Chapter 7

Advanced Functional Membranes for Water Purification

E. Kavitha, S. Vishali*

Department of Chemical Engineering, College of Engineering and Technology, SRM Institute of Technology, Kattankulathur 603 203, Tamil Nadu, India.

* meet.vishali@gmail.com

Abstract

Worldwide, the scarcity of water due to the contamination of water and water resources from human activities has become a challenge. To overcome this, we need adequate water treatment technologies. For the past few decades, research has becoming wider to innovate the advanced technologies for water purification. Several conventional methods have been adopted for water treatment. Extensive investigations have been done, and some are still in development to find an eco-friendly and feasible process for water purification. The advent of membrane separation processes has changed the scenario in the field of desalination and water treatment. The proper selection of membrane material and configuration could be an excellent approach towards water purification. This chapter deals with the various advanced functional membranes, the functionalization of membranes employed in UF, NF and membrane distillation. This chapter also deals with their applications in wastewater treatment.

Keywords

Advanced Functional Membranes, UF, NF, Membrane Distillation, Water Purification

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1. Introduction

The swift growth in population and industrialization lead to the extensive demand for quality water. Due to the increase in industrialization and change of lifestyle, a vast volume of wastewater has been generated. Globally, the major crises for the human community are the inadequate availability of potable water, which forces the public to drink unhealthy water. The consumption of contaminated water is a health concern for humans and the entire ecosystem. The familiar wastewater sources are the industrial sector, commercial zone, residential area, irrigation release, etc. The major pollutants present in wastewater are organic, inorganic and biological contaminants. Some of the pollutants like heavy metals, radioactive materials are more toxic and hazardous. Also, some of the pollutants are non-biodegradable, which severely affects the healthy life of the ecosystem. However, proper treatment, reuse and recycle of water could reduce the water scarcity problem significantly [1].

Various conventional treatment technologies include chemical precipitation, adsorption, ion exchange, membrane separation processes, electrochemical treatment, etc. All these techniques have their own merits and also limitations. In the past few years, emerging pollutants in wastewater have become a severe threat. The existing traditional

methodologies are not compatible with the treatment of emerging pollutants. So, we require advanced technologies or advancements in the existing technologies to overcome this issue. In the past few decades, membrane separation processes are gaining importance because of their ambient condition operation, no phase change involved in the process, ease of installation and operation, less footprint area, compatibility to combine with other conventional separation processes and the possibility of both separation and recovery of the value-added components from the effluent. These merits triggered the attention of researchers to work towards advanced membrane technologies and developments in the fabrication of membranes [2].

The membrane separation processes are pressure-driven, concentration-driven, thermal-driven, electric potential driven processes. The separation mechanism can be sieving or diffusion. The proper selection of membrane material and modules could be an excellent solution for treating various pollutants. In recent years, plenty of research work is going on to improve the surface characteristic of the membrane so that it could be adopted for the selective separation of various contaminants in wastewater [3].

2. Developments in the synthesis of nano-based membranes

In recent years, nanomaterial science has grasped the attention in wastewater treatment by membrane separation processes. By coating, the suitable nanomaterial over the surface of the membrane could widen the applications of membrane separation processes in wastewater treatment. Recently, there are many rapid developments in the synthesis of nanomaterials and their incorporation in the polymeric matrix to produce the mixed matrix membranes for the application of water treatment [1].

2.1 Nanocomposite ultrafiltration membrane (NUF)

The ultrafiltration (UF) membrane has been increasing for the past few years due to the merits such as low-pressure operation, low energy consumption, ease of separation mechanism based on size exclusion and backwashing of the membrane is possible, which leads to reduced membrane fouling. Polymeric materials such as polysulfone (PSF), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polypropylene (PP), polycarbonate, cellulose acetate, cellulose nitrate, carboxymethylcellulose, polyvinyl alcohol, polyacrylic acid, etc., have been utilized in the fabrication of UF membranes. In recent years, UF membrane finds extensive application in wastewater treatment.

2.1.1 Polysulfone nanocomposite UF membrane

The developments and growth in the petrochemical and petroleum refinery, metallurgical, food process, paint, and fine chemicals industries have increased oily effluent generation

[2]. Membrane-based separation technologies have proven to be superior in the treatment of oily effluent compared to other convention techniques [3–5]. Y. Zhang et al. (2009) synthesized the advanced organic-inorganic composite membrane, using sulfated, Y -Y-doped zirconia as an additive to PSF. N, N-Dimethylacetamide is heated to 40-50°C and polysulfone is dissolved by proper mixing. Then, polyethylene glycol 400 is added to enhance the yield of pores. The Zirconia nanoparticles are added to this solution and mixed thoroughly to get the homogenous solution. The membrane is cast on a glass plate to form a thin film and immersed in a water bath. Then the membrane is leached and stored in formaldehyde to avoid biofouling [6].

The characterization studies on this novel membrane showed tensile strength twice that of PSF, and contact angle also got reduced almost 50%. This membrane has been employed to study the treatment of oily wastewater. The schematic diagram of the treatment process is shown in Fig. 1. The investigations have shown significant retention of oil, which is nearly 99% and it could be a feasible membrane for the separation of oil from the effluent stream. From the literature, the incorporation of inorganic nanoparticles on the surface of the membrane could increase the permeability of the membrane and enhance the surface characteristics of the membrane [7–9].

Figure 1. The schematic representation of the experimental process for the treatment of oily effluent

2.1.2 PVDF UF membrane

Biopolymers are the natural polymers produced from living organisms and consist of monomers forming macromolecules by a covalent bond. Cellulose is an abundantly available biopolymer. It is crystalline, fibrous, hydrophilic and has a high molecular weight [13]. It is an eco-friendly biopolymer and also sustainable and biodegradable material. The Nano-crystalline cellulose combines both cellulose components such as its hydrophilicity, recoverability, biodegradability, and the benefits of nanoparticles such as high specific surface area, higher activity, mechanical and tensile strength [14]. The synthesis of NCC can be done by either chemical modification or mechanical modification methods. The chemical modification involves strong acid hydrolysis [15] and mechanical modification involves high-pressure refinement or homogenization [16,17].

Haolong Bai et al. (2012) synthesized NCC using chemical and mechanical modification techniques [18]. The synthesis process involves acid hydrolysis and mechanical homogenization. The cellulose pulp is reacted with a diluted sulphuric acid solution at 85°C. Then the pH of the solution is adjusted to neutral. After drying the solution, the solid content is suspended in N, N-dimethylacetamide and then it is subjected to high-pressure homogenization. The fabrication of PVDF/NCC composite membrane follows Loeb – Sourirajan Phase inversion technique. The experimental findings of Haolong Bai et al. (2012) are as follows: (i) the permeability and water flux could be improved significantly by composite membrane compared to PVDF membrane, and (ii) the pore size of the membrane and porosity were found to be more than PVDF membrane [18].

Table 1 Advanced functional Nano composite membranes

Nano-composite membrane	Contribution of the research work	Type of effluent	Target ion/contaminant	References
Polysulfone composite membrane with sulfated Y-doped zirconia/	Synthesis, characterization of membrane and treatment of oily wastewater	Oily wastewater	Oil	[6]
Polyvinylidene fluoride nano composite membrane coated with alumina nano particles	Synthesis, characterization of membrane and treatment of oily wastewater	Oily wastewater from an oil field	Oil	[12]

Polyvinylidene fluoride composite membrane with cellulose nano-crystals	Synthesis and characterization of membrane	-	-	[18]
Polyvinylidene fluoride nano composite membrane coated with TiO ₂ nano particles	Synthesis and characterization of membrane	-	-	[19]
Polyethersulfone coated with functionalized graphene oxide mixed matrix membrane	Synthesis, characterization of membrane and treatment of wastewater	Raw wastewater from Membrane bioreactor water treatment plant	Fe(II), Zn(II), Cd(II), Cr(VI),	[20]
ZIF-8 Nano composite membrane	Synthesis, characterization of membrane and treatment of dye effluent	Dye effluent	Dye	[21]
Hydroxyapatite nano composite membrane coated with silver nano particles	Synthesis, characterization of membrane and treatment of palm oil mill effluent	Palm oil mill effluent	Oil	[22]
Polyethersulfone nanocomposite membrane with sulfonated graphene oxide	Synthesis, characterization of membrane. Treatment of wastewater and electricity generation	Wastewater	COD removal	[23]
Polysulfone nano-composite membrane with graphene oxide	Synthesis, characterization of membrane and treatment of wastewater containing Bisphenol A	Wastewater	Bisphenol A	[24]
Polyvinylidene fluoride-polyaniline membrane with graphene oxide	Synthesis, characterization of membrane and treatment of dye effluent	Dye effluent	Allura red, Methyl orange	[25]

3. Advanced functional nano filtration membranes

Organic, inorganic and biological contaminants are present in wastewater. The inorganic contaminants, one of the major pollutants present in wastewater, are released from process industries such as petroleum refineries, fertilizers, textile and dye, paint, pharmaceutical industries, etc. [26]. The chief inorganic contaminants in wastewater are heavy metals, trace elements, mineral acids, salts, metal compounds, etc. [26]. Most of these pollutants are toxic, hazardous and non-biodegradable. These contaminants harm humans, animals and also aquatic life. However, some of these pollutants are micropollutants present in only trace quantity such as in mg/L or ng/L. Even in trace concentration, these contaminants are not desirable for the healthy life of the ecosystem. There are no adequate technologies for the treatment of micro-pollutants either from municipal wastewater or industrial effluent.

However, pressure-driven membrane technologies such as RO and NF have proven promising technology for separating these micro-pollutants since they possess higher rejection, compactness and ease of operation, and feasibility to combine with other conventional separation processes [27]. NF membranes find applications in desalination, treatment of fine chemicals, food process and biotechnology industrial effluents. In the past few decades, various developments in the surface modification and fabrication of NF membranes by technologies such as interfacial polymerization by applying nanomaterials and other additives, grafting, electron beam radiation, layer-by-layer modification, plasma surface modification, etc. [28]. All these technologies have been developed to enhance the characteristics and functionalization of NF membranes to improve the rejection rate, selectivity and to overcome fouling tendency.

3.1 Interfacial polymerization

In recent years, the fabrication of thin-film composite membranes by interfacial polymerization has gained attention due to the improvement in the selectivity and anti-fouling tendency of the membrane. The ease of operation and self-inhibiting reaction made this technique more feasible. Various monomers include bisphenol A, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, m-phenylenediamine, piperazine, polyhexamethylene guanidine hydrochloride, etc., have been employed in the interfacial polymerization for the fabrication of thin-film composite membranes [29,30].

In recent years, the incorporation of nanoparticles in interfacial polymerization has attracted many researchers. Since they possess specific unique characteristics such as antimicrobial and catalytic tendencies, they gained attention. Also, the composite membranes incorporated with nanoparticles exhibit excellent selectivity, rejection rate, permeability, mechanical strength, and hydrophilicity. The widely used nanoparticles are silica, and zinc oxide, titanium dioxide. In one of the recent studies, aluminum oxide

hydroxide particle known as Boehmite nanoparticles is used to synthesize polyethersulfone membrane to improve the separation efficiency of the membrane [31].

This advanced functionalized mixed matrix NF membrane possesses a highly hydrated surface and is hydrophilic. Recently, a combination of nanoparticles has been studied to improve the characteristics of the NF membrane. For example, polyether sulphone membrane incorporated with polyaniline/Fe₃O₄ nanoparticles aids in the removal of heavy metal ions from wastewater [32]. The combination of nanoparticles utilized in the fabrication of NF membrane is carbon nanotubes, halloysite nanotube, nanofiber, etc. [33–35].

3.2 Grafting polymerization

Grafting polymerization can be done either by UV-assisted/initiated grafting polymerization or by photo-grafting polymerization. Qiu et al. (2007) synthesized the NF membrane from the cardo-polyether ketone UF membrane via photo-grafting co-polymerization [36]. Deng et al. (2011) fabricated an NF membrane with a positive charge on its surface from polysulfone UF membrane using UV grafting polymerization [37].

3.3 Electron beam radiation

The electron beam radiation process involves the creation of active sites on the polymer without any additives. This leads to the formation of NF membrane with improved porosity, pore size, permeability, and rejection rate. Few examples for NF synthesis by electron beam radiation are as follows: (i) nylon 66 polymer cross-linked by electron beam irradiation [38], (ii) polysulfone layer grafted with 2-acrylamido-2-methylpropanesulfonic acid.

3.4 Plasma surface modification

In this process, to increase the hydrophilicity and decrease the membrane fouling, nitrogen functional groups are incorporated with the membrane by applying nitrogen-containing plasma [39]. The surface characteristics of the NF membrane can be permanently modified by plasma-induced graft polymerization.

3.5 Layer-by-layer surface modification

This process involves the addition of amine coupling and silane coupling in a layer-by-layer surface modification of NF membrane. One of the examples layer-by-layer surface modification of NF membrane is the fabrication of polybenzimidazole/polyethersulfone NF membrane to separate heavy metal ions from wastewater.

3.6 Applications of advanced functional NF membranes in wastewater treatment

Polyelectrolyte multilayer-based NF membrane fabricated by layer-by-layer surface modification has been employed to separate micro-pollutants from wastewater [40]. Polydopamine coated polyether sulfone incorporated with amino-functionalized multi-wall carbon nanotubes has been employed to treat oily wastewater [41]. The cross-flow filtration setup is shown in Figure 2.

NF hollow fiber membrane prepared by mixing sulfonated polysulfone with polyethersulfone followed with the formation of hollow fiber membrane using polyethyleneimine in the bore fluid has been investigated by Gao et al. (2020) for the separation of heavy metal ions from wastewater [42].

Figure 2 Cross-flow filtration setup [41]

4. Membrane distillation

Membrane distillation is an emerging technology in separation processes and gaining importance in recent years. It is the thermally driven membrane separation process. This process involves the separation at lower pressure and temperature compared to the traditional distillation processes and hydrophobic porous membranes are employed for this process. The separation mechanism is based on the difference in vapor pressure of volatile species across the hydrophobic membrane surface. The pore size of the membrane is relatively larger than the pores of the RO and NF membrane. The feed side of the membrane is at a slightly higher temperature compared to the permeate side and the

permeate side is at lower temperature or ambient temperature. This temperature difference across the membrane surface ensures the vapor pressure difference. Due to the hydrophobic nature of the membrane and vapor pressure difference across the membrane surface, water vapor alone can permeate through the membrane. The water vapor exiting the permeate side of the membrane is condensed and collected. The schematic representation of the separation mechanism of membrane distillation is shown in Fig. 3. The rate-controlling mass transfer mechanisms are the Knudsen diffusion model, molecular diffusion model and viscous flow model [43].

This process has been employed for seawater desalination, wastewater treatment, the concentration of fruit juices, etc. Recently, this process has been adopted for the treatment of radioactive wastes [44, 45]. In the past few years, the application of this process has been widening due to its unique merits, such as relatively low-pressure operation compared to other membrane separation processes like RO, low-temperature operation compared to other conventional distillation processes; also, there is no need to heat the feed solution till its boiling point for achieving the separation, cost-effective process, could be easily coupled with other membrane separation processes like UF and RO, alternate energy sources like solar energy could be utilized [45–49].

Figure 3 Schematic representation of separation mechanism by membrane distillation [43]

4.1 Configurations and modules of membrane distillation

There are mainly four different configurations in the membrane distillation process. They are direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) [50].

Polymeric compounds such as polyvinylidene fluoride, Polypropylene, and polytetrafluoroethylene are widely used to fabricate membranes employed in MD units [51–53]. The application of hydrophobic membranes in the MD process suffers from certain limitations, such as membrane fouling and wetting of pores of the membrane. Both these characteristics are not desirable for the effective separation process. So, recently, much research is carried out to investigate the feasibility and functional modification of commercially available membranes to overcome these limitations. Various studies have been conducted to assess the characteristics of superhydrophobic and omniphobic membranes for their successful implementation in the membrane distillation process for desalination and wastewater treatment.

4.2 Super hydrophobic membranes in membrane distillation

The main drawback of the hydrophobic membrane in the membrane distillation process for wastewater treatment is the wetting of membrane surface and fouling. The foulant blocks the membrane's pores, which in turn affects the water flux of the membrane [54]. In applying the MD module for the desalination of saline water containing surfactants, pores of the membrane will get attached to the hydrophobic tail of surfactants. Since the hydrophilic head is exposed, that makes the pores of the membrane hydrophilic. This leads to wetting of membrane pores and declines the retention of salt from saline water [55]. To overcome these limitations, superhydrophobic membranes could be employed for membrane distillation. Recently, several attempts have been made to enhance the hydrophobicity of the PVDF MD membrane. The experimental findings of Wang et al. (2017) show that there is no significant change in the water flux and retention of contaminants in the MD process with feed solution containing stable surfactants [56]. The preparation of dope solution plays a significant role in changing the structural characteristics of the membrane. For the past few years, researchers have been investigating the modification in the preparation of dope solutions to enhance membrane characteristics in the MD module. M. Khayet et al. (2002) investigated the addition of 1,2-ethanediol with a dope solution and found an increase in the roughness of the surface of the membrane [57].

The hydrophobicity of the membrane could be enhanced by using hydrophobic nanoparticles since they are superhydrophobic [58]. The addition of hydrophobic

nanoparticles, such as silica nanoparticles, calcium nanoparticles, into the dope solution could improve the roughness of the membrane surface, pore size, and hydrophobicity [58,59]. Hence, it has been proved from several studies that by using the appropriate additives in the dope solution, roughness, porosity, and hydrophobicity of the membrane could be improved significantly. Adopting the proper additive could induce crystallization, leading to the formation of the nodule to improve the roughness of the membrane.

Several methodologies have been attempted in the fabrication of superhydrophobic membranes for the MD process. Various preparation techniques for the fabrication of PVDF superhydrophobic membrane include phase inversion, non-solvent induced separation, vapor induced phase separation, etc. The following methodology has been adopted from W. Zhang et al. (2013). This methodology follows a modified phase inversion technique for the fabrication of a superhydrophobic membrane. Ammonia water, an inert solvent additive, has been mixed with the dope solution. Incorporating additive in the dope solution creates the PVDF clusters by incipient precipitation due to the localized micro phase separation. Hence, the formation of a superhydrophobic membrane is obtained as the clusters of PVDF grow to form a spherical structure with increased contact angle (up to 158°) [43].

Hou et al. (2014) studied the preparation of PVDF / calcium carbonate nanoparticles flat sheet composite membrane and employed for the desalination process by DCMD process [58]. Wu et al. (2017) fabricated the superhydrophobic membrane PVDF membrane by silica particle-assisted non-solvent induced phase separation process and applied it in the MD process. The preparation of dope solution involves the proper mixing of propylene glycol and dimethyl acetamide followed by silica particles. Then the solution is kept for ultrasonication for about half an hour. With this solution, PVDF is mixed by stirring the solution at a speed of 1000 rpm at a temperature of 80°C for 4 h to yield a homogeneous solution. Then the dope solution is cast on a glass plate and kept at ambient air for the 30s. The solidified sheet is removed and immersed in deionized water at atmospheric temperature for a day. Then the membrane sheet is removed from the water and kept for atmospheric drying, followed by vacuum drying [62]. Wu et al. (2017) studied the treatment of saline water by fabricating PVDF superhydrophobic membrane by the process mentioned earlier and employed in the MD module to treat saline water. It was observed from the experimental findings that the salt retention is more than 99% and the water flux of the membrane was observed 2.7 times more than that of pristine PVDF [62]. The schematic diagram of the experimental setup for the direct contact membrane distillation is shown in Figure 4.

Figure 4 Schematic representation of experimental setup of direct contact membrane distillation setup [62]

Zhang et al. (2020) studied the fabrication of superhydrophobic PVDF membrane by non solvent induced phase inversion technique by utilizing NaCl-H₂O as a green additive, with improved water flux and more than 99% salt rejection [63]. A recent study by Li et al. (2020) involves the fabrication of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PDTS) - Zinc oxide – PVDF and its application in DCMD. The dope solution is prepared by mixing PVDF, zinc oxide nanoparticles in the solvent dimethyl acetamide and acetone in a proper ratio. Then the solution is stirred for the complete blending of the solution. The thoroughly blended solution undergoes electro spinning and then membrane casting. The fabricated membrane is adopted for the DCMD process to treat saline water, saline water with low surface tension sodium dodecyl sulphate and calcium sulphate [64]. A Novel super hydrophobic composite hollow membrane was synthesized quite recently by Ding et al. (2021) and employed in a vacuum membrane distillation module for the desalination process. The synthesis involves the filter coating and phase inversion technique. A thin composite layer is prepared from poly-dimethyl silane and PVDF on a substrate by suction coating. The substrate is immersed in a bath with silicon dioxide, which leads to the formation of a super hydrophobic membrane [65]. Wen et al. (2021) performed the preparation of super hydrophobic membrane by using graphene oxide membrane with fluorinated silica nanoparticles. The membrane performance was investigated by employing the membrane in an air gap membrane distillation process.

4.3 Omniphobic membranes

Superhydrophobic membranes hold excellent water repellent tendencies. However, they are susceptible to wetting by organic contaminants in wastewater. The contaminants possessing low surface tension can lead to the wetness of the pores of the membrane. The

wettability of membrane pores can deteriorate the function of the membrane in effectively separating the liquid-vapor interface and which in turn can restrict its application in the MD process [66]. Since the omniphobic membranes can exhibit repellent both to water and organic compounds, the studies on the synthesis of omniphobic membranes and fabrication of MD modules for wastewater treatment and desalination have significantly gained importance in recent years. The re-entrant geometries and functional modification of the membrane are the key factors in the synthesis of omniphobic membranes to enhance their repellent tendency towards water and species with low surface tension [67]. Also, it is equally important to impart the characteristics such as chemical, thermal and mechanical strength to withstand the MD process. In the functional modification process to impart omniphobicity, a thin gas film is created adjacent to the surface of the membrane, which restricts the contact area of liquid on the surface of the membrane. However, exhibiting the omniphobic behaviour towards highly saline water with oil and surfactants is still uncertain. Boo et al. (2016) studied the performance of the membrane and found the steady performance of the membrane with excellent wetting resistance towards the feed containing surfactants [68].

Several studies have been demonstrated to impart the surface omniphobicity by creating the re-entrant geometries on various substrates [69], especially by the deposition of nanoparticles [70]. Zinc oxide is a well-known compound that exhibits rich growth morphology [71] and produces by chemical bath deposition. Studies have been conducted to synthesis omniphobic surfaces by chemical bath deposition of zinc oxide nanoparticles on the silicon substrates [72, 73]. Chen et al. (2018) studied membrane fabrication by depositing zinc oxide nanoparticles on the glass fiber to create the re-entrant geometry to impart omniphobicity [70]. The fabrication of omniphobic membrane for the MD process is adopted from Chen et al. (2018). The fabrication involves the deposition of zinc oxide nanoparticles on the glass fibre membrane using a chemical bath deposition method. After the deposition, the process follows fluorination of the surface and then a coating of polymer.

The schematic representation of the process flow diagram is shown in Fig. 5. The saline water as a feed solution is taken in the feed tank. The feed solution is heated and passed through the direct contact membrane distillation (DCMD) module. In the DCMD module, the feed solution is in direct contact with the hot side of the membrane. Due to the vapor pressure difference, water vapor alone permeates through the membrane. Then it flows through the chiller, where it is condensed and the treated water is collected in the permeate collection tank.

Figure 5 Process flow diagram of DCMD for the treatment of saline water [70]

Conclusion

In the past few decades, there has been an immense growth in the development of membrane separation processes and the fabrication of advanced functional membranes for the application in water purification. However, some of the technologies are either under research or in pilot scale and need to be enhanced for their specific applications. In recent years, the advent of nano-composite based UF and NF membranes have been gaining significant attention in the field of water purification and also produced substantial outcome. The advancements in the characteristics of membranes for the application in membrane distillation process has becoming the emerging technology. The implementation of advanced functional membranes in the industrial scale by overcoming the challenges such as membrane fouling, cost of operation, etc., could be an excellent choice for addressing the water scarcity issues. The outcome of all the advanced functional membranes in water purification has evidenced the success of technology. In the future, the advanced membranes with more economical and technical viability, could find wide applications in water purification.

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