficiently eliminated $E. coli$ growth after UV treatment due to the photocatalytic bactericidal effect of the TiO$_2$ catalyst. The bactericidal effect of UV/TiO$_2$ photocatalysis is due to the presence of reactive oxygen species like O$_2^-$, H$_2$O$_2$ and HO generated by TiO$_2$ or the direct UV illumination of the cells. The bactericidal effect of TiO$_2$ photocatalytic on the death of $E. coli$ cells was explained with HO radical attack and lipid peroxidation reaction.

Huang et al. (2014) deposited the silver nanoparticles on the silica sphere surface to form Ag-SiO$_2$. They improved the anti-fouling performance and enhanced the dispersion of silver in the membrane. Ag-SiO$_2$ mixed matrix polyethersulfone (PES) membranes were fabricated by the phase inversion method. The effect of Ag-SiO$_2$ content on the membrane performance was investigated. The antibacterial and anti-formation properties of the membranes were systematically studied with pure cultures of both Escherichia coli and Pseudomonas sp. and also with a mixed bacteria culture in an activated sludge bioreactor. The results showed that the prepared Ag-SiO$_2$/PES membrane exhibited improved filtration performance and excellent antibacterial and anti-biofouling properties.

3.4.2 Desalination

Desalination is a unique process that removes the salts and minerals from water medium and is a key solution in solving the challenges of global water scarcity. Along with conventional desalination technologies like thermal distillation, the reverse osmosis (RO) process contributed greatly to the success of sea/brackish water desalination, despite high energy consumption (Emadzadeh
et al., 2014). Besides this, membrane fouling is the other problem for the RO process. Therefore, recent studies have focused on developing RO membranes with consistent high water flux by improving the anti-fouling property of the membrane surface. To prevent membrane fouling, some inorganic nanomaterials were introduced into RO membranes during the fabrication of thin film composite (TFC) membranes. Inorganic nanomaterials can improve film formation by offering the following benefits: (i) increasing the diffusion rate of monomers to the interface, (ii) expanding the wet zone on the top of the support layer and (iii) capturing by-products and controlling reaction pH (buffer agent) (Emadzadeh et al., 2015a). Moreover, inorganic nano-additives (e.g. titanium dioxide (TiO₂), silica, silver, and zeolite nanoparticles) improve the diffusion features of the formed membrane and also enhance their fouling resistance. The nanotechnology concept has led to new desalination membranes having high permeability, catalytic reactivity, and fouling resistance. Among the numerous concepts proposed, the most promising to date include zeolitic and catalytic nanoparticle coated membranes, mixed matrix and bio-inspired membranes, such as hybrid protein-polymer biomimetic membranes, aligned nanotube membranes, and isoporous block copolymer membranes. Figure 3.5 shows the classification of novel desalination membranes (Buonomenna, 2013).

Among the various nanoparticles, zeolite nanoparticles are the most popular nano-fillers in RO membranes. The physical and chemical properties of zeolite nanoparticles affect markedly the TFN membrane performance and it leads to more permeable polyamide active layers for water desalination. Generally, it can be said that zeolite nanoparticles provide preferential flow paths for water transport when they have a tight pore distribution less than the diameter of a hydrated salt ion. Besides this, it is also believed that the presence of zeolite nanoparticles in the polyamide layer may change the structure of thin film layer at the RO membrane surface by the formation of nano-gaps at the organic-inorganic interfaces, which can reduce the cross-linking density of the polyamide layer (Dong et al., 2015).
Over the past several years, the forward osmosis (FO) process using membrane-based technology has attracted considerable attention among membrane scientists as a potential desalination process to compete with RO in the future. Despite the distinct advantages offered by FO membranes in the water desalination process, the research on how to further improve the properties of thin film composite (TFC) FO membranes, particularly at the top active skin layer, still remains as the main research focus of researchers (Emadzadeh et al., 2014). Tian et al. (2015) fabricated a novel TFN-FO membrane on nanofibrous substrate with functionalized MW-CNT. MW-CNT increased the tensile modulus by 53% and substrate porosity by 18%. TFN membranes achieved a significantly higher water flux, i.e. 61 L m\(^{-2}\) h\(^{-1}\) in active layer-draw solution orientation. Emadzadeh et al. (2015b) prepared a self-synthesized TFN-FO membrane incorporated with hydrophilic functionalized titanate nanotubes (TNTs) and tested these membranes for FO desalination. TNTs improved the surface morphology and separation performance. The water flux of the FO membrane was significantly improved from 21.0 L m\(^{-2}\) h\(^{-1}\) of TFC (control) to 31.5 L m\(^{-2}\) h\(^{-1}\) in PRO mode by adding only 0.05 wt% of TNTs. It was concluded that modifying PA layer properties by adding TNTs was an effective approach to enhancing FO performance of typical TFC membranes because the large specific surface area and high pore volumes of TNTs might provide abundant adsorption sites and diffusion channels for water.

3.4.3 Fuel cell

Fuel cells generate the electricity by a chemical reaction. They are becoming increasingly popular due to the contribution of conventional fossil fuels to environmental pollution and the reduction of the overall oil supply. Among the various types of fuel cells, direct methanol fuel cells (DMFCs) have attracted extensive attention because of advantages like their low weight, simple system design, high energy density at low operating temperature, low emission and the ease of handling their liquid fuel. The key part of DMFCs is a proton exchange membrane (PEM), which is used to segregate both sides of the electrodes in order to prevent an internal electric current between the two electrodes and provide a charge carrier for the protons (Hasanabadi et al., 2013). Nafion® (DuPont, USA), Flemion® (Asahi Glass, Japan) and Aciplex® (Asahi Kasei, Japan) are mostly used for membrane material, but these materials are expensive and are major contributors to the system cost. The development of the membranes with a lower cost and higher performance is necessary (Peighambardoust et al., 2010). Therefore, full cell researchers focused on making new PEMs with high proton conductivity, durability, thermal stability, maximum power density and low fuel crossover, and low cost. The hybrid organic-inorganic composite or mixed matrix membranes have risen as an attractive option. The combination of organic and inorganic properties may overcome the limitations of the pure polymeric membranes. The utilization of novel polymers and the incorporation of inorganic materials as fillers in the pure polymer are several approaches for the development of new membrane material. Hydrophilic inorganic materials, such as silicon dioxide (SiO\(_2\)), titanium dioxide (TiO\(_2\)), and zirconium dioxide (ZrO\(_2\)), and heteropolyacids, such as phosphotungstic acid and silicotungstic acid, have been widely studied. Inorganic materials enhanced the mechanical properties, and also contributed to the blocking of the fuels, such as methanol, by increasing the transport pathway tortuosity and improving the proton conductivity, which resulted in better cell performance (Kim et al., 2014).

Aslan and Bozkurt (2014) prepared proton conducting nano-titania composite membranes. They also discussed the production and characterization of proton conducting super acid membranes. During membrane fabrication, sulfated nano-titania was firstly synthesized by hydrolysis and precipitation of titanyl sulfate (TS) and was then blended with sulfonated polysulfone (SPSU). The maximum proton conductivity of the prepared membrane was obtained as 0.002 S cm\(^{-1}\) at 150°C.

Aviles-Barreto and Suleiman (2015) studied the synthesis and characterization of mixed matrix membranes based on the sulfonated poly(styrene-isobutylene-styrene) (SIBS) and SW-CNT loading and functional groups’ substitution with the aim of evaluating their transport properties for direct methanol fuel cells (DMFC). The addition of SW-CNT limited the passage of methanol
through the membranes due to the partial blockage of the free volume by the SW-CNT. The high water content and transport results showed two different types of water inside the polymer membranes (bound and bulk water). Large amounts of bulk water seemed to inhibit the transport of protons, decreasing the proton conductivity of the membranes. For DMFC applications, selectivity values suggested that 0.1 wt% is the optimum SW-CNT loading. Using carboxylic groups as terminal functionalization in the SW-CNT had a zero impact on the overall transport properties (e.g. m selectivity) for DMFC applications.

3.5 CONCLUSION AND OUTLOOK

Mixed matrix membranes with nano-additives can be fabricated with different methods and have numerous application areas. These membranes are named as high-performance membranes due to relatively high flux, easy cleaning, good mechanical strength and dimensional stability and they are also suitable for different areas such as water filtration or fuel cell application. Modification of classical polymeric membranes with nanomaterials has become an expanding field of research, as the introduction of specific groups can improve the structure and performance of membranes. The key steps for this membrane fabrication are as follows: (i) choice of suitable inorganic nano-additives for homogenous dispersity in the membrane matrix, (ii) understanding of the relationship between polymer and additive for the ideal membrane structure, (iii) improving the stability of nano-additives in the membrane structure after fabrication for a long service life and (iv) regeneration or cleaning of mixed matrix membranes for reuse. Much research and development is still needed in order to understand the performance criteria of these membranes and to fabricate the ideal polymer-inorganic mixed matrix membrane.

ACKNOWLEDGMENTS

The authors are grateful to TUBITAK (The Scientific and Technological Research Council of Turkey) for their financial support under grant (Project No: 111Y095).

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