Sustainable Materials and Technology

Akil Ahmad
Mohammed B. Alshammari *Editors*

# Nanofiltration Membrane for Water Purification

Springer

# Sustainable Materials and Technology

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Akil Ahmad · Mohammed B. Alshammari
Editors

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*Dedicated to Sir Syed Ahmad Khan (1817–1898)*

*An Educationist and Reformer for Indian Muslims*

*Sir Syed Ahmad Khan was born in the well-known city of India, Delhi, on October 17, 1817. He had a strong belief that any national or religious cause can be promoted only on a strong foundation through scientific temperament. With this thought, he started the Aligarh movement and later established a college called Muhammadan Anglo-Oriental (MAO) College in Aligarh, India. After this great personality's departure in 1898, all the mourners turned the procession into a political demonstration urging for the grant of university status to his college in Aligarh, India, in fulfilling the cherished dreams of the visionary. This university is now a world-famous university and known as Aligarh Muslim University. This is a sure sign to attest to the power of the influence welded by this great and visionary personality. Whatever he dreamed now flourished in making the slumbering people rise with a resurgent spirit that they could now fearlessly face the situations of their times and hope for a promising future.*

# Preface

At the present time, most of the developing and underdeveloped countries are facing drinking water problems due to increasing world population and industrial expansion. With increasing anthropogenic and industrial activities, most of the industrial discharges like organic and inorganic pollutants enter into the water bodies and contaminate the system. Therefore, there is an urgent concern worldwide to search the new water resources and purification techniques to treat wastewater to reuse in daily life.

Among all the studied water purification techniques like adsorption, flocculation, precipitation, ion exchange, etc., there have been growing interests in the advancement of nanofiltration membrane as sustainable approach which are effective and efficient for the removal of toxic pollutants even in trace amount from wastewater. Apart from other techniques, the nanofiltration membrane is considered as a simple, sustainable, economical and extensively used technique which plays a significant role in waste purification. The preparation, characterization and design of nanofiltration membranes play a vital role to make them more effective and efficient in the application of water purification.

In this book, a summary of recent information about membrane hydrophilicity, water flux, removal efficiency, characterization, design and mechanisms involved during the separation process are discussed in detail. This book helps academicians, scientists, researchers and working people in industries to understand the mechanism of nanofiltration membrane as a sustainable and promising technique in the field of wastewater treatment. This book provides a wide knowledge of nanofiltration technique to the water purification audiences concerning the recent development with various illustrations, methods and results for graduate students, scientists, academicians, researchers and industrialists. Readers from wastewater and water purification may take help as a quick reference by exploring the research literature on the subject field with commercial value-added research applications of nanofiltration membrane. This book offers significant coverage of the commercial status, trends and performance of nanofiltration membrane technique.

We are greatly thankful to all qualified researchers, scholars and leading experts to contribute their valuable work. The chapters provided cutting-edge up-to-date research findings on nanofiltration technique. We collected all the information given by eminent authors on nanofiltration and related membrane research from Turkey, India, Indonesia, Saudi Arabia, etc., and, finally, compiled this project in a fruitful way.

Al-Kharj, Saudi Arabia

Akil Ahmad
Mohammed B. Alshammari

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**Dr. Akil Ahmad** Akil Ahmad currently working at Prince Sattam bin Abdulaziz University, Saudi Arabia as Assistant Professor in Chemistry and having the experience of seven years as Research Fellow, Teaching Fellow, Postdoc and Visiting Researcher from Universiti Teknologi Malaysia, Universiti Sains Malaysia, University of KwaZulu-Natal, South Africa and Universiti Kebangsaan Malaysia, Malaysia. He has completed Ph.D. in Analytical Chemistry (2011) with the topic "Modification of resin for their use in the separation, preconcentration and determination of metal ions" from Aligarh Muslim University (AMU), India. His research interest in the areas of environmental pollutants and their safe removal, synthesis of nanoparticles and Nanosorbents (GO, CNT), photo-degradation and antimicrobial effects, water and wastewater treatment and adsorption and ion-exchange. He has published more than 100 research articles and chapters in the journals and publishers of international repute such as Scientific reports, Talanta, Chemical Engineering Journal, Journal of Industrial and Engineering Chemistry, Journal of Molecular Liquids etc. He has also edited five books of Springer and Elsevier. H-index and citation in Scopus are 24 and 2010 and in Google scholar, H-index and citation are 27 and 2653. He is guest editor of many reputed journal namely *Adsorption Science and Technology*-Hindawi, *Polymers* MDPI, *Frontiers in Environmental Chemistry and Journal of Chemistry*, Hindawi.

**Dr. Mohammed B. Alshammari** Mohammed B Alshammari was born in Saudi Arabia in 1978. He received his B.Sc. and M. Sc. degrees in Chemistry from King Saud University, Riyadh, KSA in 2007 under supervision of Professor Abdullah Almajed and Professor Hassan Alhazmi. He worked in Chemistry department in KSU for 9 years as researcher. He received his Ph.D. degree from Cardiff University, UK, in 2013 under supervision of Professor Keith Smith. His research focused in using of organometallic intermediates in organic synthesis. In 2013, He worked as assistant Professor in Prince Sattam bin Abdulaziz University and promoted to associate professor in 2019. He has published more than 45 International per-reviewed journal publications and 45 conference proceedings in the area of Organic Chemistry and Chemistry. Supervised 2 M.Sc. students. PI of 3 grants from the University, and 1 grant from the SABIC in collaboration with PSAU. His research interest in the areas of organic synthesis of organic compounds, wastewater treatment and polymers by different methodology such as lithiation reaction, Matteson homologation and others. In addition, He published number of papers about the biological activity for synthesized compounds and pollutants removal from wastewater using different analytical techniques.

# Chapter 1
# Introduction and Basic Principle of Nanofiltration Membrane Process

**Vemula Madhavi and Thotakura Ramesh**

**Abstract** One of the demanding challenges of the twenty-first century is to improve the decontamination of the water by sustainable and economically adaptable technologies. Traditional water treatment technologies, though efficient, give rise to several problems and not adaptable that obstructs the development processes. The application of membrane technology in wastewater treatment has been gaining great interest and has shown potential results for the elimination of toxic pollutants. Nanofiltration (NF) in membrane technologies is relatively recent development and is explored due to stringent water quality standards. NF has outplaced reverse osmosis in most of the applications due to high flux rates with better pollutant rejection. This chapter incurs to address the principles and concepts of NF membrane technology for water treatment including fundamental mechanism and fouling in the process. Besides, a general outline was made on the different membrane fouling types and mitigation strategies in NF process and future perspectives.

## 1.1 Introduction

Extensive growth in technology and industries, water contamination and scarcity have evolved a comprehensive challenge world-wide (Mekonnen and Hoekstra 2016; Haddeland et al. 2014). Substantial research has been devoted for evolving advanced materials and technologies to extend efficient water supply by wastewater reuse. Among all water treatment technologies, pressure-based membrane processes such as microfiltration (MF), Ultrafiltration (UF), Reverse Osmosis (RO) and Nanofiltration (NF) have been emerged as most energy efficient and technologically robust. In particular NF membranes provide better rejection of multivalent ions and organic molecules with much higher flux, rendering NF an ideal water treatment technology with high performance applications (Fig. 1.1). The applications of NF membrane technology are expanding and are not limited to elimination of heavy metals and

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pesticides from ground water, separation of organic compounds in wastewater, water recycling in industrial process streams and softening brackish water. NF membrane technology is a sustainable, energy efficient and high separation efficiency technology and has been applied in the separation and purification in industrial sectors like food, medicine, chemicals and biotechnology etc. beside waste water treatment. NF with operation pressure between RO and UF provides much higher flux than RO and high solute rejection than UF. In general, polymers and ceramic materials are used to fabricate NF membranes. Owing to the good film forming property, suitable flexibility and mechanical strength, polymeric membranes are being mostly used in fabrication NF membranes. Polymers such as polyamides (PA), cellulose acetate (CA), polysulphones (PES), polyvinylalcohol (PVA), polyimides (PI), chitosan (CS) etc. are being used for preparing NF membranes. In general, nanoparticles are incorporated into these membranes to enhance high productivity and demonstrate promising potential in solvent permeability, remarkable mechanical/thermal stability and antifouling properties (Yin and Deng 2015; Jhaveri et al. 2016; Li et al. 2017).

The significant advantages provided by NF membranes have gained much attention from over past decade such as low energy consumption, low pressure temperature and relatively easy scaling up (Fig. 1.2). In view of this context, this chapter overviews the state-of-the-art of NF membranes, fouling mechanism and current trends of fouling control is briefly discussed for their high permeability and flux properties. A general review focusing on the role of large number of nanomaterials such as metal and metal oxide nanoparticles, carbon based nanoparticles, metal–organic frameworks etc. to prepare the nanobased polymeric filtration membranes. Brief description on the recent studies of NF membrane fabrication followed by effects of nanoparticles on the properties of NF has been emphasized.

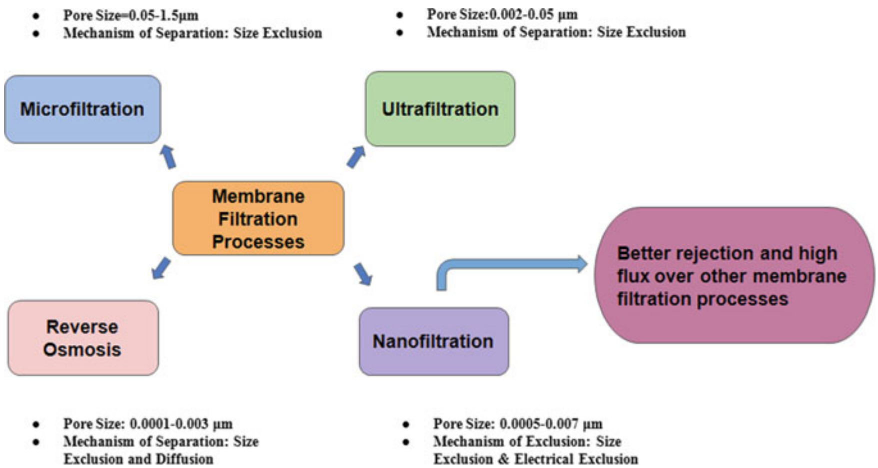


**Fig. 1.1** Membrane filtration processes for water purification and advantages of NF over other filtration processes

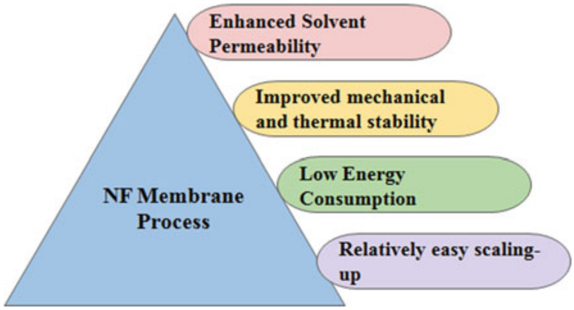


**Fig. 1.2** Significant advantages of NF membrane process for water purification

## 1.2 Principle of NF Membrane Technology

Membrane separation technology makes use of the differences in the selective osmosis performance, external energy or chemical potential as driving force to separate, decontaminate and augment the gas or liquid of the multicomponent mixture. Nanofiltration process is a subset of membrane separation technology has found to be successfully endorsed as a green water treatment technology that can replace traditional wastewater treatment methods. The separation spectrum of the process was extended beyond the traditional cut point limit of standard filtration of the very finest distinct molecule size of around 1 nm and has a high removal rate for multivalent ions and organic solutes larger than about 200 Da. It deals with the separation of materials that have been dissolved in a liquid such as hardness causing salts, particulates, turbidity, heavy metals, dyes etc. by diffusion of the solvent across the mass of the membrane matrix, prevailed by a high transmembrane pressure. The transmembrane pressure difference required for NF membrane separation is generally 0.5–2.0 MPa, which is 0.5–3 MPa lower than the pressure difference required to acquire the same permeation with RO membrane and is called as “loose reverse osmosis”. Recent advancements in membranes for NF have appreciably enhanced their abilities in very high or low pH environments, and to organic liquids (Sidek et al. 2015). The membranes fabricated from polymer are highly cross-linked, tends to give enduring stability and practical lifetime in hostile environments. The membranes are key to the performance of NF systems and are characterised by chemical and physical compatibility with pore size distribution, surface chemistry, porosity and cost. The NF membranes are produced in frame form, plate form, spiral wound, capillary, tubular and hollow fibre formats from a wide variety of materials such as cellulose derivatives, synthetic polymers from inorganic materials and ceramics from organic/inorganic hybrids. The NF membrane process characteristics are summarized in Fig. 1.3. The functions of membrane depend on three layers. The first layer is an active layer that determines the permeability and separation of components. The second is supporting layer, helps to adapt the mechanical properties and the last layer is a macroporous layer below the medium layer.

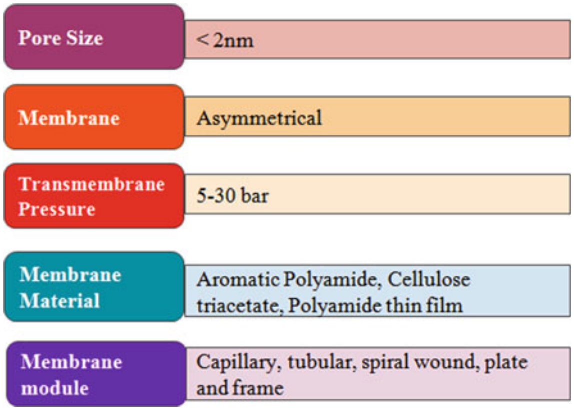


**Fig. 1.3** Characteristics of NF membrane

## 1.3 Mechanism of Separation

The NF membranes found exceptionally beneficial in the fractionation and explicitly removes the solutes from intricate process flow streams. The progress of NF technology as a sustainable technique over recent years has led to the significant improvement in its application in a number of industries such as treatment of effluents in waste water treatment, separation of pharmaceuticals, demineralisation and metal recovery from waste water etc. The NF membranes have 1 nm sized pores and hence small uncharged solutes are rejected while the inorganic salts by the charge/electrostatic effect of the membranes and ions. NF membranes demonstrate intermediate properties between those of Ultrafiltration (UF) and Reverse Osmosis (RO), operated at low pressure compared to RO and higher rejection compared to UF, both charge and size of the particle play significant role in NF rejection mechanism. The mechanisms accountable for solute transfer across NF membranes are convection, diffusion and electro-migration. Convection is the presiding mechanism at high membrane thickness-to-porosity ratios and high permeate flux. Diffusion presides at low membrane thickness-to-porosity ratios, low permeate volume flux and high charge density on the surface of membrane. Electro-migration is the presiding mechanism at solute transport for moderate membrane charge densities.

On the other hand, the decline of uncharged solutes depends on the size of the pores of NF membrane material (Fang et al. 2014). The properties of NF membranes, thereby, enable ions to be separated by the synerging of size and electrical effects of UF and the ion association mechanisms of RO. Macoun (1998) presented the NF rejection mechanisms considering the basic membrane properties of pore size, charge, dielectric constant and hydrophilicity. The summarized rejection mechanisms can be presented into following different rejection patterns.

(1) Wetted Surface rejection mechanism: water associates with the membrane through hydrogen bonding and the molecules which form the hydrogen bonding with the membrane can be transported.

(2) Preferential Sorption-Capillary rejection mechanism: membrane is heterogeneous and microporous, electrostatic repulsion occurs due to difference in electrostatic dielectric constants between solution and membrane.
(3) Solution-Diffusion rejection mechanism: membrane is homogeneous and non-porous, solute and solvent dissolve into the active membrane layer of the membrane and the transport of the solvent occurs due to the diffusion through the membrane.
(4) Charged Capillary rejection mechanism: electric double layer in the pores determines rejection. Ions of same charge as that of membrane are attracted and counter-ions are rejected due to the streaming potential.
(5) Finely Porous rejection mechanism: membrane is a dense material punctured by pores. Transport is determined by partitioning between bulk and pore fluid.

## 1.4 Fouling in NF Membranes

Fouling of NF membrane decreases the flux with time of operation due to solution chemistry effects or concentration polarisation and is probably the reason for minimal acceptance of NF membrane in large scale processing. Fouling can be defined as a deposition and accumulation of undesired solutes, colloids, macromolecules, salts etc. on the surface of the membrane on aggregation of the pores causing partial or total blockage of pores, resulting in the rejection of flow. The most common fouling types are organic, inorganic, particulate and biological fouling. In most of the cases, all four types of fouling go together (Cheryan 1998; Broeckmann et al. 2005). Fouling is an irreversible and time-reliant phenomenon and is caused by interactions between solute–solute and solute-membrane that leads to resistance in the flow of permeate. Notably, the interaction between solute and membrane assess the fouling formed by the accumulation of solute onto the surface of the membrane (Strathmann 1990; Susanto and Ulbricht 2005). However, physicochemical interactions such as Vander Waals forces, chemical binding and Lewis acid–base interactions are also majorly entailed in the interactions on molecular level.

Moreover, the parameters like temperature, pressure, pH, feed concentration, flow, equipment design contribute to membrane fouling. These factors causing fouling i.e., pore blockage possibly formed by accumulation on the membrane increase the decline to permeation. Concentration polarisation is complete obstruction of membrane, results when the solutes that accumulate on the membrane surface are greater than the membrane pores and subsequently leads to a larger local osmotic pressure. This provides decline to mass transfer by the membrane and as a result, flux rejection in permeate occurs. In order to decrease or eradicate fouling, it is essential to identify the foulants. This can be accomplished by the characterisation of the fouled membrane that follows suitable control strategies. The control strategies integrate on a number of categories, namely, membrane selection, module design, feed treatment& operation mode, cleaning (Fane et al. 2000).

## *1.4.1 Mitigation Strategies of Membrane Fouling*

To develop simple methods for the prevention or elimination of membrane fouling, few strategies and techniques have been tailored for the successful intervention. Membrane surface properties significantly impact the fouling and hence proper tailoring of membrane properties can resolve the trouble (Zhongyi 2016). The techniques are generally categorized in two ways. One method is passive antifouling strategy to avoid the early adsorption of foulants on membrane surface without affecting the unique qualities of foulants. The other method is an active antifouling, contrast to passive strategy, eliminates the proliferative foulants by destructing chemical properties of foulants. This section discusses few mitigation and control techniques to manage the adverse effects of membrane fouling.

### 1.4.1.1 Pretreatment of Wastewater

Pretreatment of water preceding to its processing in a membrane filtration, intended to minimise the chances of fouling maintaining the membrane efficiency and life span. Various pretreatment processes are designed accordance with the properties and chemical composition of feedwater.

### 1.4.1.2 Conventional Treatment Process

Conventional treatment involves the various processes including disinfection, pH adjustment, coagulation/sedimentation, flotation and filtration etc. Disinfection alleviates the membrane biofouling by preventing the biological matter. After pH adjustment, coagulation process is usually processed using coagulants/antiscalants followed by flocculation for the turbidity removal. However, the concentration of antiscalants should be carefully monitored as they may have negative effects on membrane filtration cycle and its environment. In the flocculation stage, micro-flocs aggregate to form visible free-floating particles can be separated due to the density difference between the particles and water. Finally, filtration process can remove the suspended particles. Though conventional pre-treatment methods are well established, several drawbacks such as many steps involved, require large space, utilization of larger concentration of chemicals, substantial manpower, unknown effects of membrane performance and high operating costs limit this procedure. To deal with these issues, non-conventional auxiliary methods such as membrane based methods have been proposed focusing on the mitigation strategies.

#### 1.4.1.3 Membrane-Based Methods

The non-conventional approach for the pretreatment of feed water involves MF, UF and NF has been proven to achieve high rejection rates and significant efficiency. The treatment also achieves high removal of various contaminants such as colloidal, bacterial and suspended matter. Moreover, the results revealed that the membrane filtration processes are economically feasible compared to conventional method. Ebrahim et al. (1997) investigated on the MF pre-treatment and reported that the method showed practical feasibility in reducing the fouling and SDI levels. Besides, there was a decrement in BOD and COD concentrations that make membrane method able to produce an input feed to subsequent membrane based systems. Another study by Lee et al. (2010) analysed the efficiency of MF pretreatment coupled with chlorination and deduced that the combination worked outwell in the removal of biofouling. UF pretreatment has shown a promising process to treat the waste water and reject wider variety of impurities than MF including silt, suspended organics, microorganisms etc. mitigating the membrane fouling issue. Bayath et al. (2016) treated oil waste in water using $Al_2O_3$ UF membranes to evaluate the effectiveness of UF in pretreatment of water. They reported that this membrane based method can effectively reduce the percentage of oil and grease content, BOD, COD, TOC and turbidity by 84, 73, 67, 63 and 79% respectively.

Monnot et al. (2016) improved the UF performance by imparting a granular activated carbon and the results demonstrated that DOC and colloidal material decreased by 70 and 90% respectively. NF membrane pretreatment due to its small pores has revealed promising results in producing filtrates with a considerably reduced quantity of TDS, viruses, salts and organic matter. NF has been made significant progress in the elimination of scale forming agents that undesirably influence desalting processes. Hilal et al. (2005) studied NF membrane efficiency for both seawater and brackish water and demonstrated that NF90 with the lowest pore size and the maximum roughness and porosity had the highest salt rejection of upto 95%. Su et al. (2015) examined the performance of NF membranes in pretreatment of desalination of seawater by operating an incorporated membrane system with UF dual stage and NF integrated system. The permeate flux reduced with decreasing feed temperature with the rejection of divalent ion at 95%.

#### 1.4.1.4 Surface Modification

Membrane surface functionalization and modification is one of the significant techniques that can enhance the membrane properties to mitigate fouling. Membrane surface smoothness and electrical charge are major characteristics modified for improved surface characteristics. Smooth membranes have low tendency for fouling as the surface is not susceptible for the accumulation of the foulants into the grooves or valleys. Foulants with counter charges to membrane surface charge, are more susceptible to fouling. Hence, it is necessary to intervene such unfavourable interactions and as a consequence two common surface modification techniques i.e., surface coating and surface grafting have been used to mitigate membrane fouling (Goh et al. 2018).

#### 1.4.1.5 Surface Coating

Surface coating is an easy and inexpensive technique that acts as a protective lining to restrain the adsorption and deposition affinity of the foulants and provide long term durability for the membrane. It was reported that hydrophilic coating on the PVDF UF membrane has achieved greater than 90% flux recovery rate (Abdelrasoul et al. 2013). Halakoo and Feng (2020) used a similar approach by layer-by-layer spraying on the surface of TFC PA membranes by the addition of cationic polyethyleneimine and graphene oxide particles and tested for desalination. They reported that the membrane exhibited 99.9% salt rejection for NaCl, $Na_2SO_4$, $MgSO_4$ and $MgCl_2$ at a range of temperatures and feed concentrations. Another study by Zhan et al. (2018) modified MF membrane by $TiO_2$ coating and demonstrated that coated membrane displayed higher flux compared to uncoated membrane due to high hydrophilicity of the coated membrane. Similarly, Han et al. (2015) showed 99% oil rejection by PDA coating on the membrane surface. The high permeate flux and high rejection was attributed to the improved surface wettability that reduced the attachment of small oil droplets.

#### 1.4.1.6 Surface Grafting

Surface grafting creates covalent bonding interactions on the surface with functional groups to obtain desired functions and can be performed by chemical processor with high energy radiation. It has been observed that the surface grafting, besides addition of functional groups, it could alter pore structures. In general, hydrophilicity of the surface is improved by adding polar functional groups on the surface of membrane. Wei et al. (2010) investigated on a radical grafting study using 3-allyl-5,5-dimethylhydantoin and tested for biofouling resistance and reported ameliorated microbial adsorption rejection and enhanced flux rate compared to ungrafted membrane. Recently, surface modification by UV irradiation and plasma treatment has gained more attention of researchers as it increases hydrophilicity of the membrane to alleviate fouling.

Khoo et al. (2021) investigated on incorporating $TiO_2$ nanoparticles into Acrylic acid modified Polyamide (PA-AA)TFN membrane. The $TiO_2$ grafted membrane achieved a considerable antifouling property with higher flux (>95%) recovery rate. The enhanced efficiency is ascribed to the improved hydrophilicity and smoother surface of the membrane. Yuan et al. (2014) investigated on the hydrogel tethered polysulfone membrane grafted with Cu-azide functionalized propargyl-polyethylene glycol to treat oil emulsion. The functionalized membrane demonstrated better antifouling performance and permeance. The reported flux and rejection using the grafted membrane were 120 $L/m^2h$ and 95% respectively.

In recent years, surface grafting by irradiating with Ultraviolet and plasma induced membrane surface has gained more attention to increase the hydrophilicity to mitigate fouling of the membrane (Du et al. 2020). Adib and Raisi (2020) examined polyethersulfone membrane grafted by hyperbranched polyethylene glycol using corona air plasma and found the increased hydrophilicity that influenced the enhancement of antifouling and high rejection for the treatment of synthetic oily wastewater. The permeate flux of the resulting membrane was 99.5 L/m$^2$h with 3000 ppm of oily wastewater. The improvement in the efficiency of the membrane is attributed to lower packing density. A study by Jahangiri et al. (2018) used the dielectric barrier discharge plasma method to improve the performance and antifouling characteristics of the PA membrane. The membrane exhibited >99% of flux recovery of bovine serum albumin (BVA) containing water.

## 1.5 Role of Nanomaterials in NF Membrane Synthesis

In general, polymers and ceramic materials are used to fabricate NF membranes. Owing to the predominant use and rapid advances of polymer membranes, we concentrated on the polymeric NF membranes. A wide variety of nanomaterials are incorporated in these matrices to improve the efficiency of the membranes with respect to solvent permeability and solute rejection. The utilization of nanomaterials in membrane fabrication process results in improved mass transfer processes in the membrane. Pore size and structure of membranes are strongly connected to membrane performance. Pore structure of membrane assists to enhance mass transfer whereas; pore size determines the ability to resist mass transfer inside the membrane structure. Conventional membranes go through various problems in water treatment such as permeability, selectivity, chemical stability and fouling etc. that influence the performance of the filtration process. The nanomaterials due to their tunable properties and unique structure improve the performance in terms of excellent separation and feasible to scale up at lower cost (Table 1.1). Therefore, the progress of high performance membranes coupled with nanomaterials should have the augmented properties such as fouling resistance, low cost, high salt rejection, high water flux and good chemical and mechanical stability inorder to provide extensive purification of water (Yang et al. 2019).

### *1.5.1 Metal/Metal Oxide Nanoparticles in NF Membranes*

In the class of wide array of advanced membranes, the metal/metal oxide nanomaterials based membranes have been demonstrated to be efficient and were reported to improve the operational performance, permeation rate and flux (Shahrin et al. 2019). Metal/Metaloxide nanoparticles with polymer membranes would possess augmented properties such as superhydrophilic, superhydrophobic, amphiphobic properties to

**Table 1.1** Performance of nanomaterial-incorporated NF membranes

| Polymer | Nanomaterial | Solute | Solvent permeance (L/m$^2$h) | Rejection of solute (%) | References |
|---|---|---|---|---|---|
| CA/PEG | $TiO_2$ | Chlorine | – | 95.4 | Shafiq et al. (2018) |
| PPy | $TiO_2$ | Brilliant Blue dye | 16.2 | 92 | Cheng et al. (2017) |
| PTFE | ZnO | RhB | – | 97 | Huang et al. (2017) |
| PP | GO | Rose Bengal dye | 3.1 | 97 | Hu and Cheng et al. |
| PA | GO | Chlorine | 45–50 | 90–99 | Kim et al. (2016) |
| PA | MWCNT | NaCl | 71 | – | Zhang et al. (2011) |
| TPP/HPEI | GO | Alcian blue dye | 14.9 | 95 | Hu and Cheng et al. |
| Block co-polymer | rGO-CNT | Humic acid | 20–30 | 99 | Chen et al. (2016) |
| Chitosan | MWCNT-COOH | – | 6.6 | – | Alshahrani et al. (2020) |

alleviate fouling and wetting issues (Lu et al. 2016). Shafiq et al. (2018) prepared CA/PEG membranes with $TiO_2$ and found that at 15wt% $TiO_2$ loading was optimal with high salt rejection (95.4%) and negligible chemical degradation. $TiO_2$ integrated PPy layer was utilized by Cheng et al. (2017) and reported to have super solvent permeance for ethanol at 16.2 L/m$^2$h bar along with high solute (brilliant blue) rejection rate of 92%.

Ahmad et al. (2015) investigated on the $SiO_2$ NPs incorporated cellulose acetate/polyethylene glycol membranes and reported the enhancement of thermal and mechanical stability of CA/PEG membrane with improved flux from 0.35 to 2.46 L/m$^2$h and increased salt rejection by 11.41% at optimum wt of 5% $SiO_2$. Zhang et al. (2015, 2017) utilized a membrane fabricated by Cu NPs implanted onto polyamide thin film on which carboxylated chitosan was coated and found that there is considerable enhancement in resistance towards bacteria and high salt rejection. PA-CCTS-Cu had antibacterial efficiency of above 99% and could sustain it after 90 days immersion in water. A PTFE/ZnO membrane was prepared for photodegradation experiment wherein the salt rejection and dye removal rates were upto 99.7% and 45% respectively after 10 h operating time (Huang et al. 2017).

### 1.5.2 Carbon Based Nanomaterials in NF Membranes

Carbon nanotechnology based membranes possess high selectivity, water flux, low energy consumption enabling the desired thermal and mechanical properties for formulating the membrane stable and suitable for water treatment. According to Shao et al. (2014), Graphene oxide could facilitate in preparing a thinner polypyrrole (PPy) layer formed over the hydrolyzed polyacrylonitrile (PAN-H) and found that the membrane possessed increase solvent permeance without affecting the solute removal rate. GO-PPy/PAN-H membrane has significantly improved the permeances of methanol, ethanol and isopropanol with 945, 635 and 302% respectively.

In another approach, chitosan containing MWCNTs with–COOH moiety was fabricated applying a filtration method (Ahmad et al. 2022). MWCNT-COOH/chitosan membrane showed better mechanical properties and high permeate flux (6.6 L/m$^2$hbar). In another study, Chen et al. (2016) developed a hybrid NF membrane that was synthesized by rGO-CNT in block co-polymers. It was found that rGO-CNT hybrid NF membranes have a high retention efficiency, superior permeability and superior anti-fouling properties. The optimized rGO-CNT demonstrated high efficiency in terms of the retention of above 99% and permeability of as high as 20–30 Lm$^2$/h bar for the retention of dyes, sugars and humic acid.

A new class of organic solvent nanofiltration membranes based on combination of porous polypropylene substrates, GO nanosheets and polyethlenimine, polyelectrolyte which are devoid of harmful organic solvents was designed by Hua and Cheng et al. (2017). The TPP/GO/HPEI membrane showed 95% and 97% of rejection towards Alcian blue, cationic dye and Rose Bengal, an anionic dye with a high permeance of 14.9 and 3.1 L/m$^2$h bar respectively. PA membrane modified with GO coated by tannic acid(PA-GOT) was described by Kim et al. (2016) which demonstrated exceptional resistance to chlorine with high flux of 45–50 L/m$^2$h and salt rejection of 90–99% and good antimicrobial property during filtration. They reported that the prepared membrane exhibited excellent hydrophilicity, polymer matrix compatibility and oxidative stress capability. Zhang et al. (2011) prepared a TFN-functionalised MWCNT-PA membrane and tested with feed solutions of 2000 ppm NaCl and 200 ppm terephthalic acid. The functionalised membrane showed a noticeable flux rate of 71 and 49 L/m$^2$h bar for NaCl and terepthalic acid respectively. CNT buckypaper (CNT BP) membranes were fabricated for direct contact metal distillation (DCMD) by Dumée et al. (2010) and found that the hydrophobicity, porosity and thermal conductivity of the CNT Bp were 113°, 90% and 2.7 kW/m$^2$h respectively. Additionally CNT BP membranes showed salt rejection of 99% and permeate flux of 12 kg/m$^2$. DCMD of a synthetic water solution containing 3.5 wt% NaCl with CNT BP membrane had a flux of 5–10 L/m$^2$h maintained for 40 h without cracking and fouling.

### *1.5.3 Metal–Organic Frameworks in NF Membrane*

Metal–Organic Frameworks (MOFs) are a sort of hybrid materials with inorganic–organic materials consisting of metal clusters with organic ligands to form 1D, 2D or 3D network, creating a explicit and comprehensive pore structure to aid transport of certain molecules (Stock and Biswas 2012). MOFs have been considerably explored owing to their extensive chemical compatibility, mechanical stability with the polymer matrix leading to minimum voids and imperfections in the resultant membranes (Ehsani and Pakizeh 2016). Several types of MOFs have been used to produce NF membranes. Zhang et al. fabricated the Cu(II) benzene-1,2,5-tricarboxylic acid assimilated in the PVC polymer matrix for the separation of toluene/n-heptane by pervaporation. The flux increased ten folds from 0.016 to 150 g/m$^2$h with the inclusion of MOFs in the polymer matrix.

In another study, Lin et al. (2020) prepared surface functionalized ICA-d-UiO-66-$NH_2$ nanofillers incorporated into TFN-NF membranes using interfacial polymerisation method. The ICA-d-UiO-66-$NH_2$@ PA membrane demonstrated a water permeance of 9.41/m$^2$h bar and 97.4% of $Na_2SO_4$ salt rejection capability. Zhu et al. (2015) reported that the membrane performance was enhanced on the incorporation of MOFs. The aluminium terephthalate-based MOF (MIL-53) was prepared by phase inversion technique and found the ethanol permeance of 0.7 L/m$^2$h bar and rejection of 94%.

## 1.6 Conclusions and Future Perspectives

In recent years, membrane processes have been proposed as viable alternate and best available techniques for water treatment. NF systems represent advantages of high recovery rate, low energy consumption and cost-effectiveness with least environmental impact. This work intends to allow new researchers in this field to evaluate the contemporary issues and existing solutions to mitigate problems associated with the process to meet water quality requirements. This chapter has provided a comprehensive overview of fundamentals of membrane processes, mechanism of NF process and challenges of membrane fouling. Though the process has proved to be versatile option, NF membranes require further improvements in membrane materials to overcome technical barriers resulting in the development for sustainability. Based on the current research, further progress in the membrane materials results in the expansion of sustainable ways to produce fresh water.

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