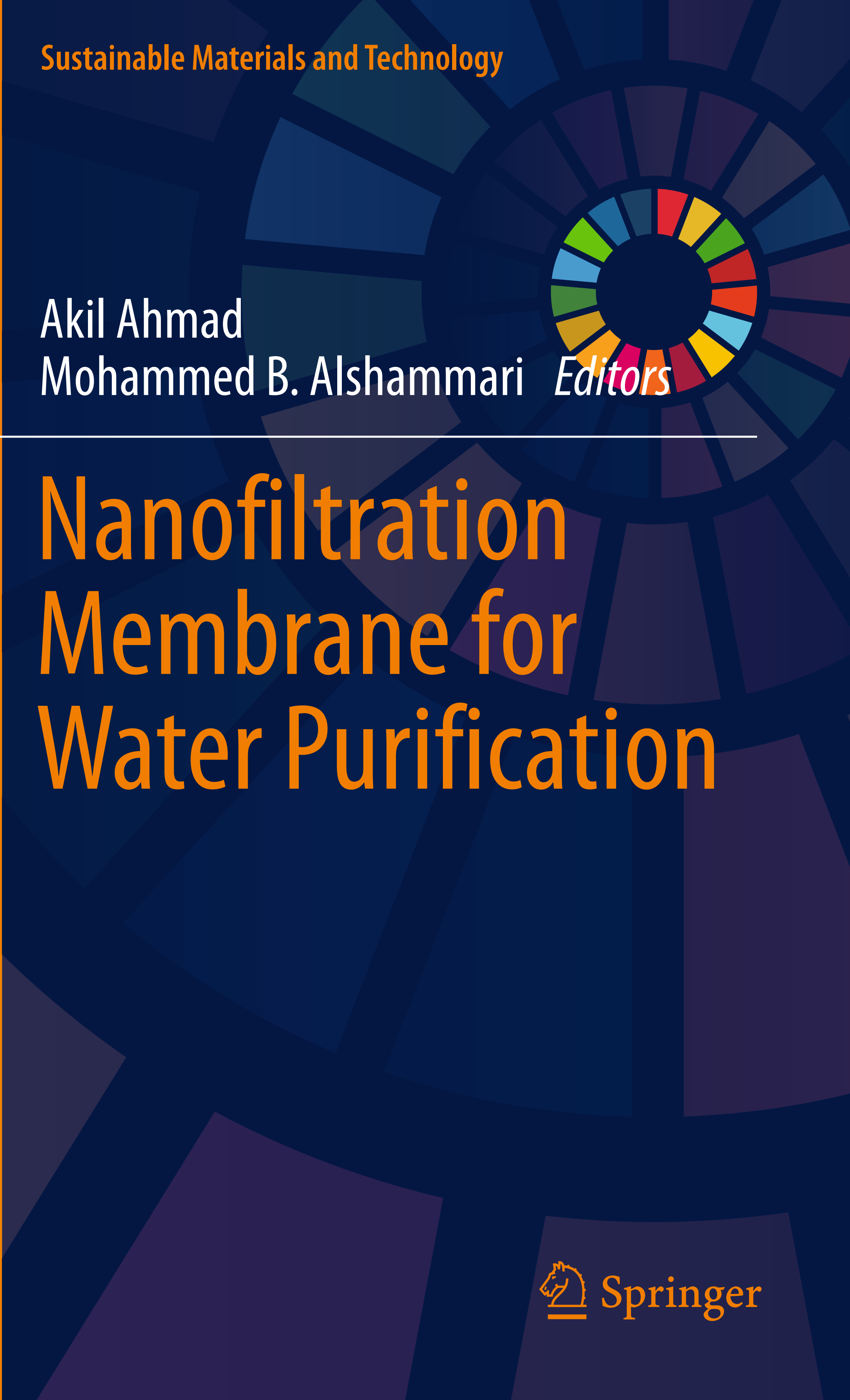
Sustainable Materials and Technology

Akil Ahmad
Mohammed B. Alshammari *Editors*

Nanofiltration Membrane for Water Purification



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ISSN 2731-0426 ISSN 2731-0434 (electronic)
Sustainable Materials and Technology
ISBN 978-981-19-5314-9 ISBN 978-981-19-5315-6 (eBook)
https://doi.org/10.1007/978-981-19-5315-6

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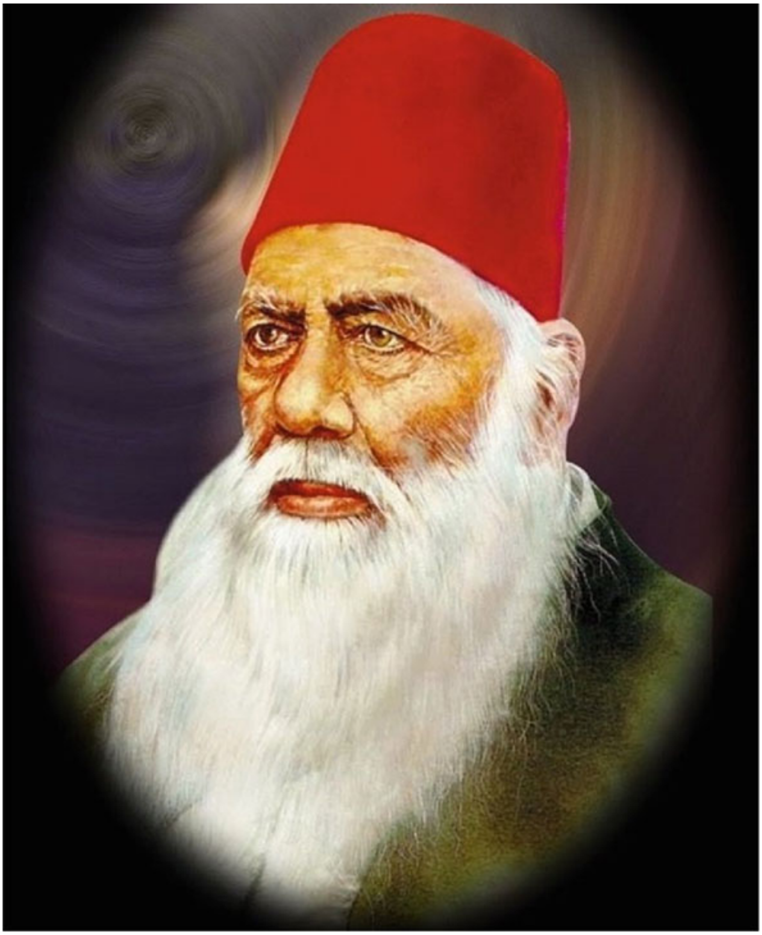

Dedicated to Sir Syed Ahmad Khan (1817–1898)
An Educationist and Reformer for Indian Muslims
Sir Syed Ahmad Khan was born in the well-known city of India, Delhi, on October 17, 1817. He had a strong belief that any national or religious cause can be promoted only on a strong foundation through scientific 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
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Acknowledgements The editors wish to appreciate the support of the Department of Chemistry, College of Science and Humanities in Al-Kharj, Prince Sattam Bin Abdulaziz University, Al-Kharj-11942, Saudi Arabia.

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About the Editors

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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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_1

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.

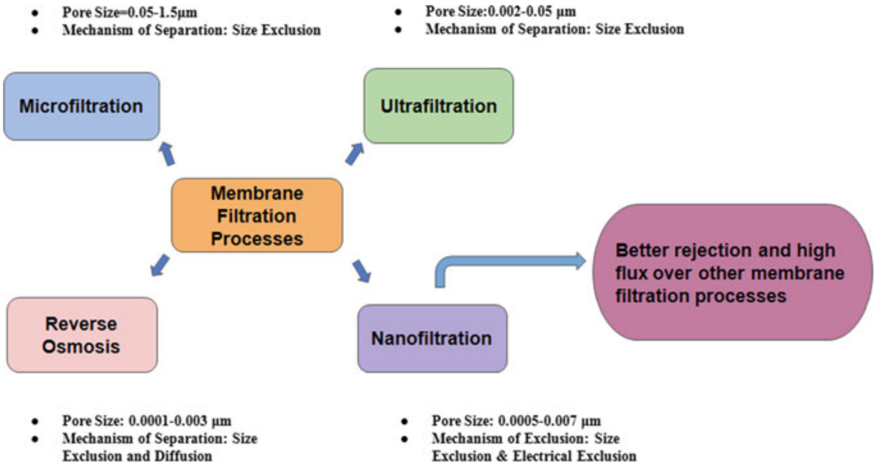


Fig. 1.1 Membrane filtration processes for water purification and advantages of NF over other filtration processes

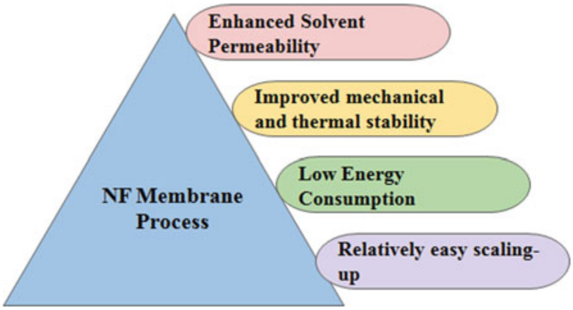
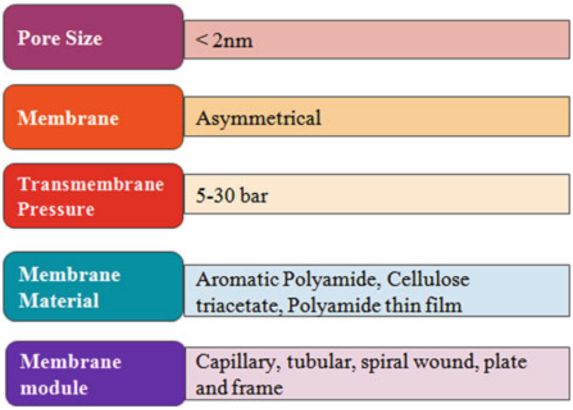


Fig. 1.2 Significant advantages of NF membrane process for water purification

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



Pore Size	< 2nm
Membrane	Asymmetrical
Transmembrane Pressure	5-30 bar
Membrane Material	Aromatic Polyamide, Cellulose triacetate, Polyamide thin film
Membrane module	Capillary, tubular, spiral wound, plate and frame

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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Chapter 2
Synthesis and Characterization of Nanofiltration Membrane

Chetan Kumar, Dinesh Kumar, and Ritu Painuli

Abstract Rapid industrialization and ever-increasing human activities lead to global environmental changes that affect the availability of naturally potable freshwater resources. Affordable and sustainable supply of adequate, clean, and safe water are major challenging concerns in the twenty-first century. Considerable efforts have been made to address the scarcity of safe water, and nanotechnology has emerged as a budding candidate with rapid development. One of the most economical and widely applied technologies for water purification is membrane separation technology. Pressure-driven membrane processes such as nanofiltration have emerged as a critical component of advanced water reuse methods. Key features such as water permeability and high salt rejection of solutes make nanofiltration membranes economically viable for water purification. Thus, the present chapter explores various methods to fabricate the improved nanofiltration membranes with techniques like interfacial polymerization, nanoparticle incorporation, UV treatment, plasma treatment, and layer-by-layer modification. The characterization of the membranes via techniques like scanning electron microscopy, Fourier transform spectroscopy, thermogravimetric analysis etc. are addressed. In addition, the prospects of nanofiltration membrane research and development are also explained.

Keywords Nanofiltration membrane · Water purification · Fabrication · Characterization

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_2

2.1 Introduction

Water pollution and inadequacy at a worldwide scale are the foremost complications modern society faces in the twenty-first century (Mekonnen and Hoekstra 2016; Satapathy and Kanunugo 2018). The limiting availability of the world's scare water resources is increasing rapidly due to the pollution of freshwater resources caused by the disposal of large quantities of wastewater, insufficiently treated or untreated into rivers, lakes, and coastal waters. UN (United Nations) reports show that 30% of the world population suffers from the unavailability of clean, safe, and consistent drinking water facilities. Thus, motivating the UN to include worldwide drinking water supply in their sustainable development aims (Yang et al. 2019). Effective water management and treatment approaches are required to achieve the goal of producing clean drinking water. Water treatment using nanotechnologies, for instance, nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), and microfiltration (RF) have been efficient to fulfill mankind's demands of freshwater. Membrane technology can be considered a concept concerning diverse separation processes and has been escalated to become a prominent technology in water purification (Swamy et al. 2013). Membrane separation technology is a pressure-driven separation mechanism involving high pressure to remove salt particles or contamination from the water (Paul and Jons 2016). Membrane-based separation techniques, for instance, NF and RO, are considered as the noteworthy candidates for consistent drinking water production (Shannon et al. 2008). These treatment technologies have been capable of providing water quality better than conventional treatment technologies.

In comparison to nanofiltration membranes (NFM), RO generally requires a dense rejection layer which usually requires the cost of high energy intake and less water permeability (Qasim et al. 2019). Whereas owing to the relatively looser structure, NFM permits rapid water production with lesser energy consumption (Fane et al. 2011). The term nanofiltration was first employed in 1980s to designate the membranes possessing features that lies between UF and RO (Eriksson 1988). As NFM are fundamentally similar to RO membranes, the description of membranes as NF is based on different features like molecular weight, the effective size of the pore, salt rejection, and weight cutoff (Simpson et al. 1987; Wang et al. 1995; Cadotte et al. 1988). On the basis of the functional group and chemistry, functional NFM are considered to change either their negative or positive charges to form surfaces. The separation in terms of performance capacity is directed by the interplay of mechanisms, for instance, dielectric exclusion, steric effects, and electrostatic effects (Labban et al. 2017). NFM is efficient in the separation of small organic molecules and inorganic salts. The main distinguishing features of NFM in comparison to RO membranes are less rejection of monovalent ions, higher flux, and higher rejection of divalent ions. These alluring properties have endorsed NF to be employed in diverse applications specifically for water and wastewater treatment, food engineering, biotechnology, and pharmaceuticals. The present chapter discusses the various methods to fabricate or modify the improved nanofiltration membranes.

The characterization of the membranes via techniques methods like scanning electron microscopy, thermal gravimetric analysis, and Fourier transform spectroscopy is also discussed. The future prospects of nanofiltration membranes development and research are also explored.

2.2 Mechanism of Nanofiltration

Nanofiltration is an exceptionally complex process that depends on the microhydrodynamic and interfacial events happening within the nanopores and at the surface of the membrane. NFM rejection can be credited to the combination of Donnan, steric, transport, and dielectric effects (Donnan 1995; Deen 1987). The ionizable groups dissociate from the surface of the membrane as well as inside the membrane pore structure, which leads to the generation of charge on a membrane (Ernst et al. 2000). These groups' nature may depend on the constituents utilized in the preparation process. The pH of the contacting solution strongly influenced the dissociation of these groups (Childress and Elimelech 1996). These membranes have a less ion exchanging ability, and they may adsorb ions from the contacting solution in some cases, causing a slight change in the membrane charge (Afonso et al. 2001; Schaep and Vandecasteele 2001). There are two mechanisms following the nature of the interaction, the solvation energy barrier mechanism (Yaroshchuk 1998) and image force phenomena (Bowen et al. 2002; Oatley et al. 2012). The solvent rolling via the confined, fined pore structure causes drag forces to the solutes moving in free solution. The solute movement is prominently affected by the local surroundings, which hinders the transport of solute. NF active layer dimensions and the restrictions in existing measurement expertise have deferred the complete information about the electric properties and physical structure of NFM. They have caused improbability over the exact nature of the separation mechanism.

2.3 NFM Modification and Fabrication Methods

The development in the NFM technology has been producing improved filtration methodologies for separating the organic and inorganic substances from solution in the liquid. Bruggen and coworkers 2008 has described various major development essential for improving the existing drawbacks in the NF applications in industries. For instance, progress in the membrane lifetime, chemical resistance, reducing membrane fouling, enhancing separation, and reducing rejection efficacy (Bruggen et al. 2008). Generally, foulants can be colloids, biological solids, inorganic and organic solutes etc. Various studies have been employed for innovative fabrication and modification techniques with noteworthy fouling propensity enhancement. These methods can be classified into interfacial polymerization (IP) and grafting polymerization. Recent advancements include incorporating nanoparticles (NPs) in thin-film layers, leading to thin-film composite.

2.3.1 Interfacial Polymerization (IP)

IP has emerged as an extremely practical and beneficial technique for preparing thin-film layers for RO and NFM. The copolymerization and reaction between the two reactive monomers result in developing a thin layer on the membrane surface (Fig. 2.1). The fabrication of thin-film composite (TFC) membrane via IP has gained noteworthy attention due to improved membrane characteristics like fouling resistance and selectivity. Figure 2.2 depicts the distinctive representation of TFC membranes with three different layers. The top layer is accountable for the selectivity of membrane followed by microporous substrate and thick polyester nonwoven backing. The bottom layer is mainly significant for instinctive support of the membrane for withstanding the high-pressure filtration (Seah et al. 2020). The procedure can be applied easily, and an exceptionally thin layer is prepared in the 50 nm range. The prepared thin layer will decide the solute retention, permeability, and overall efficacy of the particular membrane. For the formation of a thin active layer, various monomers have been employed in this technique like tannic acid, bisphenol A (BPA), trimesoyl chloride (TMC), m-phenylenediamine (MPD), isophthaloyl chloride etc. Further monomers employed for membrane fabrication include tetraethylenepentamine (TEPA), piperazidine (PIP), diethylenetriamine (DETA) (Li et al. 2014a). Table 2.1 summarizes the various monomers that have been used to fabricate TFC membranes by IP. As per the investigation of Tsuru and coworkers, the enhancement in water permeability capacity of the membranes can be achieved by the use of two-step IP with MPD and TMC (Tsuru et al. 2013). An improvement in the membrane performance and antifouling properties modified by IP was reported by using Tetramethyl Bisphenol A (TMBPA) and BPA as the monomers for membrane development. Effect of IP time and various concentrations of BPA in aqueous solution were considered for NF polyester membranes (Abu Seman et al. 2011). IP prepared a nano thin-film composite membrane for the organic solvent nanofiltration process. Polyetherimide (PEI)/amino-functionalized silica nanocomposite membrane was employed as a supporting layer to fabricate membrane (Namvar-Mahboub and Pakizeh 2013). Li and coworkers demonstrated the preparation of novel NFM by IP technique using purposefully synthesized polyhexamethylene guanidine hydrochloride (PHGH). The antibacterial study indicated that the prepared composite NFM possesses efficient inhibition against *E. coli* bacteria. Fouling test also revealed an increased antifouling performance of the prepared membrane (Li et al. 2014b). The introduction of calcium chloride as an additive during IP reaction has been discussed by Fan et al. (2014). A prominent rise in pure water fluxes of the composite NFM was noted as a function of $CaCl_2$ concentration. The effects of various organic acids with diverse acidic strength and structures were studied on

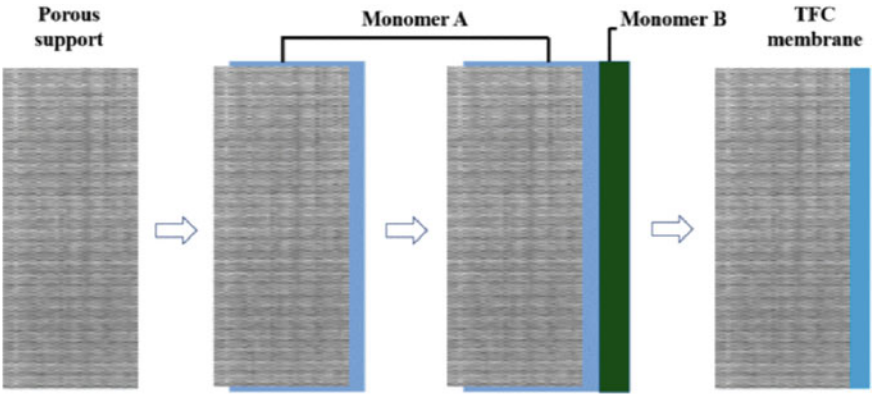

Fig. 2.1 Mechanism for interfacial polymerization [Reprinted with permission from Yang et al. (2019). Copyright 2020. MDPI-Publisher of Open Access Journal]

developing polysulfone NF membrane. It was shown that the addition of organic acids in NFM results in superior pure water flux and improved rejection and permeation in the separation of xenobiotics from aqueous media at various pH (Ghaemi et al. 2012). Kong et al. (2011) reported a strategy for preparing inorganic-polyamide nanocomposites membrane by metal-alkoxide assisted IP. The metal-alkoxide used were phenyltriethoxysilane, bis(triethoxysilyl)ethane, titanium tetraisopropoxide. The prepared membrane displayed progress in permeability capability and improved water flux and pore size. Chiang et al. (2012) created a zwitterionic surface on the NFM. They reported the preparation of NFM by IP of diethylenetriamine and trimesoyl chloride. The quaternized zwitterionic membrane also demonstrated the reduction in bio-fouling phenomena. Two monomers, i.e., trimesoyl chloride (TMC) and polyethyleneimine (PEI), were used to prepare thin-composite NF polyamide membranes via IP. Surfactants like sodium octyl sulfate, sodium dodecylbenzenesulfonate, and sodium dodecyl sulfate were also added to aqueous PEI solution for improving the rejection of divalent ions like $MgCl_2$. The addition of surfactants leads to enhanced membrane hydrophilic properties, increased membrane surface charge, and better rejection capability (Ang et al. 2020).

2.3.1.1 Nanoparticles (NPs)

NPs have gained consideration owing to their inimitable properties like antimicrobial activity, catalytic property, photoemission etc. Membranes that are incorporated with NPs can enhance their various features like permeability, selectivity, and in some cases, hydrophobicity. Zhang et al. reported the preparation of NF composite membranes possessing a polyethyleneimine-NPs hybrid active layer. The uniformly dispersed inorganic NPs (silica/titania) with tunable structures were provided in the active layers of the composite membranes. NPs dramatically enhanced the prepared

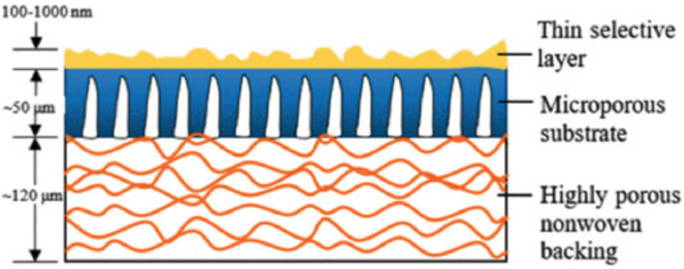

Fig. 2.2 Typical cross-section of TFC membranes [Reprinted with permission from Seah et al. (2020). Copyright 2020. MDPI-Publisher of Open Access Journal]

composite membranes' thermal stabilities and rejection capability. The stable hybrid structure of the active layer gave satisfactory long-term operational stability. The developed composite membranes showed high solvent resistance properties and nanofiltration performances (Zhang et al. 2014a). A mixed matric polymeric membrane was prepared from polyaniline/iron(II, III) oxide (PANI/Fe_3O_4) NPs, and polyethersulfone (PES). The membrane with 0.1% weight was reported to remove a maximum level of Cu(II) ions with the lowest pure water flux. The reusability of the membrane was also confirmed using Ethylenediaminetetraacetic acid (EDTA) as a regenerator (Daraei et al. 2012). Due to the unique biocatalytic performance of titanium dioxide (TiO_2), it was employed to functionalize with immobilized laccase for the water treatment process. It was reported that the prepared membrane was accomplished in enhancing BPA removal efficacy from wastewater, therefore providing an option to the traditional wastewater treatment process (Hou et al. 2014). Boehmite NPs have also been used as nanofillers to prepare polyethersulfone (PES) membranes. The developed membranes displayed improved pure water flux and hydrophilicity due to the presence of boehmite NPs (Vatanpour et al. 2012). A thin-film composite membrane was also prepared by in situ IP process using MCM-41 silica NPs as fillers. The presence of NPs increased the membrane permeability and salt rejection capability (Yin et al. 2012). Silica NPs coated with polydopamine (PDA) were employed to modify the thin-film nanofiltration membrane. The prepared membrane delivered good pure water flux, salt rejections, and antifouling ability (Ang et al. 2019). A thin film nanocomposite membrane incorporated with poly(hexafluorobutyl acrylate)-modified hydrous manganese oxide (PHFBA-modified HMO) nanomaterials were reported. The prepared membrane rejects salts and fouling resistance against organic and inorganic foulants (Lai et al. 2019). Various remarkable nanomaterials have been demonstrated to prepare membranes like carbon nanotubes (Ngoma et al. 2021), halloysite nanotubes (Ormanci-Acar et al. 2021), etc. By using all these kinds of nanomaterials in the membrane preparation, the aim is to improve the NFM.

Table 2.1 Various monomers and membrane properties for the thin-film composite (TFC) membranes fabricated by interfacial polymerization

Monomers	Membrane property	References
Monomer 1—TMC **Monomer 2**—pentaerythritol	Membrane possess 98.1% rejection for Na_2SO_4 and lower water flux of 6.1LMH	Cheng et al. (2017)
Monomer 1—1,3,5-Triformylphloroglucinol **Monomer 2**—p-Phenylenediamine	Membrane had flux upto 50.1 LMH and rejection to dye	Wang et al. (2018)
Monomer 1—1,3,5-benzene-tricarbonyl trichloride **Monomer 2**—Piperazine	High rejection performance for Na_2SO_4 (98%)and $MgSO_4$ (97.5%) with increased water permeability	Bai et al. (2018)
Monomer 1—TMC **Monomer 2**—m-Phenylenediamine	The membrane had good water flux, less reverse salt flux, and a large free volume	Shen et al. (2018)
Monomer 1—1,3,5-benzene—tricarbonyl trichloride **Monomer 2**—Hexylene glycol	Flux stability and fouling reversibility was enhanced	Hao et al. (2019)
Monomer 1—2,4,6 Trischlorosulfonylphenol **Monomer 2**—Piperazine	Membrane showed rejections for H_2SO_4 and $CuSO_4$ and had a flux of 13.98 LMH	He et al. (2019)
Monomer 1—1,3-benzenedisulfonyl chloride **Monomer 2**—polyallylamine	Membrane had more than 90% selectivity for heavy metal ions	Wang et al. (2019)
Monomer 1—Cyclodextrins **Monomer 2**—Ethylenediamine	Membrane had a superior water flux up to 28LMH, exceptional antifouling property with high flux recovery rate >91%	Xiong et al. (2019)
Monomer 1—TMC **Monomer 2**—piperazine	The membrane showed exceptional stability and antifouling properties	Shen et al. (2020)
Monomer 1—1,4-phenylene diisocyanate **Monomer 2**—TMC	Membrane showed rejection for Na_2SO_4 and $MgCl_2$ along with long-term stability after exposure to strong acid	Cao et al. 2021

2.3.2 Grafting Polymerization

2.3.2.1 UV/Photografting

UV-assisted grafting polymerization is achieved via the chemical bond between the active layer and membrane substrate without affecting the bulk polymer. At various functionalization conditions, the NFM performance was examined. Qiu et al. reported hydrophilic NFM by grafting polymerization of hydrophilic monomers onto the

UF membranes surface prepared from cardo polyetherketone. The obtained NFM grade can be achieved by observing the irradiation power or monomer concentration to graft progressively polyacrylic acid on the pores of membranes (Qui et al. 2007). Novel positively charged NFM fabricated employing sulfonated polyphenylenesulfone support with hydrophilic properties by UV-induced grafting was demonstrated. The resulting NF membrane showed high pure water permeability and was effectively developed using two different positively charged grafting monomers. The prepared membranes also displayed high efficacy in textile dyes removal from wastewater (Zhong et al. 2012). Using UV-photo assisted graft polymerization technique, polyethersulfone UFM were converted into charged NFM possessing strong polyeletrolyte hydrogel as a selective barrier. The preparation was accomplished using N,N′-methylenbisacrylamide as a crosslinker monomer and vinyl sulfonic acid as the functional monomer (Bernstein et al. 2013). A negatively charged loose NFM was prepared using UV-grafting of acrylic acid and polyvinylidene fluoride UFM. The prepared membrane displayed satisfactory antifouling properties, high dye recovery, and low sodium chloride rejection (Chiao et al. 2020).

2.3.2.2 Electron Beam Irradiation

Electron beam irradiation is an effective and noble method for penetrating the polymer layer. No exclusive additives are required during the irradiation process, and active sites on the polymer could be made very easily. Nylon-66 is a semicrystalline polymer that can be crosslinked via electron beam irradiation. Polymer properties can drastically change via crosslinking. The effect of electron beam irradiation on the nylon-66 membrane (N-66 M) sieving characteristics and morphology was reported. The gel content and the surface of nylon-66 increased with increasing dose irradiation (Linggawati et al. 2009). Nylon-66 can be crosslinked to form NFM via electron beam irradiation. It was noticed that N-66 M displayed adequate permeability, improved divalent ions rejection, and removed neutral solutes (Linggawati et al. 2012). The preparation of novel NFM via grating of 2-acrylamido-2-methylpropanesulfonic acid onto a PSf support by irradiation was reported. The prepared membrane also demonstrated high efficacy for removing carcinogenic and mutagenic Cr(VI) (Xu et al. 2014).

2.3.2.3 Plasma Treatment

It is an efficient method to enhance the surface wettability and hydrophilicity due to the introduction of polar groups onto the surface. Plasma surface amendment is a method where membrane hydrophilicity can be increased with decreased membrane fouling by generating nitrogen functional groups by applying nitrogen-containing plasma onto the polymer membrane (Kim et al. 2011). A negatively charged NF membrane was prepared via grafting of 2-acrylamido-2-methylpropanesulfonic acid on the PSf hollow fiber UF membrane. The developed membrane showed higher ion selectivity (Wang et al. 2012a, b).

2.3.2.4 Layer by Layer (LbL)

A selective NFM was prepared layer by layer using polydiallyldimethylammonium chloride (PDADMAC) and polysodium-4-styrenesulfoate (PSS). The developed membrane possesses high salt selectivity and performance stability. Using polyelectrolyte multilayers offers another mode to improve membrane performance (Ng et al. 2014). The layer-by-layer surface modification effect on performances and characteristics of cellulose acetate NFM was studied. The membranes were prepared via adsorption of alternated layers of sodium alginate and chitosan. The 15 bilayers were the optimum condition for the satisfactory performance of the prepared membrane (Lajimi et al. 2011). Two crosslinking methods, i.e., silane coupling and amine coupling for LbL-assembled NFM, were reported to increase the stability of the membrane under chlorine treatment and high ionic strength conditions. The prepared membrane showed enhanced separation capability and satisfactory stability under acidic conditions (Saeki et al. 2013). Water purification membrane by LbL assembling with positively charged poly(allylamine hydrochloride) (PAH) via electrostatic interaction was reported. The developed membranes showed good sucrose rejection and were preferred appropriate for the water treatment process (Hu and Mi 2014). The effect of sulfonation on PES substrate and layer by layer deposition of graphene oxide to fabricate nanocomposite membranes was studied. The prepared graphene oxide-based membrane exhibited a relatively high rejection of dyes (Tavangar et al. 2019). An NFM was prepared on a porous substrate with a chemical crosslinking process by LbL assembly of polyacrylicacid (PAA) and PEI. It exhibits improved separation performance with 1.5 bilayers of deposited polyelectrolytes. The membrane showed high rejection for $MgSo_4$ and $MgCl_2$ because of the electrostatic screening effect, whereas less rejection for NaCl due to size exclusion and Donnan effect (Liu et al. 2019). Layer by layer assembly-based biocatalytic NFM were prepared by immobilizing laccase into the skin layer with controlled crosslinking and immobilization. The prepared membrane was employed for micropollutants, i.e., BPA removal (Li et al. 2020).

Other methods were also reported for the development of novel NF composite membranes. For instance, a positively charged composite NFM was synthesized using deposition of PDA followed by PEI grafting on PES substrates. The salt rejection was observed to be enhanced along with the decrease in the pure water flux with increasing PDA deposition. The prepared membrane possesses superior rejection for the cationic dyes (Zhang et al. 2014b). Another novel positively charged NFM was prepared by PDA deposition followed by crosslinking on PES UF membrane substrate. The selected bridge and crosslinking agent enhanced the positive charges of the PDA layer and hydrophilicity. The developed positively charged membrane displayed high efficacy for cationic separation (Mi et al. 2021). PEI and trimesoyl chloride (TMC) were used for performing IP reactions on polydopamine coated hydrolyzed polyacrylonitrile substrate to prepare a positively charged NFM. The prepared membranes showed satisfactory potentials for the application of water softening (Yang et al. 2018). By incorporation of organic metal frameworks (MOFs) into the chitosan polymeric matrix, a positively charged NF was also prepared for the enhanced removal of multivalent cations. It was observed that the shapes of MOFs had a noteworthy effect on the prepared membrane's permeability (Ma et al. 2016). Zeolite nanoparticles embedded in situ with polysulfone support followed by IP from the polyamide layer were employed to develop TFC membranes. Compared to the thin-film membranes prepared by the traditional method, the prepared membranes had advanced loading and higher uniformity in the dispersion of NPs. The presence of NPs enhanced the surface unevenness with maintained hydrophilicity (Dong et al. 2016).

2.4 Membrane Characterization

Nanofiltration membrane durability in operating conditions relies on the membrane polymer's chemical, mechanical, thermal properties. In contrast, membrane performance relies on these properties that may be determined by membrane characterization (Rana et al. 2005). The various techniques that are used for characterization of the physical and chemical properties of NFM are mentioned below.

2.4.1 Scanning Electron Microscopy (SEM)

SEM depicts the microstructure of membrane material. The measurement is achieved via the exposure of the membrane to an electron beam at an accelerating voltage in a vacuum. It includes sample drying along with conductive material coatings like carbon and gold. It was owing to the characteristics like high permeability, enhanced surface area, low basis weight, and high pore interconnectivity. The effect of processing parameters on pore structure and thickness of anodic aluminum oxide tubular membranes was studied. SEM was used to determine the pore sizes of the membrane ranging from 14 to 24 nm (Belwalkar et al. 2008). An ion-selective NFM using polyvinylidene fluoride nanofibres and hyperbranched polyethyleneimine as building blocks was developed. The SEM images have estimated the thickness of the membrane surface layers. On the basis of SEM images, it was observed that the surface of the using polyvinylidene fluoride nanofibres scaffolds can be covered by spraying them with polyethyleneimine in methanol (Park et al. 2012). The effect of water choice in the compaction of NFM in terms of surface characterization membrane performance was observed.

SEM images showed the different planes of deposition subjecting to water grade (Semio et al. 2013). The influence of various casting solution salt dopants with similar cations and different anions on the morphology and performance of polyethersulfone membranes was evaluated. The SEM images showed substantial changes to the internal membrane structure and pore size concerning the type and concentration of the casting solution anion dopant (Mierzwa et al. 2012). The preparation of TFC nanofiltration membrane with crumpled polyamide layer by IP on single-walled carbon nanotubes with polyethersulfone composite support, using metal–organic framework nanoparticles was reported. The SEM images of the membrane with different immersion time was noticed. Before immersing into the water, the PDA/MOFs NPs and single-walled carbon nanotubes film could be easily observed under the polyamide layer, indicating the top polyamide layer as thin and transparent (Wang et al. 2018). A thin film composite NFM-based on the layer of polyvinylidene fluoride formed a tree-like electrospun nanofiber membrane was developed. As compared to conventional support membranes, prepared tree-like electrospun nanofiber membranes exhibit less tortuosity, lesser average pore size, enhanced surface porosity, and high-proportioned interconnect pore. SEM images of the prepared membranes with different concentration of tetrabutylammonium chloride (TBAC) in the spinning solution was observed. It was demonstrated that TBAC concentration considerably affected the growth of the tree-like network (Liu et al. 2020). A new polyamide thin-film NFM was reported for the purification of water. The polyamide film was deposed on a synthetic cellulose acetate via IP method. TMC and 1,3-cyclohexane bis (methylamine) were used as monomers. SEM results displayed that membrane thickness was increased with an increasing concentration of 1,3-cyclohexane bis (methylamine) (Ounifi et al. 2021).

2.4.2 Transmission Electron Microscopy (TEM)

This technique measurement is achieved via transmittance of an electron beam in the influence of a high vacuum through a sample. An image is formed through the interaction of electrons transmitted through the sample. Compared to SEM, TEM produces images of high resolutions that enable users to examine thin fine samples. This technique accomplishes almost atomic resolution. A polymer nanocomposite with graphene-based hierarchial filler as a material was prepared. The images showed that most AuNPs had a diameter between 10 and 50 nm while a small part of AuNPs observed an exfoliated graphite nanoplatelets support between 50 and 100 nm. (Crock et al. 2013). Water flux and rejection ability of nanocomposite membrane prepared from reduced GO (rGO) and silver NPs (AgNPs) were demonstrated. It was observed that the prepared membranes possess high water flux and satisfactory rejection rates for rhodamine B. TEM images of GO showed thin sheet-like morphology and sheets with wrinkled surfaces and folding at edges. The AgNPs were homogeneously dispersed on the rGO sheets. AgNPs' average diameter was in the range of 20–30 nm (Liu et al. 2017). The graphene oxide surface was grafted by active groups of biguanide via covalent functionalization and joined with magnetic NPs to make a magnetic graphene-based composite (MMGO). The fabricated hybrid was then introduced to PES polymer by immersion precipitation method. TEM images showed that the GO film was obvious and spherical NPs with approx. 20 nm were well dispersed on MMGO surface (Abdia 2018). GO/AgNPs composite membranes were synthesized to determine the size effect of AgNPs on NF capability. TEM images showed the size of AgNPs loaded on three types of GO/AgNPs composites are 8, 20, 33 nm. It was observed that when the NPs size was 20 nm, the nanocomposite (GO/AgNPs) had maximum water flux and rejection for Rhodamine B (Yang et al. 2020). Polymer matrix membranes, cellulose acetate/vinyl triethoxysilane modified graphene oxide, and gum Arabic (GuA) membrane as developed. TEM images showed the graphene oxide distribution in matrix structure was dense, whereas, in modified samples (-GuA2–M-GuA8), wrinkles were observed as the Gum Arabic NPs distribution was uniform (Idress et al. 2021).

2.4.3 Thermogravimetric Analysis (TGA)

It is a measuring technique which as a function of time with a constant mass loss or temperature or function of increasing temperature at a fixed heating amount, determines the chemical or physical changes of materials (Coats and Redfern 1963). It is utilized for determining particular characteristics of materials like polymers, ceramic glass, and plastics that undergo either mass gain or loss because of oxidation, loss of volatiles, degradation. It relies on an extreme degree of accuracy concerning mass and temperature change. It is useful for studying polymeric materials like thermosets, composites, paints, coatings, fibers, elastomers etc. In membrane technology, the thermal stability of membranes is an important aspect. As a result, it is important to study the temperature stability of membranes as the membrane process can be processed at higher temperatures. N,O-carboxymethyl chitosan NFM having PES was prepared and tested for their capacity to separate Ni(II). With increasing temperature, loss in the mass of membranes was observed. The membranes were thermally stable at 200 °C (Boricha et al. 2008). A membrane was developed by incorporating CO_2-selective adsorptive silica NPs in situ into the tertiary amine-containing polyamide membrane. TGA results showed that the degradation of silica-free membranes is more as of silica-containing membranes. Silica comprising membranes have less mass loss rates compared to silica-free membranes owing to the silica thermal stability (Xingwei et al. 2011). A novel TFC polyphenylsulfone (PPSU) membrane was prepared by casting a thin PPSU barrier layer on the surface of the electrospun nanofibrous PPSU support. The two-stage degradation in the membrane was observed in thermal stability studies. The initial decomposition was due to the degradation of the PEG 400 molecule, while the second was due to the PPSU molecule decomposition (Kiani et al. 2017).

2.4.4 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

This sampling technique is integrated with FTIR to facilitate the surfaces to be studied for infrared analysis. FTIR uses vibrational spectra measurements for identifying the materials' chemical structure. The IR spectra are employed to determine the transitional intensities and the vibrational frequencies of molecules with functional group intensities. Polysulfone composite membranes were fabricated and characterized for desalination in the NF method. ATR-FTIR was used to study the chemical structures of NFM after irradiation. Polysulfone membrane was prepared and characterized that showed bands at 1301 and 1148 cm^{-1} corresponding to asymmetric and symmetric stretching of SO_2 group. The IR analysis of Polysulfone/chitosan composite film showed a peak at 3370 cm^{-1} for –OH stretching superimposed with N–H stretching, 2926 cm^{-1} for aliphatic C-H stretching, 1102 cm^{-1} for cyclic ether linkage. The uncrossed linked poly(1,4-phenylene ether sulfone/chitosan composite film showed a weak band at 1657 cm^{-1} due to the presence of acetylated amino group (Shenvi et al. 2013). Two-step surface modification of polyamide NF was applied. Firstly, by reacting with residual acyl group of NFtriethanolamine (TEOA) with hydrophilic -OH. Then, a low surface energy material was covalently grafted on the –OH via hydrogen bonding. ATR-FTIR spectra of surfaces of PSF support membrane, NF membrane, TEOA grafted NF membrane were noted. The apparent peak at 1628 cm^{-1} was noted, approving the development of an active polyamide layer by IP method (Ruan et al. 2018).

2.5 Future Aspects of NFM Technology

The effective utilization of NFM has been owing to its inimitability of possessing selectivity for the desired separation species. A membrane with appropriate selectivity must be designated for providing the most optimal separation based on the requirement. Therefore, with this capability, NFM will continue to discover new applications in areas like desalination of brackish water, water and wastewater treatment, separation of small organics, food applications, biotechnology, etc. Additional study is needed in determining the role of novel nanomaterials in NFM arrangement and the influence of solute transport. It would also be motivated to examine new nanomaterials' safety and ecological facets for the water treatment process. This will lead to significant advancement in nanotechnology and sparkled interest in NF membrane fabrication. Thin-film composite and thin-film nanocomposite NFM have been prepared via IP process will remain the standard in the development of NFM. Other fabrication methods must secure their place for small-level development in the lab. However, these methods suffer from limitations when large-scale preparation of membranes is needed. The capability to modify NFM that are significant in the preparation process will lead to considerable development in improving the performance of NFM. For the satisfactory performance of NFM, it is imperative to precisely understand the relevant data that can be derived from various characterization methods. NFM manufacturers must support researchers in providing basic characterization data that will permit them to select NFM that will meet their needed requirements and decide on diverse operational conditions.

2.6 Conclusion

Nanofiltration is recognized as an appropriate technique for removing pollutants from the water surface for producing drinkable water. NFMs are pressure-driven liquid membrane processes that have been practically applied in various industries. Procedures for NFMs preparation have been successfully applied in fabricating membranes with improved selectivity and good flux. The prime routine employed for synthesizing thin film composite or nanocomposite membrane is still based on interfacial polymerization. Introducing nanomaterials onto the thin film has had a noteworthy consequence on the performance ability of the membrane. The characterization of NFM has been imperative in nanofiltration membrane development and research as the design of NFM process and systems rely on data involving the properties and chemical structures of the membrane. Nanofiltration has to still evolve for understanding the resources and characterization to power their execution. However, future works must concentrate on creating membranes while enhancing the capability to control, reduce, or moderate fouling.

Acknowledgements The authors are thankful to the Banasthali Vidyapith and the Central University of Gujarat.

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Chapter 3
Pretreatments Before the Nanofiltration Technique

Sevde Korkut, Vahid Vatanpour, and Ismail Koyuncu

Abstract Nanofiltration (NF) is a preferred process in water and wastewater purification, water recovery, and reuse due to its ability to retain low molecular weight components. However, there is an important factor limiting nanofiltration applications, which is the formation of fouling caused by various pollutants. Pretreating wastewater before entering into the NF process is the most feasible technique to prevent fouling. The pretreatment is aimed to keep the undesirable compounds in the feed water, decrease the concentration of these compounds in the boundary layer, prevent the gel formation/concentration polarization, and/or provide a long membrane service span. At this point, it is critical to select the most appropriate pretreatment methods or configurations based on the characteristics of the wastewater. Pretreatment technologies for NF can be broadly subdivided into chemical (coagulation/flocculation/sedimentation and advanced oxidation), physical (sand/carbon/cartridge filter), biological (MBR/PAC, biosorption), and membrane-based processes (UF/MF). In this section, the combinations of NF-pretreatment technologies studied in various wastewaters are evaluated in terms of factors such as improvement in flux, process sustainability, the water quality of the effluent, and cost.

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_3

3.1 Introduction

Water is a fundamental constituent in the transition from the conventional economic system to the circular economy. Water, which has an indispensable position in terms of industry, agriculture, energy, climate change, recycling/recovery technologies, must be sustainable and of high quality (Dharupaneedi et al. 2019; Vaziri et al. 2021). Also, inadequate access to clean water stifles economic and social growth while also posing possible threats to public sanitation. One of the leading treatment technologies preferred for clean water production is nanofiltration (NF) in particular for membrane filtration technologies. To ensure the long-term viability and stability of the NF process is critical to decreasing foulants, and hence requires applying pretreatment techniques.

Fouling is generated by dissolved in water inorganic (i.e. $CaCO_3$, $BaSO_4$) or organic (i.e. humic acids, natural organic matter) components, colloidal and suspended particulate matter, or bacteria (Van der Bruggen, Braeken, and Vandecasteele 2002; Vrouwenvelder et al. 1998). The fouling mechanism of nanofiltration membranes describes usually occurring by inorganic and/or organic substances situated in water that stick to the surface and pores of the membrane, resulting in loss of treatment performance with an inevitable membrane replacement (Al-Amoudi and Lovitt 2007). Fouling in the membrane pores can occur as a result of surface fouling, such as partial pore size reduction, cake layer formation, and gelation, caused by the blockages adsorbed on the inner pore walls (Schäfer, Fane, and Waite 2000). This phenomenon will raise operating expenses by increasing energy consumption, increasing cleaning costs, and shortening the lifespan of the membrane components (Vrouwenvelder et al. 2003). The silt density index (SDI), which is known and used globally, and the modified fouling index (MFI) are the two existent fouling indices for measuring the colloidal matters that have a fouling potential of feedwater. Both indexes are calculated by passing water through a 0.45 micron filter using the dead end method (Boerlage et al. 1997; Hilal et al. 2004). There is a scheme summarizing the main dynamics of colloidal contamination is given in Fig. 3.1 (Mohammad et al. 2015).

Biofouling is depicted in the literature as the buildup of microorganisms, namely biofilm, on a surface caused by growth and/or deposition at a level that creates operational trouble. During NF or RO, it may result in decreased normalized flux and/or greater normalized pressure decreases (Vrouwenvelder et al. 1998). Controlling biofouling can be accomplished by (i) pretreatment to remove all non-inert compounds, (ii) use of high purity and high quality cleaning chemicals, and (iii) monitoring of periodic chemical and backwashes. A cleaning approach used when fouling is not an issue may also postpone biofilm development (Hilal et al. 2004).

Surface water containing calcium (Ca^{2+}) and humic compounds can lead to significant fouling of NF membranes. Fouling was detected to be harmful at high Ca^{2+} concentrations, by the mechanism relying on solution chemistry (Yoon et al. 1998). Because of their extremely compactable floc-like shape, calcium-humate complexes produced the utmost flux reduction when compared to calcite precipitates. Ca^{2+} and

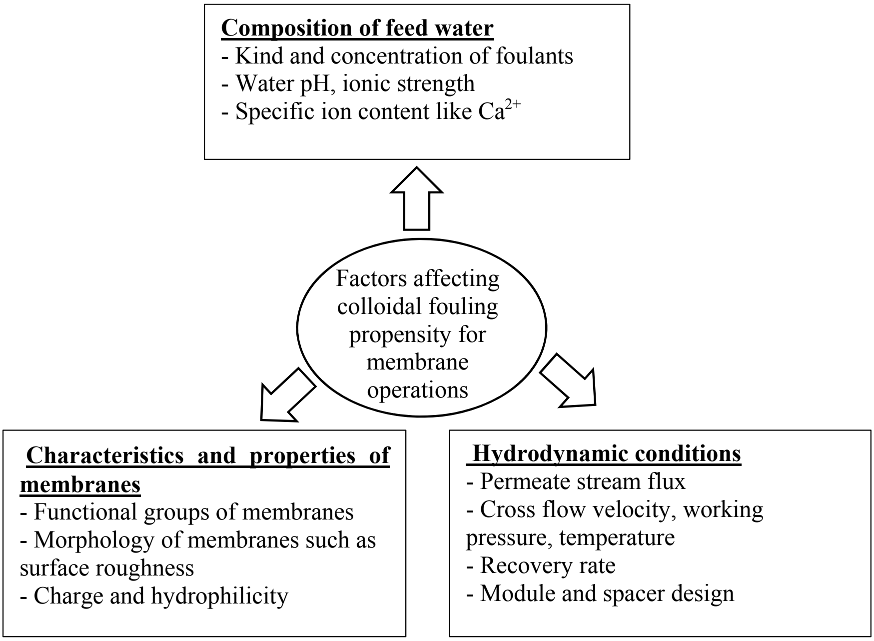

Fig. 3.1 Factors affecting colloidal fouling propensity for membrane operations (Mohammad et al. 2015)

organic matter deposition increased in proportion to the pH owing to calcite precipitation and organic adsorption on the calcite surface. Humic acid is a natural organic substance with a high molecular weight. For this reason, with its high concentration in the boundary layer, it achieved the lowest diffusion across the membrane and played a role in reducing the flux significantly (Hilal et al. 2004).

Pretreatment methods involved microfiltration (MF), coagulation-MF, and coagulation-sedimentation were combined with NF membrane. The presence of a higher negatively charged membrane surface was associated with increased fouling, showing electrostatic repulsion, but it was ineffective for fouling reduction. Organic adsorption fouling may have been led to high surface areas that have increased surface roughness in the more negatively charged membranes. A polyamide membrane is not durable against monochloramine. With the addition of monochloramine, decreasing flux and, low recovery rate fouling was decreased, as were flux and recovery (Reiss, Taylor, and Robert 1999).

The feed pretreatment before entering into the NF membrane unit is one of the most effectual solutions of fouling control. Different types of pretreatment have been applied to reduce colloidal/dissolved pollutants in the feed stream, and according to the results of many membrane operations, membrane fouling has been significantly reduced. Coagulation, flocculation, ozonation, adsorption, H_2O_2/UV oxidation, and UF/MF have all been described as successful pretreatment before to NF unit. As described in Fig. 3.2, it should be noted that those pretreatment techniques may not be able to eradicate all of the foulants in the water, implying that the NF membrane process will still require alternative fouling management strategies (Mohammad et al. 2015).

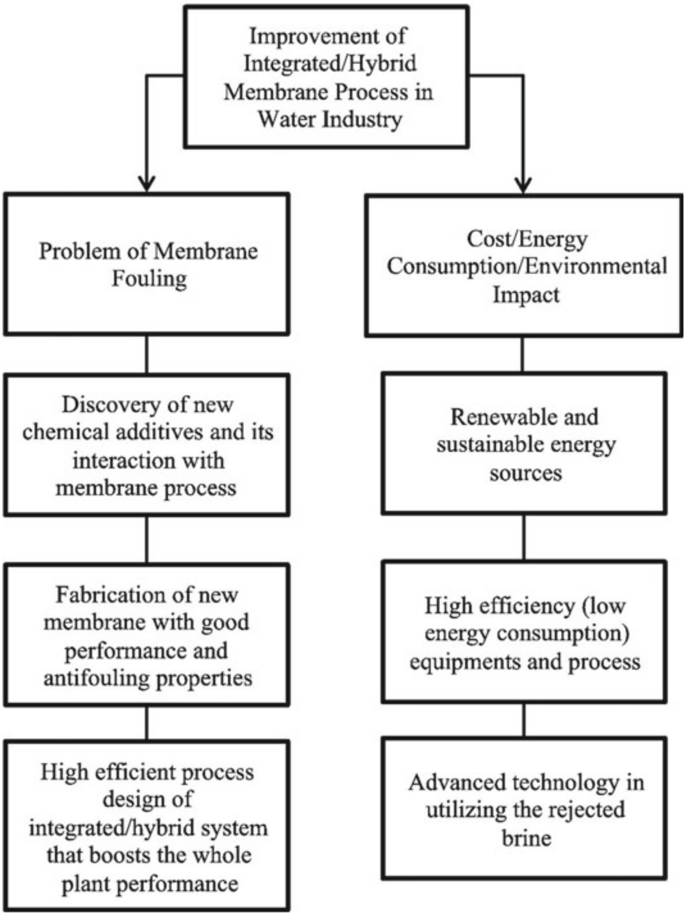

Fig. 3.2 Possible enhancements for an integrated/hybrid membrane water treatment plant (Ang et al. 2015)

3.2 Physical Processes

3.2.1 *Flocculation and Sand Filtration*

Flocculation is the process of destabilizing suspended particles by a charge neutralization mechanism, and bridging the fine sediments to form a larger floc substance (Lee et al. 2012; Karadoğan et al. 2020). It is an efficient and quick way of solid–liquid separation. In Hashlamon et al. study, coagulation/flocculation/sedimentation (CFS) and powdered activated carbon (PAC)/CFS processes were compared to each other for pretreatment during NF. Two wastewater (WW) samples that secondary treated sewage WW and diluted biodiesel WW were used in this experiment. According to the results, CFS pretreatment provides better control of membrane fouling and enhances the flux from 24 to 32.1 $L.m^{-2}\cdot h^{-1}$. Experiments occurring with biodiesel wastewater PAC/CFS process have increased the flux from 22.3 to 28.7 $L.m^{-2}\cdot h^{-1}$. The COD value in the NF permeate was decreased to 4 $mg.L^{-1}$ using pretreatment while remaining at 95 $mg\cdot L^{-1}$ without pretreatment (Hashlamon, Mohammad, and Ahmad 2017).

NF was tested in a German water treatment plant where groundwater had high hardness as expected and NOM content was high (Gorenflo, Velázquez-Padrón, and Frimmel 2003). A conventional pretreatment system that includes deferrization, demanganization combined with rapid sand filtration was established. Almost all of NOM was rejected (95%), and the removal of magnesium (Mg^{2+}) (86%) and Ca^{2+} (74%) was acceptable. The configure-flocculation of a conventional pretreatment system before NF minimized fouling and necessitated the use of fewer detergents or softening agents.

In a recent research, a pretreatment method was investigated for NF aiming to treat and reuse animal by-products in rendering plant wastewater. For this purpose, the sand filtration technique was compared with the ultrafiltration process (Racar, Dolar, Špehar, and Košutić 2017a, b). However, considerable fouling occurred during the UF pretreatment, even though SF and UF decreased turbidity by more than 93%, TC by 31%, and DOC by 45% (the flux loss at 28–43% in the first hour). Membrane fouling was not as severe during NF as it was during UF due to the effective elimination of foulants by UF membranes. NF significantly reduced COD, salt concentration (conductivity), carbon, nitrogen, and phosphate.

3.2.2 *Adsorption Processes*

Adsorption is an effective and efficient conventional technology for retention in a wide scale of inorganic and organic pollutants (Ganiyu et al. 2015). It is frequently preferred as a pretreatment process to reduce fouling and stabilize flux during membrane filtration. Many studies have been compiled, including the integration of adsorption techniques and membrane filtration technologies for the effective purification of water during the previous two decades (Kim et al. 2022). The physicochemical characteristics of the process have frequently influenced the retention of polymeric contaminants by the membrane filtration systems, and for ionized organic molecules, charge exclusion is critical in maintaining a steady state. The size exclusion mechanism of solute retention is determined by the size of the soluble molecules and the size parameters of the membrane pores. The molecular weight cut-off (MWCO) data is routinely used to predict these properties given by the manufacturer (Zahoor and Mahramanlioglu 2011).

The use of activated carbon (AC) pretreatment is one favorable method for reducing membrane fouling. However, because of the small weight of AC and the lengthy time necessary for its sedimentation, membrane permeability may be reduced. Alternatively, magnetic activated carbon (MAC) was developed and tested through the abilities of its magnetic forces and enhanced coagulation features, it could successfully convert the soluble substances to coagulated flocs. Hereby, MAC had no membrane-fouling propensity with the improving flux, whereas a notably fouling was observed by using AC as a pretreatment before NF (Wahab et al. 2021).

An adsorbent-membrane system was combined with an adsorbent based on natural matter and an NF membrane (polyethersulfone, PES) with MWCO of 1000 Da. The raw water was provided from a pilot-scale wastewater treatment plant with the aim of organic matter removal (Meier and Melin 2005). An instrumental analysis that liquid chromatography configurated organic carbon detection (LC-OCD) was applied to detect numerous fouling agents, for instance, polysaccharides, and different molecular weight acid/neutral/amphiphilic chemical substances. Because adsorbent particles and polysaccharides (100,000 Da and > 20,000 Da, respectively) were considerably bigger than the pores of the membrane, these results were connected with the organic load derived from solute molecules and adsorbent materials clogging the membrane surface pores. But once the organic compound was eliminated by the adsorption mechanism on PAC, the membrane flux shaded off fairly steady at a pretty desirable level. Furthermore, there was a loss in the removal efficiency of inorganics on account of concentration polarization in the adsorbent particle layer attached to the membrane surface.

The adsorbent/catalyst of a hybrid process used to reject bisphenol A (BPA) which is known as a common and potent endocrine disruptor was electrostatically immobilized Fe(III) tetrasulfophthalocyanine on the anion-exchange resin (Amberlite IRA-400) and added H_2O_2 to the reactor. The hybrid experiment of adsorption-catalysis processes was not as successful as expected in BPA removal. When NF was added to the system, the BPA removal efficiency reached < 85% successfully. So, BPA became highly concentrated in the reactor during the experiment. However, the concentration of BPA deposited in the reactor was higher when purified with NF without pretreatment. Furthermore, adding H_2O_2 to the BPA reactor after 15 h did not result in a rise in BPA concentration, possibly because the presence of H_2O_2 aided in the breakdown catalytically of BPA (Kim et al. 2008).

In another hybrid system with an NF with salt retention of 97%, a magnetic carbon nanocomposite (MCN) synthesized using biomass of pineapple waste was employed to extract levofloxacin, a micropullutant (Ullah et al. 2019). One of an antibiotic medication, levofloxacin, was mitigated by the MCN–NF membrane integrated system almost completely (~100%) and the data of flux were also satisfying (Ullah et al. 2019). After filtration in a 1 h period, the membranes were cleaned by deionized water. Because the MCN was entirely extracted from the slurry using a magnet, the overall backwashing time of the NF membranes and MCN was significantly less than that of the bare ones (Tanis, Hanna, and Emmanuel 2008).

Another hybrid NF system with a membrane surface that has positive charge was used for the removal of a few dyes, from a synthetic dye solution (Peydayesh, Mohammadi, and Bakhtiari 2018). Membranes were produced by a phase inversion method, and triethylenetetramine-functionalized multi-walled carbon nanotubes (MWCNT) were embedded into the PES support layer during production. All results disclosed that the size of ion and electrostatic tensions between the active layer and the solute electrolytes influenced treatment performance (Tang et al. 2015). As the rhodamine B concentration increased from 50 to 200 mg L^{-1}, the osmotic pressure of the solution also increased. This situation affected the membrane flux negatively and caused it to decrease. Besides, as the dye concentration increased, the removal efficiency of rhodamine B decreased. It can be said that the electrostatic interaction between the membrane surface and the dye molecules weakens and becomes insignificant as the reason (Zhao et al. 2016).

Only a few studies, in particular, have investigated the transfer of pollutants at the pilot size using traditional indicators like COD and dissolved organic molecules. As a result, a thorough assessment of the mitigation of numerous either conventional or emerging inorganic/organic pollutants is necessary, especially at the pilot scale. This documentation would enable the determination of real/pilot scale and enduring membrane resistance for utilizing in adsorbent–membrane hybrid processes (Kim et al. 2022). Figure 3.3 displays potential research domains for adsorption-membrane filtration hybrid systems in terms of different parameters.

3.3 Chemical Processes

3.3.1 Coagulation

One of the conventional and low-cost pretreatment systems is coagulation/flocculation/filtration pretreatment was intended to eliminate the majority of probable foulant elements from the feed water before NF. However, the selection of pretreatment process and grade is determined based on the characteristic of raw water, namely the concentration of organic and inorganic suspended particles. Several studies have been reported on factors such as flow rate, pH, and backwash frequency, which should be optimized when coagulation is selected as the pretreatment. In previous work, surface water has elevated hardness (Ca^{2+} and Mg^{2+}) was applied a multistep complex process comprised of coagulation and flocculation using lime,

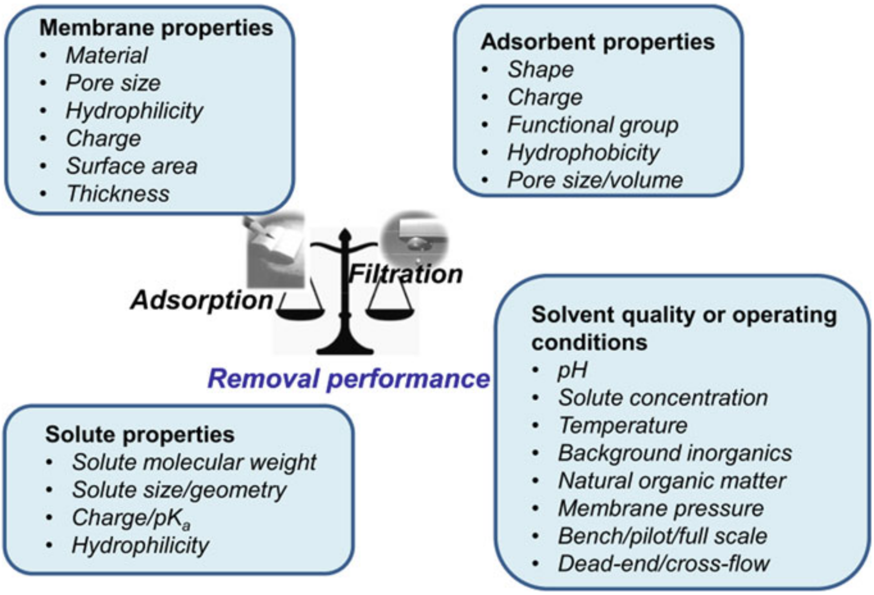

Fig. 3.3 Future research fields for adsorbent-membrane hybrid systems (Kim et al. 2022)

mechanical bed filtration, followed by weak cation ion exchange, and deep-cartridge filtration as pretreatment. Ca^{2+} and Mg^{2+} concentrations in the permeate water had successfully fallen below the limit values (Al-Amoudi and Lovitt 2007).

As typical coagulants, ferric salts (like $FeCl_3$, $FeCO_3$) or aluminum salts ($Al_2(SO_4)_3.16H_2O$) work by destabilizing hydrophobic or acidic organic macromolecules and colloidal matters to produce aggregates that are eventually eliminated as sludge. Surface water, textile wastewater, sewage treatment plant effluents, and landfill leachate have been researched on treatment using membrane filtration processes with a coagulation pretreatment (Dolar et al. 2016; Racar et al. 2017a, b). There are two studies in which 62–78% and 85% BOD_5 removal were obtained by using coagulation pretreatment in slaughterhouse wastewater, which is one of the challenging wastewater (de Sena et al. 2008; Tariq et al. 2012).

In other research, rendering plant secondary effluent (SE) was treated by coagulation/sand filtration combined with NF membrane (Racar et al. 2017a, b). Response surface method (RSM) was used to adjust the coagulation process, i.e. the dosage of $FeCl_3$ coagulant, mixing time, and pH change, to produce an acceptable residue (carbon components at a pH close to 7 and minimum turbidity) that would not foul the surface of NF membranes considerably. When raw SE was purified directly with NF, the flux was reduced, and pretreatment was applied by sand filtration (SE-SF) and coagulation/sand filtration processes (SE-C-SF). Moreover, following each treatment step, characterization of effluent water was followed in terms of several carbon measurements. As a result, the resistance of the fouling layer was somewhat greater for the tight NF90 membrane, while it was equivalent for NF and NF270, with a little

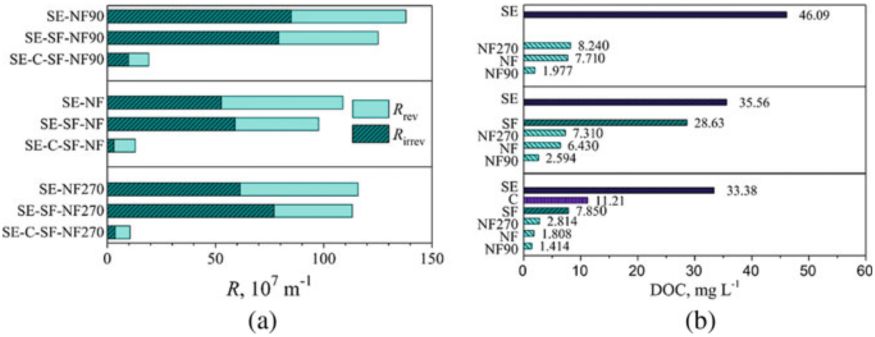

Fig. 3.4 Reversible and irreversible fouling (**a**) and DOC content of effluent of hybrid systems (**b**) (Racar et al. 2017a, b)

higher resistance after SE-SF-NF270. Washing the membranes with demineralized water had a positive effect on the flux and the flux increased. The membrane pretreated with SE-C-SF depicted the greatest flux recovery ratio. The membranes of the SE-C-SF-NF system were rusty in color, indicating that iron salts had accumulated on their surfaces. The inorganic fouling may explain why it may be reversed after washing with demineralized water. Reversible and irreversible fouling of hybrid systems and DOC content of effluent of hybrid systems were portrayed in Fig. 4a, b, respectively. Consequently, the coagulation process provided a more efficient pretreatment than other alternatives (Racar et al. 2017a, b).

Coagulation is an effective technique for removing turbidity and color, which are two important physical parameters. Besides, it is capable of greatly reducing the presence of microorganisms in the water. Coagulation occurs when large-scale microorganisms such as fungi and algae, as well as natural organic materials cling to each other, form a flock and precipitate. Following coagulation, TOC was removed at a 15 to 29% rate. The charcoal treatment completely erased the color from the surface water. The high pesticide content in raw water is reflected in its high COD and TOC values. Charcoal treatment eliminated up to 99.3–99.4% of pesticide residue. After the preceding step's charcoal pretreatment, there was a drop in COD of 21–37% and a reduction in TOC of 38–43% (Sarkar et al. 2007).

In Kim et al. study (2007), different pretreatment processes have been tested on NF membranes using river water to assess the filtration performance. MF pretreatment was more desirable for removing solids than dissolved organic materials. The quick rise infiltration resistance of the feed stream was most likely due to particle organic matter adsorption rather than cake/gel layer formation. The most effective process in removing organic pollutants was the CSOB (coagulation, sand filtration, sedimentation, ozonation, biological activated carbon) pretreatment, but it was no better than the CS (coagulation, sand filtration) process in removing inorganic matter (Kim et al. 2007).

The impact of a coagulation/flocculation system used as pretreatment is determined by the pH, the kind and volume of chemicals employed, and the raw water parameters. That procedure is mostly employed to reject organic contaminants. Nevertheless, a detrimental impact on NF permeates flux has been determined also compounds that promote biological development are not adequately degraded, which may be concluded in biofouling surrounding the surfaces and pore walls of NF membranes. Other disadvantages include the high expense of additives and the subsequent removal of produced sludge (Van Der Bruggen et al. 2004).

3.3.2 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) principles are based on the generation and participation of hydroxyl (OH*) radicals in sufficient quantity for treatment water by the reaction between H_2O_2 and ferrous (Banerjee et al. 2007). To obtain high performance, AOP employs Fenton's reagent. Ozone (O_3) and UV radiation improve the effectiveness of Fenton's reagent and are occasionally utilized for AOP (Xia et al. 2018). Integrating/coupling using membrane separation processes with AOPs provides some important advantages. Firstly, when considered as a pretreatment process, it removes macromolecular organics and colloidal matters from the feed water and decreases bio/fouling. Also, advanced oxidation technology reduces the operation load to NF and achieves cost-friendly and stable operation (Li et al. 2019) It acts as a post-treatment to oxidize organic substances in both the concentrate and permeate streams of the membrane. Lastly, it ensures coincident separation and oxidation of contaminants with a one-pot/hybrid process (Ganiyu et al. 2015). All configurations were portrayed in Fig. 3.5.

AOPs such as photo-Fenton, ozonation, UV/H_2O_2, photocatalysis, preoxygenation (O_3/H_2O_2), and electrochemical AOPs (EAOPs) have been effectively linked with membrane filtration for various contaminant rejecting from water (Ganiyu et al. 2015; Hilal et al. 2015; Li et al. 2019; Lin et al. 2019). In reality, AOPs use the hydroxyl radical (OH*) produced by UV light and H_2O_2 to broke down organic

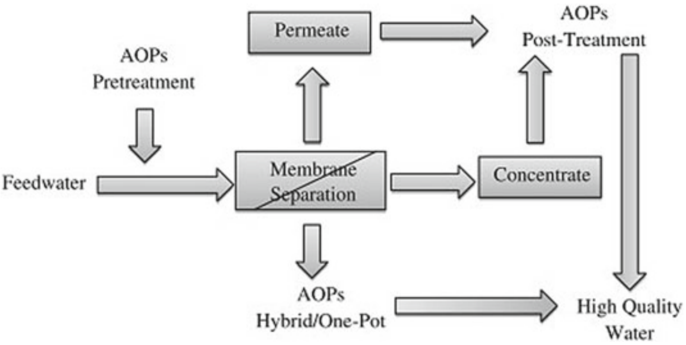

Fig. 3.5 Integrating or coupling methods of AOPs and membrane filtration (Ganiyu et al. 2015)

materials into minor molecules that can degradable biologically and, eventually, CO_2 (Lu et al. 2013; Umar et al. 2016).

AOPs were thought to be an efficient pretreatment method of decomposing organic matters, humic substances, suspended solids in reverse osmosis concentrate (ROC) (Xia et al. 2018). In the ROC treatment study (Li et al. 2019), the O_3-assisted UV-Fenton AOP as a pretreatment during the NF was investigated. In the membrane module system that has an active area of 25 cm^2, four different structures of commercial NF membranes were tested to purify the AOP effluent. According to the results, NF90 and NT103 membranes could better reject monovalent ions, while separation monovalent and divalent ions had been achieved successfully by DK and NT101 membranes. As the temperature increased their capabilities of ion rejections decreased. The highest removal rate of TDS (89.65%), UV254 (80.40%), COD (77.40%), and water recovery rate of 72% was reached after pretreatment by AOPs. In addition, pre-treatment with AOP positively affected the process, allowing the flux to be higher than the value obtained if treatment with NF alone. Flux increased by 39.7% as pressure increased from 0.3 to 1 MPa. Due to raw ROC produces substantial organic fouling when its get in touch with NF membrane that is working at low pressure, the flux range was significant as the high pressure. The variation in MWCO of NF membranes had responsibility for performances on the rejection of organic substances and humic materials. Consequently, the diffusion rate of water molecules can be raised and NF effectiveness can be enhanced after AOPs pretreatment (Li et al. 2019).

One of the novel AOPs is ferrous-activated peroxymonosulfate (PMS) has been deeply investigated and used as a pretreatment technique during NF (Lin et al. 2019). Besides, this practical and efficient AOP has been compared with coagulation on behalf of the conventional pretreatment process. Both approaches significantly reduced organic fouling at the membrane surface, according to the data. Because of the presence of ferric ions and SO_4^{2-} anions, gypsum scaling was increased when Fe(II)/PMS was employed as a pretreatment method during the NF process at a dosage of 80/80 M. Surprisingly, Fe(II)/PMS oxidation could effectively boost permeate quality in the NF process. Besides, Bisphenol A removal efficiency ranged from 53 to 78% in the Fe(II)/PMS-assisted nanofiltration process, while only 5–12% was achieved in the Fe (III) coagulation-NF configuration.

For the concentrated part of this hybrid system with high water recovery, different processes should be considered for testing in future studies. New technology such as membrane distillation or mechanical vapor recompression techniques can separate the water from the solution. Finally, zero discharge liquid becomes a possibility. AOPs need new research to monitor the treatment performance and improve the water recovery rate in case of long-term operation. The energy efficiency of the process has not yet been clarified. It may also be possible to make cost analysis by conducting real-scale and long-term studies (Li et al. 2019; Mozia et al. 2016).

3.4 Membrane-Based Processes

Microfiltration (MF) can mitigate bacteria, colloidal particles, turbidity, and chemicals in solute-linked stick with particles. Additionally, since the main removal mechanism of MF is size rejection, an increase in removal occurs in COD/TOC as a result of the retention of organic matter in particulate form. While MF does not make a major contribution to pollutant removal, it provides an advantage as it sustainably prevents flux reduction in the NF membranes and this helps to reduce operating costs. UF membranes have a similar effect for pretreatment. Only the structural difference is that the pore diameter is smaller and therefore the water flux is lower than the flux of MF.

Boerlage et al. created a modified fouling index (MFI) that uses UF modules to estimate flux reduction in membrane filtration systems and as a water quality indicator. The MFI-UF was discovered to be a viable method for assessing colloidal fouling potency in RO, NF, and UF systems (Boerlage et al. 1997). The ability of UF membranes to retain colloidal particles is determined by UF pore size represented as a molecular weight cut-off (MWCO), morphology of surface (e.g. the structure of ridge and valley or porosity), and the composition of the membrane matrix (e.g. charge, hydrophilicity). These UF membrane features also have an impact on the filtering mechanisms that occur throughout the test (cake layer formation). As a result, the effect of UF membrane characteristics on the MFI-UF was investigated to explain the presence of filtering mechanisms in the test. The MFI-UF test may be used to anticipate flux reduction and a differential pressure rise in NF and UF to evaluate a feed water's backwash frequency (Hilal et al. 2004).

A membrane hybrid process has been developed to investigate the recovery of water from wastewater in textiles, which is one of the industries with a high water footprint. Sand filtration (SF), coagulation, and hollow fiber UF processes (UF-HF) as pretreatment were compared in terms of various water quality parameters (Ćurić et al. 2021). Coagulation experiments revealed that $FeCl_3$ is preferable to $AlCl_3 \cdot 6H_2O$ (ACH), with superior outcomes for turbidity, TOC, and color removal. Coagulation is not cost-effective since a considerable amount of coagulant is required, which necessitates the treatment of a huge volume of sludge. Furthermore, the impact of decreasing the examined parameters with UF-HF was shown to be superior to SF standalone using. Finally, the UF-HF membrane outperformed the other pretreatments tested. Table 3.1 documents the UF-NF hybrid system carried out by the different teams on the research of treatment of textile effluents.

3.5 Biological Processes

According to historical background, aerobic biological pretreatment is commonly utilized as a pretreatment method of NF. To achieve the needed quality for water reuse, NF is frequently added later in the treatment procedure. Presently existing

Table 3.1 Detailed documentation into the UF-NF for remediation textile wastewater (Dasgupta et al. 2015)

Membranes	Effluent	Component(s) removed	Comments	Ref
UF: Spiral-wound PES module MWCO: 1 kDa NF: NF270 and Duraslick NF	Raw textile wastewater (textile finishing process)	$R_{salt} = 71\%$ (NF270), $R_{salt} = 54\%$ (Duraslick NF)	Maximal J_{UF} at pH 11 No correlation of pH with J_{NF} $J_{NF270} >$ 30% *$J_{Duraslick}$	(Alcaina-Miranda et al. 2009)
NF: NF90, NF200, NF270 Pilot-scale flat- sheet	Secondary textile effluent (cotton thread factory)	$R_{COD} = 99\%$ $R_{salt} =$ 95–97% (NF90) $R_{COD} = 40\%$ (UF) Permeate conductivity (NF90) < 500 mS/cm	Flux trend: $J_{NF270} > J_{NF200} > J_{NF90}$ UF pretreatment: J_{NF} ↑ 50%	(Gozálvez-Zafrilla et al. 2008)
NF: NF200, NF270 UF: 1 kDa and 10 kDa PES	Reactive azo dyes Raw textile effluents (rinsing baths)	$R_{COD} =$ 80–100% $R_{salt} = 80\%$ $R_{Color} = >$ 90%	Affected by effluent complexity	(Aouni et al. 2012)
UF: 2000, 5000, 20,000 Da NF: 150–300 Da	Milli-Q water and WWTP effluent	$R_{COD} > 70\%$ (NF) $R_{COD} < 50\%$ (UF)	Rejection by UF → Adsorption mechanism Rejection by NF → size exclusion, electrostatic interaction	(Acero et al. 2010)
NF: 600 Da UF: 8000 Da	Spiked deionized water and three surface waters containing < 10 ng L^{-1} EDC/PPCPl at pH 7.5	NF: Average retention 30–90% except naproxen (<10%) UF: R < 30%	Rejection in NF → hydrophobic adsorption, size exclusion UF → hydrophobic adsorption	(Yoon et al. 2006)

installations, for example, an activated sludge system, are often kept in place and used as a pretreatment system for the NF unit. Experiment results suggest that using a biological pretreatment increases the water flow and (overall) rejection of organic chemicals in NF (Van Der Bruggen et al. 2004).

In Chon et al. study, the aim was to evaluate the efficiency of removal of pollutants (mostly N-nitrosamines) occurring municipal wastewater reclamation employing a hybrid membrane bioreactor (MBR)-NF system. Adsorption and fouling improve the rejection of contaminants by NF membranes. Nevertheless, size exclusion was discovered to take a significant share in the hybrid treatment system, as the treatment performances of pollutants changed greatly based on N-nitrosamine molecular weight and MWCO of the NF membranes (removal efficiency: NF90 > NF270) (Chon et al. 2015).

To treat complicated leachate, biological degradation + membrane treatment has been frequently used. However, the performance of each unit based on both conventional bulk indicators and molecular data has not been thoroughly studied. Table olive processing fermentation brines (FTOP) are hypersaline wastewaters (conductivity > 75 $mS \cdot cm^{-1}$) that contains high amount of organic molecules (COD close to 10 $g \cdot L^{-1}$), and phenolic substances (in the range of 700–1500 $TY \cdot L^{-1}$). A hybrid technique with the aim of reusing FTOP was studied in this study. This merged process began with biological wastewater treatment and was followed by a UF and NF. A 6 L laboratory sequencing batch reactor (SBR) was used for the biological degradation. Each stream produced by the FTOP treatment (SBR effluent, UF, and NF) was assessed. The SBR removed COD (80%) and total phenol content (71%) successfully. The COD content of the NF permeate stream was less than 125 $mg.L^{-1}$ and the physical parameters such as turbidity, color, and phenolic substances were eliminated (Ferrer-Polonio et al. 2017).

3.6 Conclusion & Future Remarks

In summary, it can be said that pretreatment before nanofiltration is an effective method in increasing filtrate quality and reducing fouling. Regardless, while planning and selecting a combined hybrid membrane process for a plant, care should be given since the quantity of treatment required is dependent on the quality of the feed water. A good quality feed water can be treated with fewer processes, while raw water whose water quality does not meet the criteria must go through a more intensive treatment process. In addition, even if water is produced in accordance with the criteria sought, a non-profit facility design will not be preferred. For this reason, a balance between the initial investment cost and operating costs and the quality of the water produced must be taken into account.

When all pre-treatment systems are compared, the features that benefit and cause losses are compiled in Table 3.2.

Table 3.2 Possible pretreatments before NF technique with their advantages and drawbacks

Process	Advantage	Disadvantage
Flocculation/coagulation and sand filtration	Elimination of insoluble pollutants	Coagulant residuals such as aluminum sulfate (alum), ferric dose, PACl, and PAC adsorbent Production of a significant amount of sludge Costs
Adsorption	Suspended solids and organic molecules well removed	Blocking filter
MF/UF	Low pressure	Low quality of the treated water
Biodegradation	Elimination efficiency of oxidizable substances at a level of 90%	Insufficient biodegradability of dyes
Ozone treatment	Reduces operational load to NF Provide economical steady-state process Good decolorization	No removal of the COD Extra costs

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Chapter 4
Graphene Oxide Based Nanofiltration Membrane for Wastewater Treatment

Pooja V. Devre, Chandrashekhar S. Patil, and Anil H. Gore

Abstract Polymer-based nanofiltration (NF) membranes are an important class of membrane technology and have been used for filtration and purification of kinds of liquids such as industrial chemicals, solvents, beverages, liquids, water, wastewater on large scale containing ions and molecules. The permeability of the pristine polymeric NF membrane towards a variety of liquids can be modulated by incorporating different kinds of nanomaterials into it. Graphene oxide (GO) is an important class of carbon-based nanomaterial having various properties to make it a suitable meant for manipulating the intrinsic characteristics of the various polymer membranes for filtration applications. Hydrophobic core and hydrophilic surface functionality of GO structure help to modify the applicability of membrane in a variety of ways practically. This chapter mainly focuses on the introduction to various filtration technologies according to sizes of the membrane. Moreover, a method for functionalization, fabrication, and applications of GO-based composite NF membranes is also discussed. Finally, typical uses of GO-based NF membranes for water and wastewater treatment are also summarized.

Keywords Nanofiltration · Graphene oxide · Polymer · Membrane · Wastewater · Pollutants

4.1 Introduction

Nanofiltration (NF) membranes are well known for their unique surface properties and nanopores size with the application of wastewater treatment, pharmaceuticals industries, and food processing (Peng and Escobar 2003; Van der Bruggen and Vandecasteele 2002; Tang et al. 2011). NF membrane is a conservative polymer and broadly

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_4

used for nano separation having the properties of good segregation, easy manufacture, and quite economical (Sun et al. 2010; Ong and Chung 2014). Unlike there are few drawbacks of NF like poor chemicals and thermal resistance, membrane contamination and materially growing under brutal operation environments, specifically in organic solvents (Marchetti et al. 2014). Herein, due to their easy availability, high mechanical strength, and chemical stability, carbon-based graphene and its derivative graphene oxide (GO) have recently been studied as membrane material (An et al. 2016; Dervin et al. 2016; Liu et al. 2015; Sun et al. 2016). By using the modified hummer's method GO could be produced at bulky low costly through the oxidation of graphite source (Dreyer et al. 2010). GO contains a monoatomic dense structure having sp^2 and sp^3 hybridization in form of C–C and C–O bonds respectively with different oxygen-containing groups like carboxylic, epoxy, and hydroxyl groups at the essential plan and termination of the GO sheet (Dreyer et al. 2010). The edgewise aspect of GO ranges is in between nanometres and micrometres (Meyer et al. 2007). As per the HARN (high aspect ratio nanoparticles) arrangement of GO particle were possibly stacked on sheets one on another to build slim sheet of the membrane (Dikin et al. 2007) having a significant performance for different applications such as gas separation (Li et al. 2013; Kim et al. 2013) pervaporation (Tang et al. 2014; Hung et al. 2014) and membrane filtration (Hu and Mi 2013) to date. Furthermore, GO functionalized as miscellaneous matrix membranes belonging to enhanced separation rate and improved the properties of the membrane (Yang et al. 2017), (Kochameshki et al. 2017).Wastewater is a global concern, to minimize the shortage of drinking water, NF is a pleasant invention concerning the environment, especially in form of GO membrane tending to remove the unwanted materials in form of metal ions, organic solute, inorganic solutes, etc.

4.2 Type of Membrane Filtrations

There are four commonly accepted types of membrane filtration, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, depending on the size of the pores as shown in Fig. 4.1. They are classified based on the pore size of the membrane material required to separate the feed from the liquid (Fig. 4.1).

(a) Microfiltration (MF)
(b) Ultrafiltration (UF)
(c) Nanofiltration (NF)
(d) Reverse Osmosis (RO).

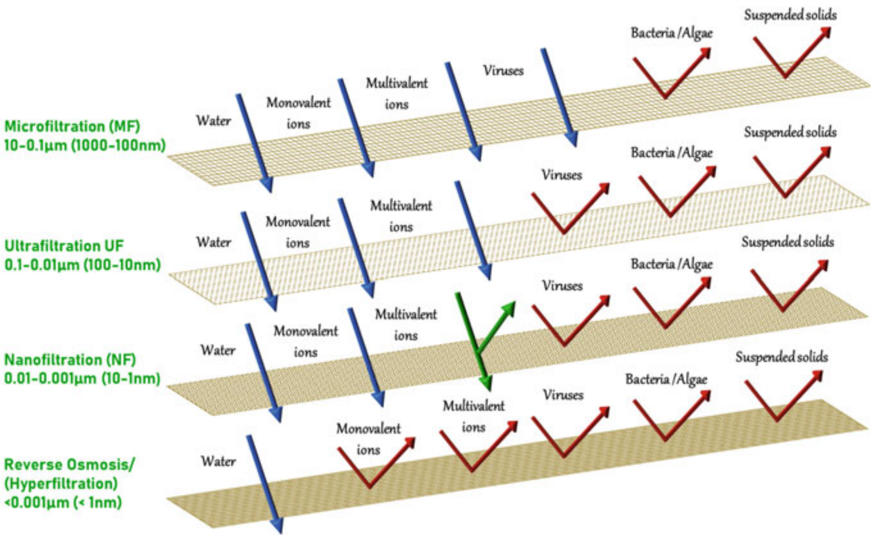

Fig. 4.1 Schematic representation of types of membrane filtrations techniques

4.2.1 Nanofiltration (NF)

NF has recently become one of the most widely used membrane purification processes in every purification technology with high practical value; especially for water purification. This may be due to the large number of chemical species separated by this process. Typically, for NF, high-energy-consuming operations involve the creation of sufficient pressure to reject the jump and the low molecular weight chemicals on the surface of the membrane. NF is the method of filtration having membrane with the nano size of pores as shown in Fig. 4.1. NF membrane has 1–10 nm pore and they are smaller than that used in microfiltration and ultrafiltration, however fair greater than that in reverse osmosis membrane.

4.2.2 Nanofiltration Membrane

NF membrane is the separation method of unwanted elements, ions, from mixture of waste sources. The process of NF membranes is parallel to reverse osmosis membranes having a thin-film composite layer (<1 μm) on upper most permeable layer (50–150 μm) for small ion selectivity. NF membranes can be allowing some monovalent salts to pass through however reject multivalent salts and uncharged solutes as shown in Fig. 4.1.

4.3 Graphene Oxide Based Nanofiltration Membrane

4.3.1 Graphene Oxide

Graphene contains 2D (two-dimensional) honeycomb structure, ultrathin thick nanomaterial that has undergone substantial study and development for commercial purposes. Its promise as separation material in form of membrane was first discovered over research on nanostructured graphene, that was used in desalination as molecular separation. Graphene membrane with nanoporous having significantly enhanced accessibility of water and refutation of salt than RO membranes, according to simulated studies. Conventional hammering or sophisticated techniques as like chemical etching, plasma etching, templating, and helium ion beam drilling can be used to manufacture nanopores. It is, however, difficult to achieve exact control over porosity, hole magnitude, and hole magnitude scattering. The expensive expense of scaling up film biosynthesis is also a constraint. A freestanding graphene oxide (GO) membrane, alternatively, is more viable alternate for desalination. This membrane is made up of a stack of graphene nanosheets that have been laminated together by GO deposition, casting, or vacuum filtration. water should be able to pass through the interlayer gaps of the multilayer GO laminates while ions are kept out. The average arrangement of GO coats in water, on the other hand, is superior to the diameters of most hydrated ions. Thermal or chemical reduction, as well as covalent interlink techniques, have been proposed to minimize spacing and boost stability in water. Changes in comparative moistness for the duration of drawing up the reaction, followed by physical detention of the coats, have recently been used to achieve precise regulator of interlayer arrangement. Development of GO has aided the development of innovative desalination processes, albeit these membranes are currently only useful in NF-range separations.

4.3.2 Manufacturing of GO Nanofiltration Membrane

For the duration of the filtration of GO solution GO membrane has been prefabricated (Dikin et al. 2007), spinning coating (Nair et al. 2012), drop liquid–air molding (Krueger et al. 2011), layer-by-layer (LbL) dip coating (Hu and Mi 2013), and the liquid air interface by evaporation self (Chen et al. 2009). By different prefabricate methods the filling structure of GO surface could be diverse (Tsou et al. 2015). Furthermore, filtration is the most traditional and uncomplicated approach. Through this procedure interspacing between the GO nanosheets become closer due to their perpendicular direction of the flow of driven hydraulic pressure induced by compression. By changing the volume of GO filtered the breadth of the membrane can be easily managed. It was observed that the consistency and the tinny structure of GO nanosheets were extremely correlated to filtration pressure (Tang et al. 2014). The highest selectivity depends on the uniform arrangement of the GO surface may directly be proportional to the pressure that controlled a proper deposition rate. Even though GO membrane and their microstructure are affected by the features containing the area of GO source and the characteristic of cross linkers or tiny grouts too. The structural, chemical and adsorption properties of GO Nanosheets could alter by the crucial modification of the degree of oxidation, which dominates numerous interlay arrangements and membrane characteristics (Morimoto et al. 2016; Lee et al. 2016; Amadei and Vecitis 2016; Wei et al. 2014a; Krishnamoorthy et al. 2013). To get an identical spreading of GO aimed at the synthesis of membrane and its functionalization of GO resource. In the case of GO structure, oxygen-containing moiety has ruling effects. Due to having the polar oxygen-carry functional group, and their good interaction with confident polar solvent molecules like water, ethylene glycol and so on (Paredes et al. 2008).

4.3.3 Functionalization of NF and Techniques

NF is a process which has the ability to reject the selective molecules and ions through the membrane which is functionalize through the modification of pressure given by to the membrane. The mechanism of transference strongly subject to the arrangement of membrane, to the interaction among the membrane and transferred molecules. NF (NF) is a solvent-separation technology with involvement of many features with reverse osmosis (RO). Unlike RO, that contains great elimination of essentially all liquefied solutes, NF offers great elimination of multivalent ions, as such calcium, and little elimination of monovalent ions, such as chloride. As per Fig. 4.1 there are several types of membrane filtration techniques are discovered for water purifications.

4.3.4 Mechanisms of GO Based Nanofiltration Membrane Separation

Nair et al. discovered that the channel of gases and liquids might completely block helping the permission of water vapour stimulatingly in GO membrane having millimicron thickness (Nair et al. 2012). They accredited the low abrasion of nanonetworks through the vacant interstice between the nano oxidized region of GO sheets for the fast transport of water vapour. Sun et al. confirmed that the typical polymeric membrane, showing GO membrane could have ultrafast moving of water too which is lesser than the water dispersion coefficient in the nano channel are 4–5 orders of size (Spitz Steinberg et al. 2017). Motivated by these discoveries, remarkable work on GO membrane have been piloted on the way to filtration. Figure 4.2 shows the applications of the GO NF membrane for the possible parting mechanism concerning the organic molecules, charged ions, and inorganic molecules as well. The large molecules could be separated by the GO membranes. Mi et al. introduced protocol to modify the nanochannel of GO internal arrangements for specific size rejection of ion and large molecules (Mi 2014). Hence, GO membranes with accurate interlayer spacing by injecting cross-linkers with a detailed size among the GO sheets could design for water cleansing, recycling of discard water, and pharmaceutical isolation. Furthermore, GO can be partly decreased to reduce its hydrated functional groups for a reduced inter-planer spacing. To the removal of oxygen-containing groups GO material can be reduced by either thermal tempering or chemical reduction (Pei and Cheng 2012). To the removal of the oxygen functionalities especially for the hydroxyl group thermal annealing is an uncomplicated and productive method (Gao et al. 2010). A rising in temperature could be ease the thermal reduction of GO. Though the utilization of energy in this method is in elevation and the oxidation degree is tough to switch. GO can chemically reduce at low temperatures using reducing agents such as hydrazine (N_2H_4), metal hydrides ($NaBH_4$), and which hydroiodic acid (HI) (Pei and Cheng 2012). The oxygen-containing group could have been targeted by these reducing agents, can control the reduction reaction. For the ion level separation and water permeability, reduced GO nano level networks could be more fascinating to reach (Gao et al. 2010). However, the modified GO could be by the reductant to achieve a nano-size membrane that is enriched in hydrophobicity. Further, the GO membrane could also have rejected the small molecules and charged ions (Nan et al. 2016; Lim et al. 2017). GO is negatively charged at a large pH scale caused by the deprotonation of the carboxylic groups at the termination of the GO nanosheets. The pristine GO membrane shows a high rejection towards divalent ions or organic anion molecules (Hu and Mi 2013; Han et al. 2013). Though GO membrane having the negatively charged characteristic could be altered. Zhang et al. designed highly positively charged GO basis membranes to enhance the rejection rate of heavy metal up to 95%, for these properties they took on amine-rich molecules along with hyperbranched polyethylene (HPEI) and PAMAM dendrimer (Zhang et al. 2015). With the different zone of GO sheets, tremendous selectivity can also be attained to remove some minor hydrate ions by the durable adsorption via interface of the ions (Zhao et al. 2011). The GO membranes tend to block the functional groups having oxygen atoms, it caused by the transition metal cation could be able to form the coordination interaction with oxygen containing functional groups (Sun et al. 2013). With sp^2 bunch of GO by cation interactions, likewise, the permeability rate of alkali and alkaline earth cations can also be remarkably reduced (Sun et al. 2014). The probable separation mechanism using GO-based NF membrane is depicted in Fig. 4.2.

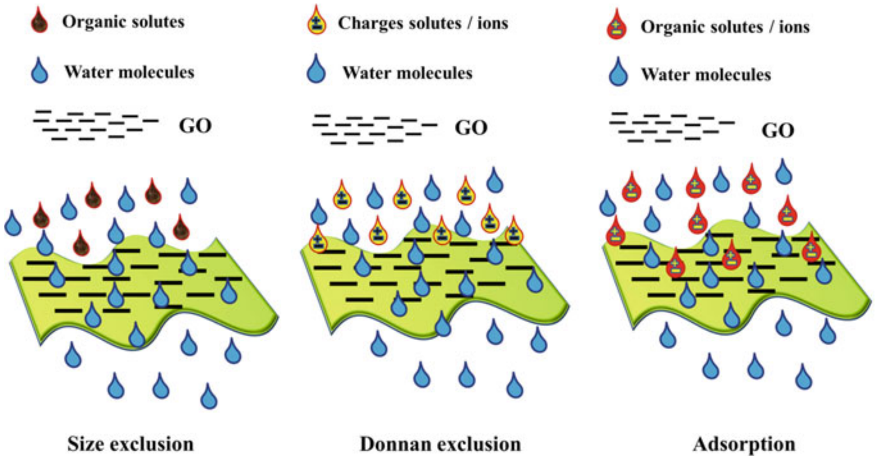

Fig. 4.2 Schematic showing probable separation mechanisms for GO based NF membranes viz., size exclusion, Donnan exclusion and adsorption. Reconstructed from Zhang and Chung (2017)

4.4 GO Nanofiltration Membrane Applications

Due to the interlayer spacing of GO sheet, pinholes, and imperfections on the nanosheets may also assist the water transportation (An et al. 2016). However the latest studies bare that the bulk viscous intemperance and spatially extended friction (Chen et al. 2017) responsible for the affected drop in water permeability clue by the oxygen functionalities existent in GO sheets (Montessori et al. 2016). The interface between water molecules and hydroxyl groups might slow down the flow rate due to the side sticking effect from the hydrophilic area of GO membranes and hydrogen (Wei et al. 2014a, b). A high consistency of GO membranes could reduce water permission too (Yang et al. 2013). The significance of the pristine GO membrane having 1.5 mm thickness can only demonstrate the fluidity of 1.04 L m^{-1} h^{-1} $bar^{-1}$of water (Aba et al. 2015). Likewise, without concession of the rejection of high-water fluidity, GO membranes have been designed to keep several strategies in mind including (1) Synthesis of ultrathin (<100 nm) size of the GO membranes on a porous support and (2) outline of further porous microstructures in the interior surface of the GO to improve the permeability and the performance of the NF. Han et al. produced ultrathin GO membranes with a thickness of 22–53 nm supporting on porous polymer through vacuum supported filtration for the purification of the water. The sequel ultrathin NF membranes own a high retention rate of 99% to organic dyes and high fluidity of 21.8 L m^{-2} h^{-1} bar^{-1} (Han et al. 2013). For the synthesis of the GO layer for NF, it only needed an infinitesimal amount of the GO materials due to its ultrathin characteristic. For the fast water conveyance without compromising rejection to organic solutes the accumulation of nanoparticles and carbon nanotube into GO surfaces has been stated to broaden the gaps of nano networks between GO surfaces (Xu et al. 2013; Han et al. 2015; Gao et al. 2015; Chen et al. 2016). Huang et al. described that to enrich the permeability of GO membrane to using of copper hydroxide nano edges the expiatory template with nano edge channelled GO membrane (Huang et al. 2013). Additionally, to the enrichment of water durability without compromising the elimination, the copper hydroxide nano edges were initially combined in to GO membrane and dissolve to form magnified water flow systems. Through the alteration of the microstructures of GO membranes, it could be substantively amended the maximum water permeability for NF applications. Subsequently, the tremendous forbearance of GO towards toxic environment and organic solvents, assemble the promising material in form of GO membranes for organic solvents NF. Aba et al. established that on ceramic hollow fibre surface of GO membrane with a cut off of molecular weight less than 300 Da and permission fluids of 3.97 L m^{-2} h^{-1} bar^{-1} and 6.35 L m^{-2} h^{-1} bar^{-1} for methanol and acetone respectively (Aba et al. 2015). In recent time, for ultrafast organic solvent nanofiltration have been evolved by negative or positively charged reduced GO membranes (Huang et al. 2016). Table 4.1. Shows the applications of GO membrane for the rejection ratio of different types of ions.

Molecular that are larger than 3.4 nm sizes of neutral solutes could be successfully reject by the membrane. Likewise, the smaller solutes with positive charge could also be rejected by surface functionalizing GO with HPEI. Subsequently these GO based membranes are stable in organic solvents, strongly acidic, alkaline and oxidative media, they have great potentials to be used in the pharmaceutical industry for value added separation. In summary, membrane flux demonstrated promising performance in NF in the form of GO membrane. With the support of membrane networks and altered with finely modified GO chemistry, the membrane selectivity could be well tuned. Unlike polymeric membranes, GO membranes are chemically stable, empowering their great potential in inorganic solvent purification.

4.5 Conclusion

In conclusion, the huge area of the planet presently relies on the purification technique to acquire drinking water, and large industries to contaminated water or remaining solvents. Thus, highly selective technologies to provides the treatment of wastewater are needed. The NF membrane is an efficient technology for water treatment and has been explored as a new upcoming generation material for the extreme efficiency membranes that is probable to resolve water crisis problems. GO membranes and modified forms of GO membranes are effectively utilized as filler in NF membranes and have improved performance in NF processes, with the decrease of energy consumption and, implicitly, costs as well as in many other applications with wastewater treatment. Also, removing heavy metals ions and organic molecules by adsorption of surface on the GO membrane. It is needed to researcher and experts would put more exertion on in the arena of nanomaterials and try to shrink the inclusive cost of the process. Concerns allied to the scale-up of the production of nanomaterials and their derivatives, and uses in situ, are also important features for

Table 4.1 Comparison of different GO based membranes for the rejection ratio of different types of ions

Sr. No	Name of GO based membrane	Application	Rejection % of		References
			Ion	%	
1	GO/PSF	Water purification	Na_2SO4	95.2	Lai et al. (2016)
			$MgSO_4$	91.1	
			NaCl	59.5	
2	GO/PSF	Water treatment	BSA	99	Lee et al. (2013)
3	GO/Pc	Water treatment	Mg (II)	92.6	Wang et al. (2012)
			Na(I)	43.2	
4	GO/H-PAN	Oil/water separation	–	99	Perreault et al. (2013)
5	GO/APAN	Oil/water separation	–	≥98	Zhang et al. (2017b)
6	GO/PEI/DPAN	Solvent resistant NF	–	96.8	Zhang et al. (2017a)
7	GO/PES	Water treatment	–	96	Zinadini et al. (2014)
8	GOF/Al_2O_3	3.5 wt% seawater desalination	–	>99.9	–
9	GO/PAN	Water purification	Sucrose	99	Hu and Mi (2014)
10	GO/Nylon	Water treatment	Organic probe molecules	>99	Akbari et al. (2016)
			Monovalent and divalent salt	30–40	
11	GO/PES	Humic acid removal	–	85.3–93.9	Wang et al. (2016)
12	OF-3/GO/PDA-PSF	Heavy-metal removal	Copper (II)	90	Rao et al. (2017)
13	GO/Al_2O_3	3.5 wt% seawater desalination	–	≥99.7	Xu et al. (2016)

upcoming progress. In addition, disadvantages of the nanomaterial themselves may require advance analysis and experts would put on more exertion in the arena of nanomaterials and try to shrink the overall cost of the process. Concerns allied to the scale-up of the production of nanomaterials and their derivatives, and uses rooted, are also important features for upcoming progress.

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Chapter 5
Nano-filtration Application in the Textile Industry for Wastewater Treatment

Mrinal Kanti Adak, Krishna Kumar, Ajit Das, and Debasis Dhak

Abstract The rapid growth of population with industrialization leads to a huge negative effect on the sustainability of the environment. Water scarcity through the pollution of the water body is one of the biggest problems for the survival of human civilization as well as life on the Earth. So, the development of water treatment technology is a great challenge to the scientific community for environmental sustainability in the upcoming days. As an energy-efficient technology, nanofiltration shows high importance for drinking water treatment owing to its reliability, integrity, longer cycle lifetime, and lesser cost. Textile wastewater is one of the main sources of pollutant water with hazardous dyes, inorganic salts with higher chemical stability. In this respect, nanofiltration membranes show high importance owing to their superior rejection rates to dyes and inorganic solids. This book chapter gives a powerful discussion about the role of nanofiltration in textile wastewater treatment, mechanistic pathways, different parameters activity, and limitations of this technique. The discussion also includes a future prospective way to recover the limitation with large-scale industrial application.

Keywords Nanofiltration · Wastewater · Textile wastewater · Dyes rejection · Salt rejection

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_5

5.1 Introduction

Life on the Earth is on the base of water. The increasing population, human activity leads to a reduction of the volume of freshwater resources (Anand et al. 2018; Das et al. 2021). In this situation, water management is very important for environmental sustainability. A lot of purification techniques like distillation, ion exchange, membrane filtration has been employed for wastewater treatment. But the challenges come from their higher effectiveness, energetically affordable with environmentally sustainable performance.

In this respect, membrane-based technology shows high performance in water management through drinking water production, desalination, reusability of water, and wastewater treatment (Anand et al. 2018; Lee et al. 2016). In the membrane technology, nanofiltration (NF) shows promising performance in terms of their pore sizes, porous framework, and rejection ability (Cheng et al. 2015; Wu et al. 2014). The selectivity, permeability of NF is depending on the above factors and is related to ion properties that are present in water flow. NF can discard waterborne pathogens, dissolved organic matter, heavy metals, metalloids and show a good impact on water management (Chon et al. 2013; Chon and Cho 2016). The membrane phase doesn't affect during the filtration process that "facilitates" it than other traditional separation techniques (Oatley-Radcliffe et al. 2017). Industries like beverages, textiles, food, dairy, and pharmaceuticals have used this technique to eliminate multivalent ions (Ang et al. 2020; de Souza et al. 2018; Lin et al. 2015a).

5.1.1 What is Nanofiltration?

Nanofiltration can be defined as the in-between process of reverse osmosis and ultrafiltration that contain nanometer (order 0.5–10 nm) size and 5–40 bar working pressure (García Doménech et al. 2020; Van der Bruggen et al. 2008). Generally, nanofiltration membrane enclosed with positively and negatively charged surfaces and these charged surfaces control the rejection of different multivalent ions (Ang et al. 2020). The generation of charge is due to the existence of dissociating functional groups at the surface or through the adsorption of charged species (Oatley-Radcliffe et al. 2017). Charged nanofiltration shows more facilities than reverse osmosis in terms of their selective operation and lower energy costs in oil and gas industries (Alzahrani and Mohammad 2014; Colburn et al. 2016). The presence of positively and negatively charged species in NF membrane deals with the separation efficiency for practical purposes. The separation mechanistic pathway of NF follows channel screening, solute membrane attraction, and the Donnan effect (Gu et al. 2019; Ren et al. 2017). According to Donnan exclusion, the membrane charge and charged ions decide the potential factor of NF membrane through high ion refusal ability (Colburn et al. 2016; Yaroshchuk 2001). The development of nanoscience technology leads to the variation of materials sizes that differ in their working performance. In this respect, the properties like chemical resistance, mechanical strength, antifouling are the best directions for the improvement of the NF technique. The main factor for application purpose depends on the nature of separation ability, broad pH variety, minimal power utilization, low operative expense, minimal toxicity, and flexible structure of nano filtrate (Anand et al. 2018; Subramani et al. 2014). The challenge of the nanofiltration technique is highly risen in the current decades due to increasing demand for high-quality drinking water, wastewater treatment, desalination, large-scale application (Van der Bruggen et al. 2008) etc.

The potentiality of nanofiltration techniques faces a challengeable hurdle in terms of their membrane stability, lifetime, fouling (like organic fouling, scaling, biofouling), and concentration of treated wastewater (Van der Bruggen et al. 2008, 2003). The membrane fouling comes from deposition or adsorption of organic or inorganic substances in the membrane surfaces that lead to a hazardous situation for membrane lifetime (Chon and Cho 2016; Chon et al. 2012).

5.1.2 Importance in Wastewater Treatment

Typical industrial wastewater contains phenolic organic compounds, ammoniacal solution, heterocyclic nitrogenous compounds, cyanides, ammoniacal solution, etc. (Kumar and Pal 2015). The numerous kinds of industrial progression and used chemicals lead to the generation of such types of hazardous compounds. In the textile industries, these processes are like sizing, weaving, scouring, bleaching, mercerizing, carbonizing, dyeing, and finishing. The use of extremely colored organic dyes and insect proofing through pesticides also causes the generation of non-biodegradable pollutants during wet processing through the rejection of large amounts of water (Aouni et al. 2012). Inorganic salts (NaCl, Na_2SO_4, etc.) participate in the dyeing process leads to a high amount of salt rejection through wastewater. According to a reported study, for 1 kg of textile production two-hundred-litre water is required that indicated a massive amount of wastewater generation (Cardoso et al. 2016). Among all the chemicals, synthetic dyes or pigments are vastly applied in the textile industries (~7×10^5 t annually (Holkar et al. 2016; Long et al. 2020)) and are responsible for the discharge of hundreds of thousands of tons in every year through wastewater (Cao et al. 2020; Jin et al. 2007).

In wastewater treatment, different methods like adsorption, coagulation, wet oxidation, and advanced oxidation show importance but limitation comes from high cost, complicated technique, and environmental aspects. In this respect, biological treatment show highly prospective in terms of their environment-friendly techniques but reality faces difficulty through toxic contamination, sensitive plants, the possibility of large-scale application, slow process (Kumar and Pal 2015). Again, causes of serious pollution throughout the world lead to stringent discharge regulation and high cost of water that favor the advanced treatment process. In the recovery of pigments or dyes, process like activated carbon or resin adsorption is important but not sufficient. The use of the traditional decolorization technique disfavored the reusability of materials and change their chemical properties through adsorption or oxidation (Cao et al. 2020; Roy et al. 2020). At this point, membrane-based nanofiltration technology show high utility based on high degree of separation, low energy consumption, mild condition, no chemical additives, and reuse of the auxiliary chemicals with the production of purified water (Aouni et al. 2012; Cao et al. 2020). The molecular weight cutoff of NF (100–2000 Da) gains extra facility for the pigment/dye recovery purpose due to pigment/dye molecular weight range fall in this region (Cao et al. 2020). The applicability of the NF membrane also comes from the absence of electrostatic interactions that keep intact flux rates constant in presence of organic pollutants (Chidambaram et al. 2015).

This book chapter discusses the use of the nanofiltration technique and its applicability in textile wastewater treatment and its further development. The effect of modification of NF membrane and its charge decides the efficiency of the filtration techniques. The parameters like nature of dyes, salt concentration, pH medium, temperature etc. are also briefly discussed here.

5.2 Materials for Nanofiltration

Generally, the NF membrane is prepared by three-layer with specific features i.e. polyester support web, microporous polysulfone interlayer, and ultrathin polyamide barrier at the top (Majamaa et al. 2011; Ong et al. 2014). The surface charge of a polyamide membrane depends on the pH values (vs. iso-electric point (IEP)) and depending on it organic molecules are interact with the surface. Lower pH values than IEP causes interaction of negatively charged organic molecules through substance blocking and flux decline. Positively charged organics follow the same at higher pH than IEP (Chidambaram et al. 2015). NF membranes are amphoteric that determine through IEP and most of the NF membranes are negatively charged. The deprotonation of carboxyl groups causes the generation of negative charge at membrane surface where protonation of amine functional group is responsible for the positive membrane surface charge (Ernst et al. 2000). In the fractionation of dye and salt from wastewater, the loose-nanofiltration technique also shows good result in terms of their high effectivity (Li et al. 2018). The loose NF membrane is mainly organized through immersion precipitation, interfacial reaction, and layer-by-layer assembly (Zhang et al. 2019). The high activity of loose NF membrane work on size exclusion and Donnan effect leads to good retention results for both dye and salt. The approaches like coating, incorporation, blending, vacuum draw is used for the construction of loose NF membrane (Long et al. 2020). Cationic polymer polyethyleneimine is used for the generation of the functional polymeric layer in NF membrane that exhibit high stability, solvent resistance, antifouling with hydrophilicity characteristics. A lot of techniques like cross-linking, phase inversion, interfacial polymerization, dip-coating, layer-by-layer has been used for the fabrication of NF membrane (Li et al. 2018; Sun et al. 2012). The fabrication of positively charged NF also done through the deposition of dopamine and polyethyleneimine. In the simultaneous salt and dye recovery process, hybrid loose NF with bipolar membrane electrodialysis (BMED) show significant result for the waste extraction. The fractionation of dye and salt mixture through diafiltration by NF membrane exhibit good productivity and applicability in large scale application (Lin et al. 2015b). In this respect, loose negatively charged NF membrane prepared by the chitosan-montmorillonite nanosheet into polyethersulfone show significant result (Zhu et al. 2015). The modification of loose NF with electrodialysis show some light in the obstacle of dye cake layer formation during textile wastewater treatment (Ye et al. 2020). Though a lot of facility presence in loose NF but limitations come through presence of negative charge at pore walls, less study in real wastewater system, and sophisticated preparation process (Long et al. 2020). The higher surface area of hollow fiber configurated NF facilitates in wastewater treatment through the advantages of high surface area, permeate channel, and self-supporting structure (Ong et al. 2014). The effectivity of nanofiltration show higher efficiency in addition to forward osmosis (FO) and the resulted FO-NF system was used for the treatment of coke-oven wastewater. In the experiment, polyamide composite membrane was able to remove cyanide, phenols, thiocyanate, fluoride, sulphate, phosphate, and magnesium under optimized condition from a real wastewater plant (Kumar and Pal 2015). The incorporation of nanoparticle in membrane is efficient for the improvement of flux, antifouling and salt rejection characteristics. Lakhotia et al. used CeO_2 nanoparticle with polyethersulfone porous support and polyamide thin film for the preparation of hybrid NF membranes. The hybrid NF shows high activity than pure polyamide and capable to reject greater than 90% salt with antibacterial and antifouling characteristics. The membrane shows high salt rejection effectivity for low valence cation and high valence anion (Lakhotia et al. 2018). Layered stack formation with graphene oxide (GO) in NF membrane is an important possibility for higher effectivity. The stability of layered structured of GO is enhanced by the incorporation of cross-linking reagents (Xu et al. 2020). The use of covalent organic framework, metal organic framework, layer double hydroxides for hybrid NF formation also show some interesting result (Zhang et al. 2021; Zhao et al. 2018).

The main challenges in the NF membrane come from flux decline and fouling that should be minimized through the variation of different process parameters. In this regard, the correlation should be drawn between NF membrane characteristics and separation mechanism for better filtration performance (Thamaraiselvan et al. 2018).

5.3 Textile Wastewater Treatment

In the textile industry a huge amount of wastewater has been released during dyeing process (dye bath water) and washing process (wash water) to the directly in the natural water sources (Aouni et al. 2012). As a result, a huge quantity of organic, inorganic, and solid pollutants causes negative impact on the environment. The effectivity of NF membrane for wastewater treatment depends on several factors like solute–solute or solute-membrane interaction, feed properties, nature of dyes, and operating conditions (Cao et al. 2020) etc.

5.3.1 Nanofiltration in Textile Wastewater Treatment

Nanofiltration membrane NF200, NF270 is used for the treatment of black, blue and red EVERZOL dyes at 10 pH with the addition of certain amount of sodium chloride. The permeate flux depends on the molecular weight of the dyes and increases proportionally with the pressure loss. The presence of sulfonate groups in the dyes vastly related with the negatively charged membrane that reflected in the large conductivity retention rates (>85%). This nanofiltration method is capable for >95% COD and colour retention during the treatment of real wastewater from Spanish textile industry (Aouni et al. 2012). NF270 membrane is used for the investigation of dye molecules and membrane interactions at different pH ranges. Positively charged dyes Acid red 87, Direct blue 53, Acid black 1 and negatively charged dyes Azure A, Basic blue 9 and Basic green 4 were used to check the membrane selectivity. The result shows that strong sulfonic acid covering dyes not absorbed where weak carboxylic acid show high flux decline and membrane fouling properties at acidic pH range. Positively charged Azure A and negatively charged Acid red 87 show 51.17 and 48.42% flux decline at alkaline and acidic pH respectively (Chidambaram et al. 2015).

Positively charged NF membrane PA6DT-C has been used for the separation of positively charged dye methylene blue from house wastewater. The membrane shows 98% rejection ability at 5 bar pressure with ~17 LMH bar^{-1} membrane flux (Cheng et al. 2012). In a comparative study between the performance of reverse osmosis and NF membrane Liu and coworkers has been used BW30 and NF90 respectively for biologically treated textile wastewater (Liu et al. 2011). The higher porosity of NF membrane leads to better performance with higher permeate flux and severe flux decline than other rougher membrane surface (BW30). The effectiveness is also compared in terms of membrane fouling, and COD removal rate. Chitosan based fabricated NF membrane with tunable thickness is used for the treatment of salt/dye mixture. The membrane is effective for the removal of dyes and the rejection rate increases with membrane thickness. In the rejection process the membrane predominantly prefer higher physical size dyes and show higher retention characteristics for same charged dyes (Long et al. 2020). The positively charged polyamide-imide based NF membrane show robust characteristics and follow Donnan exclusion effect for the rejections of salts that follow the order as $MgCl_2 > NaCl > MgSO_4 > Na_2SO_4$. In the dye rejection process the lower molecular weight dye shows higher tendency for the reduction of flux (Ong et al. 2014). Polysulfone/polyethersulfone supported thin-film NF membrane is used for the rejection of dye desalination. The negatively charged surface characteristics are eligible for >99.9% rejection of anionic dyes reactive brilliant blue X-BR and acid red B. For salt rejection, the negatively charged surface NF membrane follow $MgSO_4 > Na_2SO_4 > MgCl_2 > NaCl$ (Wei et al. 2013). The pore size of different NF membrane decides its rejection ability to the corresponding dye or salts. In this point, molecular weight cutoff values decide the range of molecular weights for dye selection to the corresponding membrane (Thamaraiselvan et al. 2018). Catechol and polyethyleneimine (PEI) co-deposition on NF membrane show good performance on the rejection of dye molecules, salt, and heavy metals from textile wastewater. This positively charged membrane surface prefers to reject cation with higher valence (Xu et al. 2016).

Cation polymer PEI layer on hydrolyzed polyacrylonitrile and in-situ phosphorylation with inositol hexaphosphate (IP6) with cross-linked Fe(III) leads to loose NF membrane. This membrane removes >99% methyl blue, congo red, and acid fuchsin with 11.54, 10.96, and 11.76 $\mathrm{Lm}^{-2}\ \mathrm{h}^{-1}$ fluxes respectively at 0.2 MPa. The salt rejection capacity is relatively much lower than dye molecules. The rejection value is higher for $MgCl_2$ (30.51%) and lower for Na_2SO_4 (5.89%). The presence of cross-linking favors the formation of dense selective active layer where phosphate groups are connected through PEI segments via electrostatic interaction (Li et al. 2018). The high dye and low salt removal capability significant for the reuse of the salt. The loose NF membranes Sepro NF6 and NF 2A also show this feasibility with less than 33.3% salt rejection and greater than 99.6% dye rejection. In the diafiltration technique these NF membranes show 95.51 and 96.62% desalination capacity (Lin et al. 2015c). Simultaneous dye and salt separation causes the formation of dye cake layer with cake-enhanced concentration polarization. These types of factors generation reduce the flux of operating NF membrane (Table 5.1). According to Jone-Dole equation (Zhang 1996), the viscosity of salt (NaCl) is increased with the rise of its concentration and show negative effect on membrane flux. In the flux value determination concentration polarization also show an important factor through variation in osmotic pressure. The pore blocking and dye deposition factors also take part in flux value determination (Lin et al. 2015a). Vergili et al. performed a techno-economic analysis of a ZLD (zero liquid discharge) system for textile dye-bath and wastewater treatment and reported that various configurations (including UF/tight NF, loose NF/tight NF, loose NF/RO, and UF/tight NF/RO) were all technically feasible and economically viable. Two methods were used for the evaluation of the profitability of using NF for dye-bath effluent reuse (Vergili et al. 2012).

5.4 Different Parameters Effect on Nanofiltration

The several parameters directly related to the performance of a membrane, their reusability and lifetime.

5.4.1 Nature of Dyes

In NF membrane, the rejection of dye molecules depends on its molecular weight and as well as their charged characteristics. A negatively charged NF membrane

Table 5.1 Textile dyes removal through nanofiltration membrane

NF membrane	Pollutant	Conditions	Result	References
NF200, NF270 (polyamide)	Black, blue and red EVERZOL dyes with NaCl	pH range 3–10, pressure 3–12 bar	>90% colour retention rate	Aouni et al. (2012)
	Wastewater from Spanish textile industry		>95% COD and >98% colour retention	
PA6DT-C	Methylene blue	20 ± 2 °C, pH < 8.0, pressure 5 bar	98% rejection	Cheng et al. (2012)
NF270	Acid red 87, Direct blue 53, Acid black 1, Azure A, Basic blue 9 and Basic green 4	2 h operating condition with 2000 ppm NaCl, pH = 3, 7, and 10	48.42% flux decline for negatively charged dye molecule at acidic pH	Chidambaram et al. (2015)
Fe (III)-phos-(PEI)/HPAN membrane	Methyl blue (MB), congo red (GR), acid fuchsin (AF) and crystal violet (CV)	Operating pressure 0.2 MPa, pollutant concentration 0.1 g/L	99.92, 99.53, 98.99, and 92.86%	Li et al. (2018)
Sepro NF6 and NF 2A	Direct red 80, Direct red 23, congo red	Operation pressure of 6 bar and cross flow rate of 55.5 L h^{-1}) All experiments were carried out at 251 C	>99%	Lin et al. (2015c)

(continued)

surface will hindered the negatively charged dyes through electrostatic repulsion effect that leads to high rejection value and vice versa (Zhang et al. 2019). Higher dye concentration causes reduction of fluxes through higher fouling with the generation of higher osmotic pressure (Ong et al. 2014). The charged factor on dye decides

Table 5.1 (continued)

NF membrane	Pollutant	Conditions	Result	References
NF90	Textile effluent	Crossflow velocity of 0.40 m/s, operating pressure of 0.52, 0.80, 1.10, 1.32 MPa	Colorless, remove COD and BOD	Liu et al. (2011)
Chitosan based NF membrane	Methyl viologen, methylene blue, orange G, brilliant blue G250, rose Bengal, and methyl blue; salt $CaCl_2$ and $MgSO_4$	Operation pressure 4 bar. Pollutant concentration 1000 ppm	>99% dyes rejection; 94.8% $CaCl_2$ and 87.8% $MgSO_4$ rejection	Long et al. (2020)
Polyamide-imide based NF membrane	$MgCl_2$, NaCl, $MgSO_4$, Na_2SO_4 salt and Reactive blue 19, Reactive black 5, Reactive yellow 81	Operation pressure 1 bar	>98% dye rejection	Ong et al. (2014)
NF90, NF270, MPF34, MPF36, TS80, XN45	Acid red 87, Acid black 1, Basic green 4, NaCl	50 mg L^{-1} dye and 2000 mg L^{-1} NaCl solution	Acid red 87 100% remove at pH 3 in XN 45 and MPF 36	Thamaraiselvan et al. (2018)
Polysulfone/polyethersulfone supporting NF membrane	Brilliant blue X-BR and acid red B, $MgCl_2$, NaCl, $MgSO_4$, Na_2SO_4	Flow rate of 1.1 L/min, 25.0 ± 1.0 °C under 0.4 MPa	96.20% $MgSO_4$ and >99.9% anionic dye rejection	Wei et al. (2013)

its hydrated radii that determine the separation factors of NF membrane. The negatively or electroneutral charged dye molecules with higher hydrated radii show better rejection rate (Long et al. 2020).

5.4.2 *Salt Concentration*

The enhancement of salt concentration shows negative impact during dye removal through NF membrane. Though, higher molecular weight dye rejection don't much effect by salt concentration due to Sieving mechanism. The reduced rate of dye removal at high salt concentration may be caused by the loss of electrostatic interaction of membrane ions and generate 'shielding effect' of NF membranes (Lin et al. 2015c). The salt concentration sometimes leads to swelling of membranes that causes expand in pore size. Such type of pore enhancement assists the passing of dye molecules through the surface (Lin et al. 2016).

5.4.3 *Effect of pH*

The performance of membrane depends on the pH of the wastewater. Most of the lab-scale based studies use acidic, neutral, and alkaline feed solution to investigate their membrane superior characteristics. In alkaline medium, the amide groups of NF membrane become hydrolysed and responsible for the large pores formation with enhancement of dye rejection rate (Shao et al. 2013). Again, sometimes the pH values of dye decide the fate of membrane surface during separation. As an example, the deposition of negatively charged dyes on positively charged membrane causes foul in the membrane and reduce the flux (Ong et al. 2014).

5.4.4 *Effect of Temperature*

The increase of temperature generally enhances the flux through water viscosity reduction, and increment of membrane volume (Ong et al. 2014). Generally, inorganic NF membrane show higher mechanical strength and stability at high temperature than organic NF membrane (Cao et al. 2020).

5.5 Limitations

(i) A lot of challenges like membrane lifetime, fouling, separation selectivity etc. are still pending for effective treatment through NF membrane.

(ii) Minimization of fresh water should be used during diafiltration process.
(iii) There are also some problems with NF methods like production of secondary waste, insufficient dye rejection and energy dissipation of hot process streams. For the reduction of NF fouling, pretreatment processes like coagulation/flocculation, ozonation and adsorption have been used.
(iv) Sometimes uneven surface porosity, membrane density, uneven charge distribution effect the rejection mechanism and selectivity of NF membrane.

5.6 Future Prospectus and Conclusion

The book chapter discuss about the use and applicability of NF membrane in the purpose of wastewater treatment for better future prospectus. A lot of study has been done on the improvement of NF membrane according to their performance on real wastewater treatment with large scale application, low cost, easy applicability, and environmental suitability. Though a lot of research has been done on this purpose but real wastewater treatment with raw actual concentration is still rare. The work still is searching for high stability membrane at the different pH, temperature variation, and hazardous conditions. The membrane fouling, selectivity, cleaning, reusability, green synthetic process should be followed in terms of their environmental susceptibility and friendliness. The details mechanistic pathway may help design of the NF membrane. In this regard, the simultaneous development of practical and theoretical research may take a new direction for the desired characteristics membrane.

Acknowledgements MKA thanks Indian Institute of Technology Delhi, India for a Post-doctoral fellowship (IITD/IES1/2021/329/72). KK thanks to UGC India to provide financial assistant in form of UGC-JRF/SRF [Award Number 20/12/2015(ii)EU-V].

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Chapter 6
Dye Removal from Industrial Water Using Nanofiltration Membrane

Pragati Chauhan, Mansi Sharma, Sapna Nehra, Rekha Sharma, and Dinesh Kumar

Abstract Water pollution and depletion have developed into global problems over the years, causing damage to the existence of aquatic and people. Water pollution by dye-containing apparel businesses is now recognized as a common wastewater cause. Such industrially polluted water reaches agriculture and consumes the water immediately, causing irreparable human and ecological damage. Consequently, the most appropriate strategy for protecting waterways is the advancement of various sectors to reuse wastewater. A few ecologically acceptable solutions often employed in practical uses are membrane-based nanotechnology. The membrane-assisted remediation technique shows attractive benefits such as power savings, absence of undesired materials, economical and eco-friendly, uninterrupted filtration, and efficiency. Reverse osmosis, nanofiltration, and ultrafiltration are examples of these techniques. Nowadays, ultrafiltration is increasingly vital due to its efficacy in removing contaminants from wastewater. This chapter introduces water pollutants, mainly dyes, and various membrane filtration technologies. This chapter also covers recent membrane filtration methods, their process, application, and dye removal challenges.

Keywords Dye · Removal efficiency · Nanofiltration · Remediation · Nanomembrane · Textile wastewater

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_6

Abbreviations

3D printing	Three-dimensional printing
BSA	Bovine serum albumin
CA	Cellulose acetate
CNTs	Carbon nanotubes
DWCNTs	Double-walled carbon nanotubes
EDTA	Ethylenediamine tetraacetic acid
EDX	Energy dispersive X-ray analysis
FT-IR	Fourier Transform Infrared Spectroscopy
GO	Graphene oxide
IP	Interfacial polymerization
LBL	Layer by layer assembly
MF	Microfiltration
MMMs	Mixed matrix membranes
MWCNTs	Multi-walled carbon nanotubes
MWCO	Molecular weight cut-off
NC	Nanocellulose
NF	Nanofiltration
PA	Polyamide
PAA	Polyacrylic acid
PAN	Polyacrylonitrile
PA-TFN	Polyamide thin film nanocomposite
PC	Polycarbonate
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEI	Polyetherimide
PES	Photoelectron spectroscopy
PS	Polyethersulfone
PET	Polyethylene terephthalate
PIP	Piperazine
PP	Polypropylene
PSD	Particle size distribution
PSF	Polysulfone
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
RO	Reverse osmosis
SEM	Scanning electron microscope
SLA	Stereolithography
SNIPS	Self assembled and nonsolvent induced phase separation
SWCNTs	Single-walled carbon nanotubes
TFC	Thin-film composite

TFN	Thin-film nanocomposite
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TIPS	Thermally induced phase separation
TMC	Trimesoyl chloride
TPC	Terephthaloyl chloride
TPP	Two-photon polymerisation
UF	Ultrafiltration
XRD	X-ray diffraction

6.1 Introduction

Several difficulties confronting humanity nowadays are the worldwide water dilemma (Ismail et al. 2020). The fabric business used much water, with each kilogram of cloth using around 60–100 kg for the dyeing and cleaning procedure (Kang et al. 2020). As a result, the textile sector has become one of the leading wastewater generators. However, although this wastage is challenging to treat, several textile businesses discharged it into the external atmosphere. The quantity of water waste created by fabric manufacturing is estimated at between 2 and 180 L of effluent for each kilogram of fabric output (Wang et al. 2021a, b). Polymers, graphics, meals, printing and fibers, fabrics, medicines, and paintings are a few industries that employ dyes. The business consumes a huge amount of water and generates industrialized effluent that contains harmful cancerous chemical dyes and elemental compounds. They had a substantial impact on marine ecology and public safety. Thus, they had to be eliminated from industrial wastewater (Wang et al. 2021a, b). Different therapeutic procedures, like coagulation-flocculation, adsorption, biological treatment, membrane filtering, and oxidation, are used to eliminate the colors inside the industrial wastewater. Traditional approaches such as oxidation, adsorption, and biological treatment have drawbacks. For instance, the challenge of recovering important elements like dyes and elemental compounds is a time-consuming procedure and has uncontrolled consequences (Lin et al. 2020). Membrane filtering methods such as nanofiltration (NF), microfiltration (MF), reverse osmosis (RO), and ultrafiltration (UF) have various advantages, such as prototypes, durable and resistance, superb performance, selectivity, and ecological. Numerous membrane varieties depend on pore dimensions, including NF, MF, RO, and UF. The pore width of the MF membrane ranged from 0.1 to 10 m, and the pore width of the RO membrane ranged from 10 to 150 m. The pore width of the UF membrane ranged from 0.1 to 1 nm. The UF film performed well for big molecule parting but not for small separation. Because RO film has the lowest pore width related to UF, MF, and NF, it better separates tiny molecules from ionic molecules. Although RO may accomplish effective dye removal, the RO process's pressure limits it's probably due to the high expense of employing high-pressure (Khajavian et al. 2020). Because NF is classified among UF and RO. It offers considerable benefits of that kind as low osmotic pressure gradient, higher permeate flux, multivalent salt retention, and the ability to reject organic components with molecular weights ranging from 200 to 1000 Da (Oulad et al. 2020). Moreover, the working pressure of the NF membrane is not as large as the RO membrane, which is around 2–40 bar (Jin et al. 2020). Although NF retaining is not as excellent as RO, NF is regarded additionally favourable since its running rates are cheaper than RO due to the greater the operational strain, the greater the working expense. The NF membrane rejects dyes better than the UF membrane and has greater water flow than the RO membrane. This has perfect separation even though covalently bonded ions and chemical dye ingredients contribute to water pollution dye inorganic salts (e.g., Na_2SO_4 and NaCl) and organic. Such features harm dye or salt specificity because of the NF membrane probably barely isolates the dye/salt mixture separately (Guo et al. 2021). The large rejections of dyes and inorganic salts raise osmotic pressure and, as a result, operational energy usage. A flexible NF membrane with hole sizes between NF and UF was created to address these issues. It has rather open active layers; hence it has higher water flow than a standard NF membrane while also having strong salt permeability and dye rejection. Coating, layer by layer method, and interfacial polymerization (IP) technologies are accessible for creating the flexible NF membrane. Polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyetherimide agarose, chitosan, alginate, polyimide, polysulfone (PSF) (Lin et al. 2020; Dlamini et al. 2021; Geravand et al. 2021; Khajavian et al. 2020) are popular industrial polymers utilized for NF membrane construction. Polyetherimide (PEI) is now among the polymers capable of supporting and producing larger NF membranes. This research aims to build NF membranes using PEI to clean fabric wastewater, specifically to provide maintainable treated wastewater that complies with Indonesia's eco-engineering development. Along with its non-toxic, reusable, and biodegradable qualities, cellulose is now frequently employed to create and use novel materials. Several chemical and physical processes can be used to transform cellulose into nanocellulose (NC). NC is more appropriate for significant contaminant treatment than micro-size substances due to their highly effective total area and nano-size (Shiohara et al. 2021a, b). However, being the most prevalent basic resource in the environment, cellulose has several benefits, such as plentiful basic material resources, processability, and low price, contributing to its extensive possibilities in membrane filtration techniques. A variety of reasons have contributed to the increased interest in employing membrane technologies to produce drinking water. The most significant is the tendency toward increasingly rigorous drinking water quality rules, which membrane technologies can only satisfy cheaply. For several years, the considerably large development and maintenance expenses of membrane plants comparison to standard plants have impeded the rapid deployment of MF in the water supply sector, where the advanced tracking of the product is quite low. However, due to significant initiatives, standardization, and growth in module, membrane, and membrane system manufacturing capacity, which enable lower apparatus prices and enhance the efficiency of the film procedures. Another reason for the growing utilization of membrane technology in water treatment is that membrane treatment is less expensive than traditional treatment. So, unwanted elements can be eliminated with just one treatment process. However, available treatments would need a few stages (Abdel-Fatah 2018). This is especially the case for NF, which eliminates organic and inorganic molecules in a single step. This chapter will discuss recent different NF methods, their procedure, application, and challenges for dye removal. Furthermore, we will also discuss conventional membranes and nanofillers in pressure-driven membrane processes.

6.2 Nanofiltration Membrane

NF films are a modern pressure-driven membrane between UF and RO membranes (Long et al. 2020). The title "nanofiltration" was invented by Filmtec Company for the characterization of "loose RO" or "tight UF" membranes having holes larger than roughly 1 nm in diameter. The following estimates (Abdel-Fatah 2018) are used to define the NF layer:

(1) Reasonable channel of ionic species (>30%) throughout the surface.
(2) Porous sizes of 2 nm.
(3) Unbiased species molecular mass snip in the 150–2000 Da spectrum.
(4) Substantial refusal of divalent ions (>90%).
(5) Refusal of beiges and favourable species depending on shape and size.

The improved achievement of the NF membrane, like lower power usage, vascular permeability, and lower investment price, make it attractive in a range of segments, such as ocean and saltwater water recycling, process water, wastewater treatment, pre-treatment of desalinated water, as well as the liquor, meals and medicinal industries (Li et al. 2020a, b). The NF membrane is a promising candidate for brackish distillation, and sea facilities that require highly high saline rejection are required and acceptable. The salt rejection of NF films ranges between 10 and 90%, whereas RO membranes may reject up to 99.5% (Long et al. 2020). The regulating processes of NF membranes include a complicated mix of the Donnan effect, solution diffusion, electromigration, and dielectric exclusion (Li et al. 2020a, b). NF membranes in interaction with aqueous fluids of varying pH have a charged surface due to the adsorption of charged species. The breakdown of surface functional groups from an aqueous solution results in electrostatic charge repulsion between the ionic species and membrane surface (e.g., sulfonic acid and polymeric contain carboxylic groups). Different methods for dye removal from wastewater are shown below in Table 6.1.

6.3 Nanocomposite Membranes

Nanoparticle's membrane is a unique class of filtered membranes made comprised of nanoparticles embedded in a polymeric substrate. The selection of materials for

Table 6.1 Different methods for dye removal from wastewater

Strategy	Process	Advantages	Disadvantages	References
Coagulation/flocculation	On the addition of coagulants or flocculants, molecules aggregates	Low cost, simple operation method, small land occupation	Potential secondary pollution, low efficiency, sludge generation	Zeng et al. (2020)
Electrocoagulation	Metal cation flocculants enhanced the molecule aggregation	Excellent dye removal	Less electrode reliability, high anode, and energy consumption,	Nawaz et al. (2021)
Adsorption	Noncovalent interaction between compact backing as well as dye	Inexpensive, good treatment of several dyes and efficient	Regeneration or dumping, mud generation, expensive adsorbent discarding	Rahimi et al. (2021)
Bacterial bioreactors	Microparasitic deprivation	Naturally friendly, mild operating conditions	Long degradation time, low biodegradability for azo dyes, vulnerability to dye harmfulness	Karisma et al. (2017)
Advanced oxidation	Producing free radicals by ozonation, Fenton reagents etc.	Greater efficiency of both insoluble dyes and soluble	Harsh reaction conditions, costly reagents,	Korolkov et al. (2018a, b)
Membrane filtration	Removing dyes based on charge effects and size, by separation films	Environmentally friendly, low cost, continuous, simple operation and high efficiency	Low separation choosiness of multivalent salts/dye, exchange between confinement and permeability and membrane fouling	Korolkov et al. (2018a, b)

particular separating procedures is a difficult task. Mechanical integrity under operating conditions and longevity, isolation, and manufacturing productivity are significant requirements in general. The overall goal is to impart the operational capabilities of nanoparticles to the polymers. Metallic nanomaterials (such as Al_2O_3 and TiO_2), e.g., increase the temperature and physical durability of polymeric films and the permeation flux (Yang et al. 2020a, b). Therefore, injecting adsorbents boosts the membrane's hydrophilicity, increasing its wettability. To improve fouling resistance, photocatalysts (e.g., bimetallic nanoparticles and TiO_2) and antibacterial (e.g., nanosilver and CNTs) nanomaterials are commonly used (Qaseem et al. 2020).

6.4 Conventional Membranes

Membranes function as a barrier layer, preventing some materials from passing through. Polymeric and ceramic membranes are two types of conventional membranes shown in Fig. 6.1. The two classes of conventional membranes listed below are noteworthy.

6.4.1 Ceramic Membranes

Inorganic resources like zirconium oxides, alumina, silicon carbide, titanium, or glassy substances are utilized to create ceramic membranes. Melting temperature is higher in ceramic membranes than in polymeric membranes. Ceramic membranes typically feature a three-layer sandwich construction. The base layer is the initial coating, the transition coating is the middle or second layer, and the functional coating is final. As the term implies, the layered structure provides good mechanical support to the film structure. The alteration film prevents units from going over the film. The functional coating is a key component for identifying the membrane. The membranes system is categorized into several categories based on this layer, such as MF, UF, and NF (Yang et al. 2020a, b; Qaseem et al. 2020). Ceramic films are created with the sol–gel process and surface modification techniques.

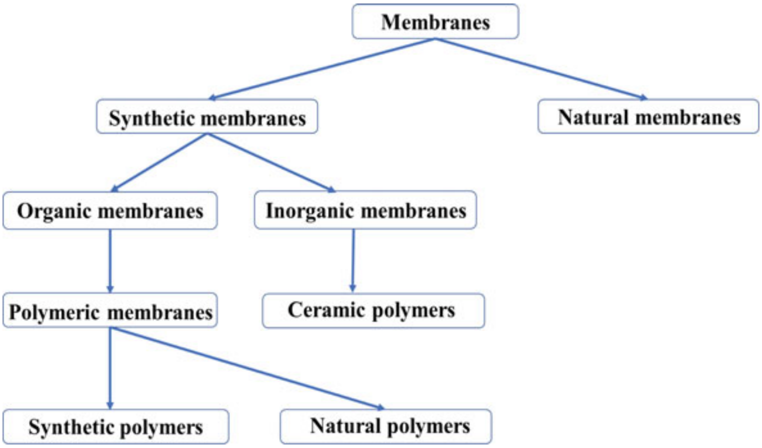

Fig. 6.1 Classification of conventional membranes

6.4.2 Polymeric Membranes

Polymeric membranes are the company's favorite option due to their low cost and versatility. The most significant property needed in polymeric membranes is a preference for a specific component. Controlling the pores of membrane materials during production is similarly simple. The installation necessitates a high degree of flexibility and a limited area. Every time, we must select a polymer-based on the task at hand. Polymeric membranes are commonly composed of cellulose acetate (CA), polyimide, polyacrylonitrile (PAN), polyethylene (PE), polycarbonate (PC), polytetrafluoroethylene (PTFE), and polypropylene (PP). In general, polymers such as polyvinylidene fluoride (PVDF) UF membranes are incorporated with nanomaterials such as carbon nanotubes (CNTs) or metal/metal oxide to increase polymeric membrane production (Zeng et al. 2020).

6.5 Pressure Drove Membrane Method in Nanofillers

One of the most recent uses of nanomaterials is its inclusion into membrane materials to improve membrane properties such as selective transparency, wettability, and durability. The distinct chemical and physical features of nanoparticles have spurred attention in investigating the creation of nanomaterials for specialized magnets, optically, catalysis, and electronic applications. The integration of different nanofillers inside polymeric membrane has multiple benefits, including increased hydrophilic nature, suppression of foulants and pollutant build-up, improvement in thermomechanical characteristics, and increased membrane removal rate. Metallic nanoparticles, like silica, titania, carbon nanotubes, ceramics, carbon molecular sieves, zeolites, and metal–organic framework are often used as nanofillers in nanocomposite membranes. Polymer polymers that were widely used included PSF, polyphenylene oxide (PPO), polyethersulfone (PS), polyesters, polyimide (PI) and PEI (Nawaz et al. 2021).

6.5.1 Alloy Nanofillers

Inorganic minerals like silica, zirconia, alumina, and zeolites were commonly used as fillers to increase membranes results in terms of mechanical, thermal, and chemical stability, as well as permeability qualities. Nevertheless, because the dimensions of the particles were within the micrometer range, the film applicability was confined to MF and UF by pore diameters of around 0.1 and 0.01 m (Zeng et al. 2020). Though, by introducing resources having at minimum one measurement in the nanoscale series, the range of mineral compounds has been expanded to include NF and RO membranes. Apart from hydrous manganese dioxide, NaA-type zeolites,

$Mg(OH)_2$ and $CaCO_3$ discovered in current years, most inorganic nanoparticles used in membrane alteration are metals or metallic oxides (Rahimi et al. 2021).

6.5.1.1 Zeolites

Zeolites are permeable coordination inorganic materials through distinct channels molecular structures size. Different univalent and bivalent cations such as K^+, Na^+, Mg^{2+}, and Ca^{2+} can be easily switched in an interaction solution. Because of their aptitude for molecular sieving, which can accurately separate particles depending on size, zeolites have received interest as effective membrane technology both for liquid and gas processes. For water desalination purification, many types of zeolite membranes have been developed. These membranes have a few unique features that standard polymer membranes cannot match. Some features include customizable pore diameters, minimal fouling propensity, thermal and chemical stability (Karisma et al. 2017).

NF thin-film nanocomposite (TFN) films with PSF provision were implanted by zeolites nanoparticles. These novel membranes demonstrated up to 93.4 and 49% nanomaterial coverage ratio, better water permeability, and salt rejection. Nano H_2O Inc. used zeolites as nanoparticles in the first industrial use of TFN membranes. It was stated that the produced films exhibited a dual greater liquid flow than standard polyamide (PA), thin-film composite (TFC) membranes, and a salt rejection of 99.7% (Korolkov et al. 2018a, b).

6.5.1.2 Silica (SiO_2)

Silica is a common inorganic filler that has a great deal of interest in creating mixed matrix membranes (MMMs) divided into nonporous silica and methodical mesoporous silica. In general, silica pitches are incorporated hooked on polymer matrices by sol–gel methods to produce inorganic oxide units at the nonorange inside the polymeric matrix (Shiohara et al. 2021a, b). PES nanocomposite membranes with mesoporous silica detected a rise in sublayer size of porosity and improved pore connectivity between the bottom and sublayer (Apel et al. 2018). At a putty lading of 2 wt%, the mesoporous particles significantly increased membrane's hydrophilicity, with a flow of 180 L/m^2 h as well as a denial rate of 96.1% of bovine serum albumin (BSA). Polyetherimide (PEI) thin-film NF film-coated by SiO_2 for decolorization in aqueous and organic solutions. As for surface polymerization in varied SiO_2 concentrations, dual individual terephthaloyl chloride (TPC) absorptions (0.1 and 0.5 wt%), as well as PEI, were utilized (0.1, 0.05, and 0.03 wt%). TPC (0.1 wt%) with SiO_2 nanoparticles resulted in a 13.3 L/m^2 h greater instability as well as 100% refusal of the cationic dye crystal violet (0.1 wt%) (Liu et al. 2018).

6.5.2 Carbon Form Nanofillers

CNTs, graphene oxide (GO), and graphene have all been employed to create water distillation membranes. Carbon-based materials have grown in popularity because of their exceptional physiochemical characteristics. Carbon-based materials include nanofibers, nanoparticles, nanotubes, nanowires, fullerenes, and nanorings. Nanocarbon constituents have unique qualities such as high diffusion properties, easy functionality modification, initiation of hydrophilic and hydrophobic properties, and higher chemical durability (Emilsson and Dahlin 2018).

6.5.2.1 Carbon Nanotubes (CNTs)

CNTs are made up of tubular graphene sheets wrapped up into pipe structures with nanosized diameters and a grid fence look. CNTs are further categorized as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and double-walled carbon nanotubes (DWCNTs) based on the graphene shell layers multi-walled carbon nanotubes (MWCNTs) shown in Fig. 6.2. CNT characteristics are intimately related to the atomic arrangement, nanotube length and width, and morphology (Pandey et al. 2019). CNTs can be employed as catalysts, adsorbents, or membranes for treating wastewater and salinity due to their adjustable properties and performance-enhancing. CNTs have appeared as exceptional possibilities in membrane technology, which has revolutionized detoxification and wastewater treatment procedures because of their antimicrobial activity, rapid liquid flow, customizable pore size, large surface area, surface composition, and electrical properties (Choi et al. 2019).

To avoid the air flow barter exhibited in most traditional membrane materials, CNTs may be structured as freestanding CNT inserted towards a polymer matrix for water treatment. The potential of compact and dense CNT networks to offer remarkable water flow is of particular importance for CNT membrane development (Kavand et al. 2019). Electroactive CNT-based membranes can remove salts, peptides, dyes, viruses, and phenols through the water. Because of surface quality and volatile hydrophobicity, advanced nanotechnology allows for a regulator of CNT dimension, which aids in the manufacturing of CNTs-coated RO membranes having greater flux. Thin-film nanomaterial membranes using CNTs lead to high water flow and a 99% denunciation amount of Na_2SO_4 (Elsaid et al. 2020).

Zhang et al. (2019a, b, c, d) investigated polymer-supported complex membranes made of interconnected MWCNT-GO. These membranes were tested by cleaning strontium-containing wastewater, and they demonstrated greater flow rates than other NF membranes. Moreover, this membrane refused around 93% of the ethylenediaminetetraacetic acid (EDTA)-chelated Sr^{2+} in basic solution. Hu et al. (2019) used MWCNTs in a phase transition method to create UF nanocomposite polyacrylonitrile (PAN) membrane (MMNMs). Based on MWCNT reinforcing capabilities, MMNMs exhibit 36% resistance to membrane compaction, resulting in improved transport qualities in PAN membranes.

Furthermore, the accumulation of MWCNTs to the PAN molding solution enhanced the tensile of MMNMs. As a result, MWCNTs in MMNMs provide greater thermal/mechanical stability for applications requiring higher transmembrane pressures. In another investigation, Voisin et al. (2020) created compound films from MWCNT and PA polymer. MWCNT insertion into membrane improved both saline reject effectiveness and nanocomposite films' structural properties relative to virgin PA membranes, with a minor drop in dynamic durability.

6.5.2.2 Graphene and Graphene Oxide (GO)

Because of its honeycomb lattice structure, graphene is potentially substantially used for water transfer. It can serve as a foundation for the new part of transparent membrane technology and selectively distillation methods (Voisin et al. 2020). The utilization of graphene in RO films has greatly aided water detoxification operations. Nanographene was discovered to enhance salt elimination from 33 to 100% (Qiao et al. 2021). The utilization of graphene in the NF water purification method allows for the efficient removal of organic dyes. Like, graphene-coated PVDF demonstrated good dye retention. The graphene-based films demonstrated varied salt rejection rates ranging from 20 to 60%, in this order: Na_2SO_4 > NaCl > $MgSO_4$ > $MgCl_2$ (Hou et al. 2019). GO is created by oxidizing graphene, which is hydrophilic, instead of graphene, which is mostly hydrophobic. The addition of GO to membrane materials can improve their thermomechanical characteristics. The application of GO, like other nanomaterials, transforms the character of the membrane from a hydrophobic to a hydrophilic profile, enhancing porousness presentation. Procedure of repulsion of salt ions by positively and negatively charged GO membranes are shown below in Fig. 6.2.

The impact of polyvinylpyrrolidone (PVP) and GO on the efficiency of a PVDF membrane filter. According to the findings, adding PVP and GO to the membranes improved their antifouling efficiency and wettability. As a result of hydrogen bonding between the GO and PVP, the authors discovered increased performance (Hu and Liu 2020). Silica particles are coated on GO nanosheets to create a PSf membrane using GO and SiO_2. With a rejection rate of 98% and good water flow, the membrane demonstrated promising antifouling activity towards protein (Wang et al. 2020) (Fig. 6.3). Table 6.2 tabulates the different roles of the inorganic and carbon-based nanofillers in nanocomposite membranes for wastewater treatment.

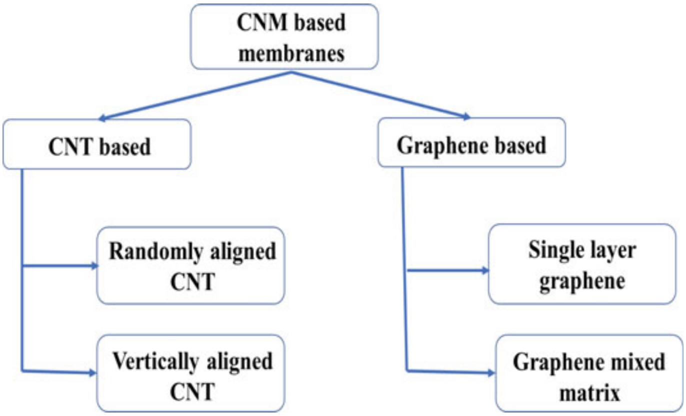

Fig. 6.2 Classifications of carbon nanomaterial-based membranes

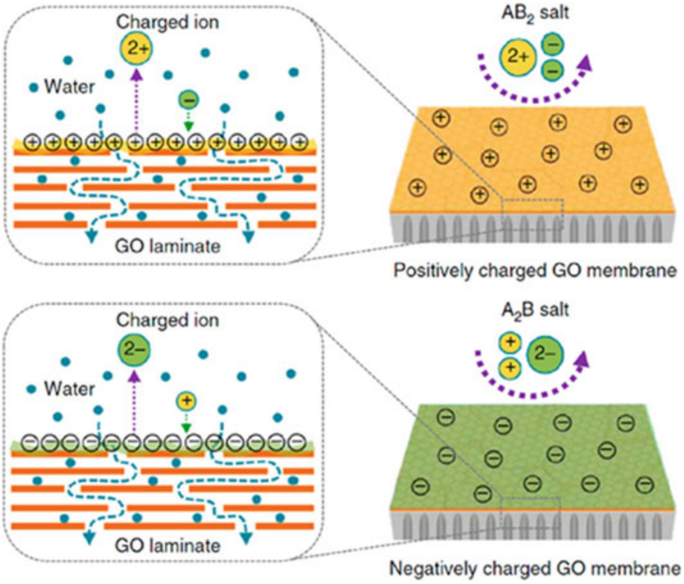

Fig. 6.3 Procedure of repulsion of salt ions by surface charged GO membrane

Table 6.2 Role of the inorganic and carbon-based nanofillers in nanocomposite membranes for water treatment

Nanomaterials	Polymers	Membrane	Presentation	References
Cerium oxide (CeO_2)	PA	NF	More hydrophilicity 99% salt rejection	Kavand et al. (2019)
Iron oxide	PVC + CA	NF	Greater water porousness Good elimination of lead	Elsaid et al. (2020)
Iron oxide (FeO)	PES	NF	High water flux, good salt rejection, more antifouling behavior	Zhang et al. (2019a, b, c, d)
GO-MWCNT	PVDF	NF	Higher water flux Good antifouling performance Higher rejection rate	Hu et al. (2019)
rGO/TiO_2	PES	NF	Better permeability Good antifouling properties	Voisin et al. (2020)
Carboxylated CNT	PES	NF	660% more water flux than PES film 87.25% Na_2SO_4 refutation	Qiao et al. (2021)
NH_2-MWCNT	PA	NF	95.72% refutation of NaCl salt More hydrophilicity Greater separation	Hou et al. (2019)

6.6 Nanomaterials in Nanofiltration Membrane Method

NF membranes treat wastewater or harshness reduction (Ca^{2+} and Mg^{2+}). The surface energy and hydrophilicity of NF membranes are essential surface features. To achieve an increased barrier, these qualities can be modified by including nanoparticles in the host material. Due to improved interface wettability, the use of water-soluble nanomaterials can minimize the clogging of NF membranes (Yang et al. 2020a, b). Carboxylated MWCNTs were used in one study to modify PA NF membranes. There was a 33% increase in water flow with strong hydrophilicity and antifouling qualities. These films performed well in terms of clogging tolerance, porosity, and salt rejecting (Wu et al. 2021a, b).

Yang et al. (2020a, b) created the PAN NF film with two iron-based nanomaterials, maleate and goethite ferroxane. Due to the obvious high repelling connections among both the functional groups of the dye as well as the nanoparticles, these iron-based nanoparticles exhibited excellent dye persistence. Furthermore, these membranes were more hydrophilic, had better water transparency, and were anticorrosion. The introduction of GO to poly(m-phenyleneisophthalamide) NF membranes improved antifouling and water flow.

The appropriate dye supply of the composite membrane was at least 90%. An antifouling NF membrane made of acid-oxidized multi-walled CNTs and PES. Due to the growth of huge macrovoids in the membrane's support layers, the salt rejecting and water porousness of the PES/MWCNT membrane improved. The surface segregation actions of MWCNTs have been observed to minimize fouling during BSA solution filtration. They concluded that surface roughness is crucial in antifouling performance. Following the Donnan exclusion process, the negative ions of MWCNTs also aided in enhancing salt refusal (Wu et al. 2021a, b). Nthunya et al. (2019) created PES NF membranes by incorporating GO nanocarbon materials into a PES medium. The refusal ability of PES/GO composite films was shown to be stronger than that of pure PES membranes. Furthermore, the GO nanomaterial caused a negative surface charge across the whole pH range. The GO-blended PES membrane had a low surface aspect, greater water flow, and better color removal than the empty membrane.

6.7 Nanomaterial-Based Membrane Synthesis Techniques

The graft polymerization, sol–gel method, stretching, layer-by-layer method, interfacial polymerization, phase inversion technique, track etching, sintering, electrospinning, and coating are all used to produce nanomaterials into the matrix of a membrane. The sol–gel approach is not widely employed because of bad thermal stresses and nanomaterial dispersion in the membrane. A few tries have been made to synthesize organic–inorganic membranes using the sol–gel technique (Wu et al. 2021a, b). The following key synthesis techniques are thoroughly covered.

6.7.1 Phase Inversion Method

This method is often referred to as the phase parting method. The measured phase change from a polymer's liquid to the solid phase is performed in this process. To remove the polymer from the solvent, an antisolvent is utilized. Water is mostly employed as an antisolvent. Immersion precipitation is a popular approach (Wu et al. 2021a, b). In general, four mechanisms are exploited in this strategy shown below in Fig. 6.4a:

- Method for lowering the temperature of the solution
- Involvement of polymer compound in gas anti-solvent
- Revelation of polymer compound to antisolvent vapor
- Solvent evaporation in the presence of air or at extreme temperature.

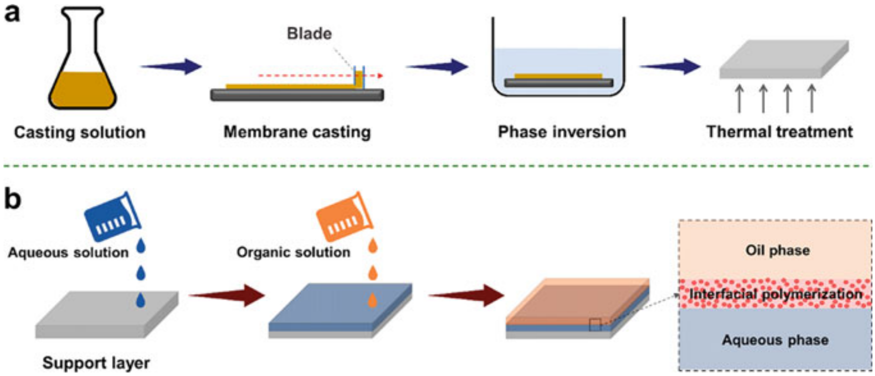

Fig. 6.4 **a** Phase inversion and **b** interfacial polymerization methods

Polymer insolubility, solvent solubility, and antisolvent temperature can impact phase inversion rate and membrane properties. Because of its low cost, the phase inversion method is a technologically dependable approach (Liu et al. 2019). The method of phase parting is additionally categorised into the different methods.

6.7.1.1 Nonsolvent Induced Phase Separation Method (NIPS)

Nonsolvent induced phase separation method is carried out on dissolving a gas antisolvent reaction in a solvent-polymer solution. Water is either a nonsolvent or an antisolvent in most cases. Loeb and Souriranjan first employed this approach to synthesize membranes. Using this method, they can create the polymeric RO membrane. Acetone is used as a solvent and CA as a polymer. Water is allowed to flow through the solution of both components. As a pore-forming agent, magnesium perchlorate is employed. These membranes outperformed commercially available membranes (Chen et al. 2020). For copolymer-based membranes, NIPS can be adjusted. This process is referred to as nonsolvent-induced phase separation and self-assembled.

6.7.1.2 Self-assembled and Nonsolvent Induced Phase Separation (SNIPS)

The varied configurations of polymer chains may be advantageous for a specific use of polymer membranes. In membrane synthesis, the copolymer procedure is an option. The extruders are utilized to combine the polymer, which is subsequently crushed by mold and etching. NPs may be introduced during the extrusion process. Selective localization of nanoparticles can aid in selective chain creation, allowing us to create nanomaterial-originated polymeric films (Bethke et al. 2018).

6.7.1.3 Thermally Induced Phase Separation (TIPS)

As a solvent, a greater boiling point polymer solution and a low molecular mass are employed in this approach. This liquid is chilled once the dope is cast. After cooling, two distinct phases are created. The method's distinctive characteristics are the lack of thermal energy dissipation and antisolvent. According to research, various polymeric films have a problem to synthesis using NIPS; nevertheless simple to synthesize using TIPS (Yang et al. 2021).

6.7.2 Interfacial Polymerization (IP)

IP is more commonly utilized to manufacture layers than other processes. IP is performed due to benefits such as increased load-bearing capacity and describes data of nanomaterials such as zeolite in the PA layer and procedure shown in Fig. 6.4b. Surface roughness is increased by nanoparticles, while surface hydrophilicity stays constant (Chu et al. 2020). IP is used to create modified mesoporous silica nanoparticles. The key elements of the synthesizing method are piperazine (PIP) and trimesoyl chloride (TMC). Amino groups are used to modify silica nanoparticles then introduced to the PIP phase. Due to their contact, the covalent link between TMC and the aqueous improved PIP phase/mesoporous silica nanoparticles are formed. The particle concentration is critical for manipulating pure water flow (Keucken et al. 2018). PA thin film nanocomposite (PA-TFN) membranes are also made from hydrophilized ordered mesoporous carbon shown in Fig. 6.5. This interaction enhanced the membrane's performance. A membrane's liquid permeability using 5wt% loading is greater than other loading values (Muthu 2017). To manufacture the PA membrane, metal alkoxides such as titanium tetraisopropoxide, phenyltriethoxysilane and bistriethoxysilyl ethane are utilized (Yaseen and Scholz 2019). Aminosilanized TiO_2 nanoparticles are modified into m-phenylenediamine (m-PDA) and TMC. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) are used to assess nanoparticles' functionalization. Scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDX) are used for morphological and surface studies. Thermogravimetric analysis (TGA) investigates heat resistivity. This film increased the salt refusal rate by 54% (Zhang et al. 2019a, b, c, d).

Acid-treated MWCNTs and silver nanoparticles are combined in the thin film nanoparticle film. Silver NPs account for 10% of the thin film coating, whereas Nosecount for 5% of the support layer. The permeability of pure water is enhanced by 20% and the permeability of seawater by 23%, respectively (Copaciu et al. 2013).

The fluoropolyamide membrane is also infused with silica nanoparticles. This membrane rejected salt at a rate of 94%. Several efforts have been undertaken to improve CNT-based film production methods. Attempts are being made to build films with a greater solvent declining rate (Zhang et al. 2019a, b, c, d). PVA medium is transferred on a 20% capacity proportion of PSF support both with and without

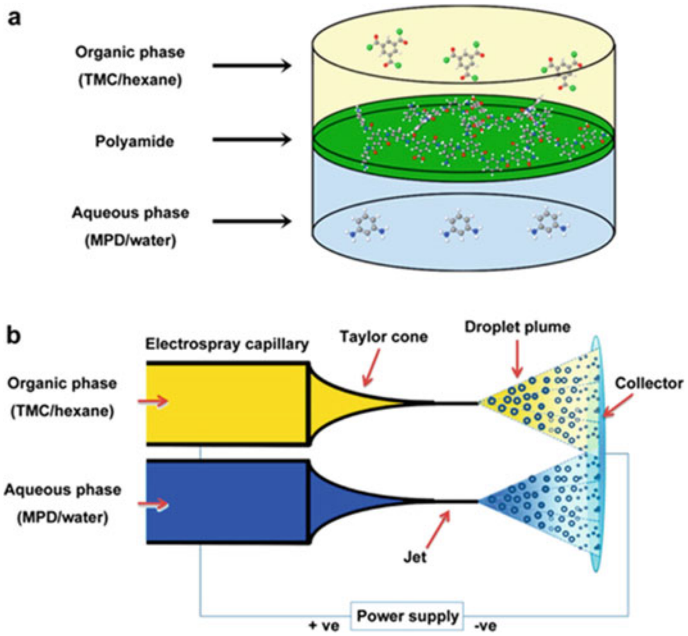

Fig. 6.5 Representation of the polyamide membrane fabrication method **a** conventional interfacial polymerization reaction, **b** electrospray method

well-distributed synthesized aluminosilicate SWCNTs. Water flow was enhanced as a result of the existence of an aqueous nanotube.

6.7.3 Layer by Layer (LbL) Assembly

It's fascinating to look back over the previous 20 years at the historical evolution of this strategy. We were unaware of any earlier work on multilayer manufacturing utilizing electrostatic interactions when we began working on it in 1989. We only found out about Heterogeneous Particle Heterostructures much later, in 1966. The reversal of the zeta voltage of charges colloids following the sorption of an opposite charge ionic liquid has previously been seen by experimentation in the early 1990s, for example, in flocculation research (Copaciu et al. 2013). However, we were previously unaware about the coating of thrombin creation by successive adsorption of a heparin and heparin complex that also exhibited charge reverse, on the polyfunctional sorption on cellulose fibres publication of a slightly comparable Successive Ionic Layer Adsorption and Reaction approach for creating polycrystalline inorganic layers. None of these study teams appeared to be aware of one another (Zhan et al. 2018).

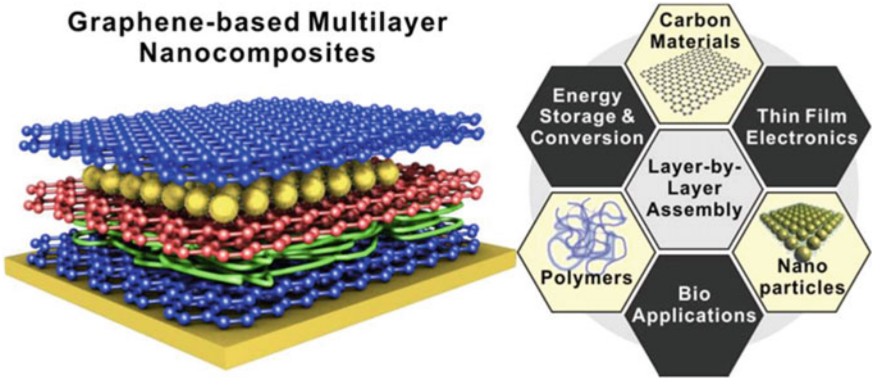

Fig. 6.6 Significance of graphene-based nanocomposites equipped by layer by layer (LbL) assembly

Here is a uniform unintended application of LbL accumulation techniques nowadays. Meanwhile, approximately 1991, one may discover procedures in natural science that employ or advocate two-component coatings for specific studies, with no one realizing that it was applying layer by layer principles (Li et al. 2020a, b). Consider how long that kind of investigation could advantage by understanding what is going on at the molecular level and how the study of cell biology (Shan et al. 2018). Significance of graphene-based multilayer nanocomposites equipped by LbL assembly in different fields are shown in Fig. 6.6.

This process deposits an alternating layer of oppositely charged elements, with wash stages between them. This is accomplished by using immersion, spin, spray, and electromagnetic approaches (Chen et al. 2021). Because of the existence of opposing charges, we may employ multilayer membranes. The element resounding GO nanomembranes is being cast-off to divide the liquid depending on its shape and charges. There is room for advancement in creating GO-based nanomembranes (Ma et al. 2018a, b). These layer-by-layer construction methods are simple to represent. If $+$ and $-$ are both negatively poly ions bound, then two bi-layer may be signified as $W + W - W + W - W$, wherever W is the wash layer shown in Fig. 6.7a, b. The contact between both layers is not limited to electrostatic attraction.

Hydrophobic attraction is another powerful force (Chowdhury et al. 2018). Other factors are encouraged to play an important part in multilayer systems. As a result, layer-by-layer synthesis may be utilized to create hydrophobic liquids, hydrogen-bonded films, other unconventional systems, and nanoparticles (Liu et al. 2021). The LBL membrane synthesis approach create forward and reverse membranes, NF, pervaporation membranes, and desalination (Ma et al. 2019).

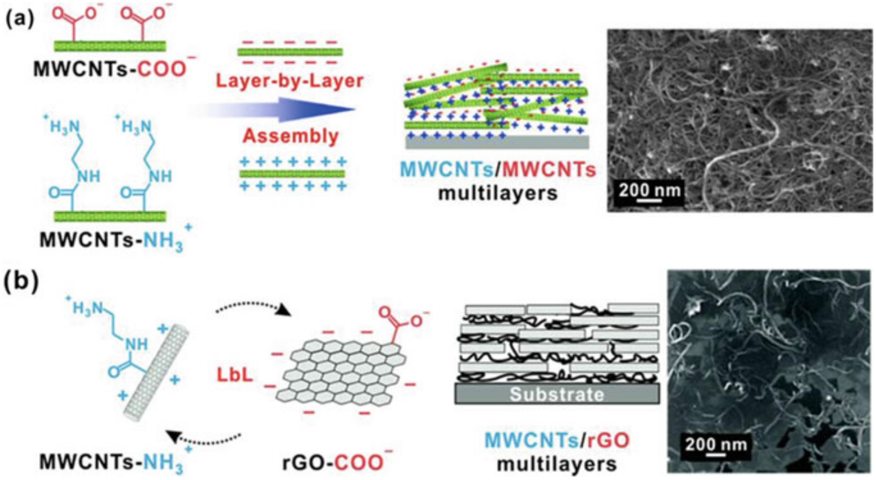

Fig. 6.7 **a** LbL collected MWCNT thin film by positively and negatively charged MWCNTs. **b** Hybrid LbL multilayers of MWCNTs and rGO

6.7.4 Stretching and Sintering

Machine-driven stretching is an essential factor in chain arrangement and polymer alignment. As a result, semicrystalline materials such as PTFE benefit from it (Buekenhoudt et al. 2013). The polymer is extruded, stretched, and formed into pieces. Stretching is completed based on the applications. The process's operating parameters are extrusion speed and temperature haggard polymer thickness (Zhu et al. 2018). In the sintering procedure, powdered materials are crushed and sintered at a predetermined temperature. The sintering method is used to create MF membranes (Zhang et al. 2019a, b, c, d). Stretching has been utilized to produce polymer membranes for MF, MD, and UF processes since 1970. The material is warmed beyond its melting temperature & injected onto coating shapes with a fast descent until a polymeric film is formed in this manner. The films are then rendered permeable by stretching them. As a result, it is the best approach for creating microporous membranes. Stretching does not require solvents. Hence, it is cost-effective (Le et al. 2019). This approach is appropriate for polymers with high translucent. Minerals in the polymer align along with the sketch, resulting in a strong point. The porous structure is generated by the polymer's amorphous component (Zhao et al. 2018). Cold stretching and hot stretching are the two phases of stretching. Cold stretching is utilized to aggregate micro porousness in the produced film, while hot stretching is utilized to control the eventual permeable construction of the film. Following the preceding procedures, a power-driven tension is applied perpendicular to the drawing way. This approach produces membranes through a rather homogeneous permeable construction and an absorbency of around 90% (Zhu et al. 2019). The physical qualities of the film substantial, such as melting point, crystallinity, processing parameters, and tensile strength used, determine the porosity properties and structure of the film. Sintering is powdering polymer particles and pressing the resultant powder onto a film. At that time, it is sintered at a temperature lower than the polymer's flashpoint. This approach produces membranes with an uneven PSD and a microporous structure. Their sponginess ranges between 10 and 40%. The aperture dimensions of these films vary from 0.2 to 20 mm, depending on the dimensions of the polymer atoms utilized (Lee et al. 2015a, b).

6.7.5 *Track Etching and Electrospinning*

Using a track etching grounded micro and nanofabrication process, researchers can create membranes with precisely regulated and consistent pore diameter, structure, position, and concentration. The most significant feature of this technology is its ability to generate various sizes and pore densities after the nano to the microscale. All of that can be regulated individually (Bai et al. 2018). Track-etching technique was initially described in the 1960s. It is grounded on treating polymers with either electron, energetic heavy ions, UV-light, X-ray irradiation, following the development of lined spoiled tracks across the bare polymeric membrane. The most often employed polymers for this method are poly PVDF, PC, and polyethylene terephthalate (PET) (Abdel-Fatah 2018). The broken grooves are translated into gaps by either utilizing suitably designed chemical solution etching circumstances or applying an electrical field. The utilization of toxic ion injectors allows adjusting track-forming particles' linear energy transfer, pore channel angle distribution, and pore length. An electric deflector, a magnetically scattering device, a sensor, a triggering, and a specimen stack are typical components of a single irradiation system. To begin, the ion beam is mechanically lens blurred and tuned such that just one beam travels through the hole at a specific frequency (Sigurdson et al. 2017). The ion beam then irradiates the stack of foils. The ions are detected by a solid-state element sensor installed overdue the sample. Once an ion is detected, the whole ion stream is diverted by a system of an electrical compressor (Cortez et al. 2017). In general, constant and homogenous damage throughout the ion pathway can yield polymeric membranes with consistent pore diameters. Pore formation by radioactivity accompanied by etching with a wet chemical is dependent on chemical etching circumstances following radioactivity. Therefore, time and etching solvents are essential parameters to govern pore structure and width, while irradiation time influences pore density. Cylindrical pores may be created utilizing symmetric etching and a single etching solution (Benkhaya et al. 2020). A track-etched PET films with tubular holes as an example of symmetrical wiping by first exposing the 12 m bushy PET foil with individual active heavy metal ions. Insubordinate pulse detection of polystyrene particles flowing over the pores investigated the variation in diameters over the pore length.

The polystyrene atoms are examined like they moved complete the holes separates the 2 pools of a mixture of electrolytes to determine the impedance of the holes whenever power was applied among such reservoirs. The mean particle size diameter rose etching in straight-line pores, and a time of around 100 nm was achieved after 30 min of etching (Spence 2018).

Narrowed holes can be created through irregular etching, which involves immersing the film in 2 distinct solvents. The mechanism of osmotic events occurring during pore morphology development using iron track etching has been found. Asymmetric chemical etching was used to create conical shape nanopores by etching the foil by one end with such a powerful acid solution. At the same time, another side was exposed to a more diluted stopping solution (Luo et al. 2016). At the point of pore breach, the chemical halting was electrically assisted by neutralization of the etchant. To eliminate OH^- ions via the birth pore, a positive voltage was applied to a sensor placed in the acid solution, which prevented further pore formation. An electrostatic attraction can be supplied to a membrane immersed in an electrolyte without using any etchant to produce holes as an alternative to chemical etching. In this scenario, the UV radioactivity duration earlier applying an electrical field to form Ionic electric routes is longer than in the traditional chemical etching track-etching procedure. One of the key advantages of this technology is that the pore width may be reduced to less than 1 nm by substituting chemical etching with prolonged UV irradiation times. Track-etched polymeric membranes have fascinating transportation qualities due to their capacity to produce tiny nanoscale pores and unique pore features. As a result, they are being extensively researched for energy conversion, filtration and separation, and molecular sensing. Luo et al. (2018) have gone to great lengths to describe the characteristics of the track-etched permeable polymer membrane, emphasizing their molecule transport and ion mechanisms.

Although these apparent benefits over alternative manufacturing processes, the process's complexity remains a substantial barrier to its widespread adoption. Other disadvantages also include reality because track-etched films are usually of microscale thickness, resulting in the loss of molecules and ions when moving through the gaps and interacting with the long porous structure. It is also important to highlight the difficulty in incorporating such membrane into microfluidic systems. After all, basic membranes components are hard to relate, such as PET or PC, to typical polydimethylsiloxane (PDMS) or microfluidic materials (Luo et al. 2018).

Electrospinning is the electrostatically induced rotating of fibers made of polymers, resulting in polymers' porosity patterns. This approach can create porous polymeric membranes with hole dimensions ranging from the micro to nanoscale, good pore interconnectivity, high gravimetric permeability, low-density, microscale interstitial space, large surface-area-to-volume ratio-controlled thickness with adequate powered strength are some of the benefits of these membranes (Qiang et al. 2019). The produced polymer solution is first put into a capillary tube, either by dissolving or melting in a solvent. The capillary tip and the ground collector are then subjected to a high electrical field. The electric field-induced charge resists the polymeric convective interfacial pressure held at the vessel's tip. When the electric power increases, the hemispherical form at the top, the polymeric liquid changes form to a conical shape termed a Cylinder. Whenever the induced electrostatic force reaches a certain level exceeding the interfacial tension of the polymeric fluid, the solutions are ejected from the point of the Cylinder. The path that the supercharged jet of suitable solvent takes may be electronically regulated, permitting polymer threads to be gathered and utilized to construct parts of a system.

6.7.6 Three-Dimensional Printing (3D Printing)

Preservative industrial often called fast prototyping or 3D printing, is a comparatively new process with significant promise for biological membrane manufacture. The technique's most significant benefit is the capacity to build complicated forms or characteristics in 3D with a broad variety of substances, including ceramics, traditional thermoplastics, graphene-based materials, and metals of various sizes (Collivignarelli et al. 2019). This method may be classified into 4 types:

1. Photopolymerisation is when photoreactive materials are healed using a UV light or laser.
2. Powder printing is a type that has the required material's powder is placed on a substrate before releasing a chemical agent to build a 3D selectively and shape sinter it.
3. Material extrusion involves melting and extruding a strand of polymer materials to construct the desired structure by heating the thermoplastic over its Glass transition temperature (Tg).
4. Lamination is bonding layered tiny layers of fabric trimmed into a specific shape to prove the concept.

Photopolymerisation, particularly the laser lithography-based technology called stereolithography (SLA), is now the greatest extensively cast-off method for producing polymer membranes. A UV laser outlines the required cures and structures the photoreactive material up or down the movable phase in this procedure. Once the required outline has been generated on the surface of the photoreactive polymer solution on the phase, the phase is moved directly down into it or out from the polymer top, creating a sustainable 3D sculpture. This UV-laser cures the polymer on the interface (Qiang et al. 2019).

Although 3D printing has enormous promise in the medical, art, industry, and construction industries, it is still in adolescence and suffers from significant constraints such as print resolution. As a result, producing membranes with nanoscale holes remains difficult. However, the bulk of 3D printing systems has a microscale precision edge. New advancements in the usage of the two-photon polymerization (TPP) process for 3D printing have shown the opportunity of increasing the determination limit to the 100 nm scale (Guo et al. 2019). The greater determination was achieved by employing an elevated aperture objective to irradiate a femtosecond optical maser beam closely concentrated on a photoreactive composite. Because most photoreactive composites engage in the UV region, a near-infrared light optical maser may be cast-off to encourage TPP, allowing polymerization to be limited to a narrow area around the laser beam's focus point. While this technology has advanced rapidly in the previous decade, it still has some limits to overcome, including material kinds, limited electromechanical toughness lacking extra post-treatment processes, and expensive manufacturing costs. To that same fullest capacity, no publications had been published on the usage of 3D printing to create porous polymeric membranes with nanoscale holes. Recent breakthroughs in increasing the determination limit of specialized 3D printing technologies and, on the other hand, open the way for the hopeful manufacturing of permeable barriers in the coming years (Collivignarelli et al. 2019).

6.8 Applications of NF Membrane for Dye Removal

6.8.1 Textile Industry

The textile sector is now the industry of most concern because of the large dye wastewater created during the dye manufacturing and application processes. This effluent comprises colors, salts, auxiliary compounds, and hazardous substances that, if released directly, cause major water contamination and soil salinization. The most regularly utilized solutions meant to remediate textile effluents, as well as their mechanisms, benefits, and drawbacks, are well established. Although coagulation and physical adsorption are low-cost and simple processes, dye repossession appears unachievable or prohibitively expensive. Although advanced oxidation or biodegradation are viable methods for dye degradation, the high operating costs must be addressed before the application scale can be expanded. As NF is beneficial in inefficient resource restoration, it may be an alternate way to release textile effluents. Most relevant investigations concentrated on enhancing the Partition specificity of salts and dyes of the NF membranes, which appeared higher closely connected to membrane modification.

More practicable tweaking feed parameters and operating circumstances in real-world applications are needed to improve NF decolorization performance. The parameters of typical textile dyes are also significant for the efficacy of NF decolorization. Feed characteristics and operating circumstances can impact solute membrane and solute interactions, with the major implications being dye adsorption and dye aggregation on the membrane. Dye molecules containing heterocycles and benzene rings are hydrophobic and readily organize macromolecular clumps to enhance the size restriction effect. In most cases, a higher salt content causes additional significant meditation polarisation and apparent junior holding of the solutes, though the combined effects overwhelm dye retention by NF. Van Bruggen et al. discovered that even when the working settings were adjusted from 2 bar, and 50 ppm to 8 bar and 2000 ppm, the rejection of direct red by the NF membrane did not change considerably. Furthermore, the addition of inorganic compounds in the dye concentration would result in an electrochemical scattering and a weakening of the charge aversion between the colors and the membranes, leading to more acute gradient polarisation and lesser dye rejection in fabric wastewater containing a high percentage of salt

(>1%). The parting of peroxides from salts allows for reusing salts and water, dye rejection, and permeate flow rise as salt concentration decreases (Wittmann et al. 2021).

The salting-in impact on dye molecules, on the other hand, would cause colors to spread more equally in solution, reducing concentration polarization and membrane fouling. Parting salts from colorants are vital for creating quality during concentration and desalination of colors throughout dye synthesis with a small proportion of salts. The NF method would aspect increasing entangling possibility with declining salt proportion. The provender pH can change the electrostatic interactions that influence dye rejection and fouling development by regulating the charges on the membrane surface and dye molecules. The pH from acidic to neutral boosted colorant elimination by an NFT-50 membrane from 77 to 97% due to increased charge repulsion between the membrane and the dye. Membrane fouling is unavoidable in the long-lasting functioning of the NF procedure for dye removal and must be avoided. The key to avoiding fouling aggravation is to reduce the exchanges of solute/solute and solute/membrane. Membrane contact can be reduced by film feed pre-treatment and modification, while the critical flow idea allows it to limit attenuate membrane fouling and foulant interaction. Furthermore, functional field improvements such as ultrasonic and electric techniques are useful methods for intensifying solute movement and increasing the perilous flux of the NF film (Merlet et al. 2020).

6.8.2 Bioproduct Manufacturing

Bioproducts are useful substances derived from bioenergy, such as animals, plants, and microbes. However, on the other hand, the undesirable color of bioproducts degrades their worth and quality, and removing dye is essential to getting large products. On the other hand, there is a rising need for extracting pigments from bioproducts owed to the coloring capabilities and possible well-being benefit of usual pigments. Traditional decolorization strategies, such as ion interaction resins and porous carbon adsorption, are less continuous activities with greater processing and renewal costs as well as product loss and massive solid waste generation. It may not be appropriate for pigments retrieval. The recovery of colorants extracted from extraction solutions, which often comprises broken adsorbents, colloids, and highly concentrated salts, is the most difficult for pigment extraction by adsorption techniques (Wittmann et al. 2021). NF is potential for bioproduct pigment recovery and dye removal as a green separation technology that does not require chemicals.

6.8.2.1 Sugar Production

Sugar manufacturing is an example of how colors in molasses or syrup juice must be eliminated to increase sugar and sugar quality recovery. Using NF for dye removal in sugar manufacture is intriguing since it minimizes chemical consumption and retrieves natural colors compared to standard chemical procedures, including sulfur dioxide and lime. Though, the use of NF colorant removal in sugar manufacture is hampered by poor pigment/sucrose severe membrane fouling and separation selectivity, resulting in significantly low pigment purity and sucrose loss. First, the NF membrane's aperture size determines its decolorization efficacy. Roy et al. (2020), for example, showed that at what time the membrane Molecular weight cut-off (MWCO) was reduced from 6–8 kDa to 500 Da, color removal increased from 58 to 76%. However, a noteworthy reduction in permeate flow occurred due to increased pore blockage and osmotic pressure of the NF membrane.

Guo et al. (2019) discovered that, while the permeate flow and decolorization efficiency were ideal, the sucrose refusal was rather significant, necessitating a sucrose recovery interactive process procedure in the concentrate using a PANF film with an MWCO of 300,500 Da (Zhan et al. 2018). As a result, improving the separation discernment of sucrose by modifying the hole dimensions of the NF film. Because pigment molecules are hydrophobic and somewhat negatively charged, boosting the hydrophilicity and negative charges of the NF membrane. That appears to be a viable avenue for improving pigment retention without sacrificing sucrose transmission.

However, such an action would reduce membrane hydrophilicity and, as a result, enhance pigment adsorption in film, offsetting the salt-induced pore enlargement and narrowing the pore size. The development of membrane fouling during sugar decolorization reduces permeate flow and enhances sugar retention. In addition to pre-treatment membrane modification, integrating NF with other separation technologies and adjusting operating conditions may be utilized to prevent recovery colors and membrane fouling from the NF concentrate. Luo et al., for instance, developed a to purify sugar cane extract, an inclusion complex process in which color removal was up to 96.6% at membrane fouling. The pilot size in the decolorization stage by tight UF (also known as loose NF) could be efficiently managed. Zhang et al. (2019a, b, c, d) presented a more difficult utilization procedure for cane molasses, including membrane filtering and resin adsorption. The non-ionic resin was used to remove the aquaphobic caramel dyes in this procedure to prevent aquaphobic fouling development and re-establish the "salt-induced pore expanding" action on the moveable NF membrane. As a result, the NF's permeate flow increased by 1.5 times, while sucrose rejection and membrane fouling were decreased by 48% and 90%, respectively. After diafiltration to remove salts and sugar, the polyphenol dyes were extracted from the NF retentate.

6.8.2.2 Juice Production

Juice is an essential part of people's daily diet; however, colored compounds in raw materials (e.g., anthocyanins and phenols) have a detrimental influence on physical qualities such as color, nutritional content, and flavor. As a result, removing the colored compounds from the juice is advantageous. Old-style juice decolorization methods and clarifying, on the other hand, typically include the inclusion of chemicals and more temperature operations. Which have the drawbacks of low efficiency, high cost, and nutritional degradation. In instruction, membrane filtering has been presented as an alternate approach for juice manufacturing to maintain bioactive ingredients in juice (Han and Wu 2019).

Technically, integrated membrane processes (e.g., microfiltration-NF and UFNF) were used to decolorize strawberry juice to decrease membrane fouling. Furthermore, the total antioxidant action in carrot and orange juice was treated with various parting techniques and discovered that film filtration beat the others in preserving antibacterial activities. Film fouling persists—a significant concern in NF juice colorant removal. Reducing growing back-diffusion of concentrated solution away from the film or concentrated solution radiative movement towards the barrier can help prevent fouling development and concentration polarisation. The operating pressure substantially reduced the irretrievable fouling of the NF membrane during the pear and apple juice colorant removal operations (Dai et al. 2020).

In theory, the principal contaminating in juice is negatively charged polysaccharides, proteins, and bacteria. NF films with large smooth surfaces and negative charges are useful in weakening the generic interaction between foulants and membrane, resulting in lesser fouling development.

6.8.2.3 Downstream Fermentation Processing

Fermentation may be utilized to make medicines, biofuels, food, and other products. In general, the fermentation process has a lot of color content, mostly due to pigments present in melanoidins or raw materials produced by the Maillard method. Carbon adsorption has been extensively utilized for colorant removal of inflamed goods, and NF also offers significant promise in this application. The colorant removal of fermentable sugar by NF is a successful way to reduce the broth's pigment level. Second, NF makes significant efforts to decolorize the fermentation broth and effluent. Furthermore, NF has been used to purify various fermentation products, including alcohol, baker's yeast, silage juice, succinic acid, soy sauce, and D-lactic acid (Yang et al. 2019). It is value noting that fermentation wastes are typically acidic and hot, necessitating the use of more strong NF films (e.g., chemically resistant and thermally stable).

6.8.3 Others

In accumulating the applications listed above, the NF-based colorant removal process shows promise in the fine chemical and bulk industries. Like coking, wastewater comprises a significant concentration of aromatics, leading to high toxicity, chroma, and biological perseverance. Some chemically produced medications' manufacture and packaging operations generate effluent with profound contamination in the fine chemical sector. As a sophisticated separation technique, NF can separate organic compounds and pigments to suit the needs of sewer water reuse. Though, because of the organic material and large fluidity of certain wastewaters, the use of profitable NF films may result in substantial contamination and viscous concentration streams. Thus, the growth of innovative NF films with high salt permeance and hydrophilicity and effective film washing procedures may overcome the difficulties as mentioned above. Furthermore, effluent pre-treatment can lower the NF handling load (Butnaru et al. 2020).

6.9 Challenges

Whereas various research has established the applicability of NF in commercial fluid color removals, such as inadequate detachment selectivity, short cell wall lifetime, and severe membrane fouling. Undeveloped color removal methods must be discussed to enhance the commercial use of NF for color removal.

6.9.1 Insufficient Separation Selectivity

Because NF membranes were initially developed to remove tiny organics and polyvalent ions from water, most commercially existing NF films have an MWCO of roughly 100,300 Da. Though, in many colors' removal benefits such as bioproduct manufacture and dye reclamation, there is a requirement to greater separating specificity of dyes and other solutes. The dyes must be preserved, but additional tiny molecules must cross through. Even though the high solubility and anticorrosion capability in the long period process are uncertain, explained in Table 6.3. Moveable NF films with MWCOs more than 500 Da have been manufactured on a wide measure, and their benefits assist the growth of NF color removal technologies. However, the NF membrane's irregular pore size distribution reduces parting choosiness significantly as colors can flow over the membranes through the big holes. Lately, decreasing the hole dimensions variation of the NF membrane by advanced materials and operational efficiencies has been a hot issue. Bulk functionalization and additive introduction are efficient ways for inhibiting polymer aggregation or uneven interface mass transfer in typical membrane materials (e.g., PA and PES). Furthermore, by employing novel resources with adjustable pore size and structure, like block copolymers and 2D nanosheets, homogenous nanopores may be unswervingly formed on the film, and loaded aligned synthetic channels and 2D nanomaterials may enhance (Han and Wu 2019).

Table 6.3 Problems in the more development of NF for decolorization

Causes	Key challenge	Consequences
Different pore size	Insufficient separation selectivity	Low product quality
Harsh operation condition	Short membrane lifetime	High operational cost
Studies in pilot scale	Immature membrane process	High industrialization difficulty
Complex feed composition	Membrane fouling	Shorter membrane lifetime

While appropriate solvents and process parameter adjustment can vary the pore size distribution in membrane manufacturing methods. Surface alteration strategies such as grafting, LbL deposition, and coating can be utilized to arrange the charge of the separation layer and pore dimensions. The uniform adsorption and release of reactive monomers, particularly for the PANF film ready by the IP technique, are critical for gaining flaw-free TFC film with uniform pore size circulation. Thus the base membrane can be tuned by solvent treatment, surface functionalization, and interlayer construction. Other sophisticated methods, such as atomic layer deposition, chemical vapor deposition, and track-etching, have created same-sized pore films (Butnaru et al. 2020). However, because of the low absorbency, the porousness of the resultant films is very low; in addition, their effective use is limited.

6.9.2 Limited Lifetime of Membrane

Although PA and PES are the most often utilized NF film resources because of their superior biodegradability and hydrolysis resistance, their low constancy in carbon-based solvent and alkali acid would reduce their life. PES film's low aquaphilicity results in regular biochemical washing, and deprived antifouling presentation significantly reduces membrane lifetime. While PA film is more effective at antifouling, it has a significantly lower chlorine tolerance. Furthermore, the compound assembly is more susceptible to severe cleaning conditions and back-pressure during an unsystematic shutdown. Refining the affinity of the support and separation layers and reducing the frequency of membrane cleaning may result in a longer membrane lifetime. Hydrophilic modification of PES membranes is a continuing issue. A strong aquaphilic coating can limit generic contact between foulants and membrane to reduce the spring-cleaning incidence and preserve the film from eroding chemicals.

In the case of PA membranes, particular groups or stable structures monomers can directly provide the PA coating with strong chlorine and acid resistance. However, the reduced responsiveness generally reduces the selectivity and porousness of the produced film. While the features of the PA film, such as hydrophilicity, and cross-linking degree, may be improved by inserting essences. The fundamental problem for large-scale manufacturing is their low dispersity in monomer solutions (Yang et al. 2019). Furthermore, a sacrificial layer formed by post-modification further protects the PA coating. Nevertheless, including a sacrifice coating would raise filtration confrontation and thus would not fix the problem entirely.

6.9.3 Serious Membrane Fouling

Film entangling, mainly pigment adsorption on the NF film, is unavoidable throughout the colorant removal process, resulting in a dramatic flux decrease and a fluctuation in parting choosiness. Pre-treatments like ozonation, coagulation or flocculation, and initiated carbon adsorption are the greatest operative techniques for reducing membrane insnaring. However, their secondary solid waste and high cost restrict their significant applications. Enhancing the charge distribution and aquaphilicity of the NF film and adjusting the working parameters are common tactics for reducing membrane fouling. Recent investigations, for example, demonstrated that dually zwitterionic polymers and electric parting layers permitted NF films with high aquaphilicity and good retention of cationic or anionic colors (Butnaru et al. 2020).

6.9.4 Process of Immature Decolorization

Although numerous unique NF membranes have been produced, dyes retaining have continuously been studied in the laboratory. The use of NF films in colorant removal at the preliminary size is uncommon, and UF leftovers are the dominant character in this field. Colorant removal is a complicated method involving several unit processes, and NF may only play a small portion in the whole procedure. Though maximum studies concentrated on only the NF phase, there is a paucity of a comprehensive study on the entire colorant removal process (Cao et al. 2020). The difficulties associated with decolorization techniques may be divided into three categories. To begin, efficient pre-treatment approaches and low-cost are needed to prevent concentration polarisation and film insnaring during NF. Second, the colors included in the NF concentration must be degraded or extracted. Moreover last, further colorant removal of the NF infuse is required by post-treatment methods (e.g., crystallization, ion-exchange resin adsorption, or activated carbon) to get the good goods. In future studies, researchers should focus on treating the actual solution and the entire colorant removal method rather than only examining the perfect colorant solution (Doménech et al. 2020).

6.10 Conclusion and Future Prospective

Nanocomposite films provide a critical and novel part in pressure-driven solutions to address the issue of water shortage. MF, UF, RO, and NF are strong pressure-driven methods that disperse various constituents to produce renewed water. Nanocomposites of the next generation, like CNTs, GO, silica, zeolites, and other metal oxides have proven to be outstanding materials for improving membrane properties such as antibacterial, antifouling, permeation, and hydrophilicity while maintaining chemical and mechanical constancy. Indeed, the features of nanoparticles are determined by their exclusive dimensions concerning the greater definite area. This characteristic has controlled the creation of films for more effective separation technologies and water treatment. Pressure-driven methods based on nanomaterials are expected to develop in the future, leading to fast advancements.

This chapter has demonstrated that NF is significant in the number of applications in the water handling industry. When purification is not the primary factor in selecting a membrane and operating circumstances, several NF choices offer excellent opportunities to modify plant features. The choice of the membrane is generally determined by the treatment effectiveness of the smallest component in the foundation water that has to be detached. Earth alkali ions like manganese, calcium, sulphate, dyes, nitrate and present organic compounds are examples of the tiniest substances. Many of the examples discussed in this chapter arose because no alternative procedure was capable of meeting the requirements of the required therapy. In a world anywhere, the demand for hygienic water is always rising as well as the accessible bases of high-quality water are diminishing. NF must become an even more essential option for freshwater treatment in the future. For about uncharged small molecular weight molecules, the elimination efficiency of NF membranes may be inadequate for the removal of developing micropollutants like endocrine disruptors or pharmaceutically active substances. In this scenario, RO is a better water cleaning method. Nonetheless, NF will continue to be an important and powerful method in purifying drinking water in the future.

The latest invention of catalysis film has widened one of the most attractive ways to extraction and catalysts. They provide various benefits such as altering the equilibrium state, improving the continuous stream, rate of exchange and lowering recycling and dissociation costs. Nonetheless, catalysis films have a variety of disadvantages due to their expensive production costs, poor resistance to high temperature, short membrane lifetimes and harsh chemicals, fouling, and low permeability. We anticipate that novel inorganic nanoparticles and their assembly can help us address these restrictions and problems. Novel inorganic nanoparticles and their assembly offering new multipurpose barriers for catalytic and filtration with more excellent stability, extended life, and enhanced efficiency. Therefore, a more rigorous theoretically and experimentally study is critical for gaining a basic knowledge of the characteristics and function of novel nanomaterials and exploring their uses in future revolutionary NF techniques.

Acknowledgements Rekha Sharma gratefully acknowledges the support from the Ministry of Human Resource Development Department of Higher Education, Government of India under the scheme of Establishment of Centre of Excellence for Training and Research in Frontier Areas of Science and Technology (FAST), for providing the necessary financial support to perform this study vide letter No, F. No. 5–5/201 4–TS. Vll.

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Chapter 7
Volatile Organic Compounds Removal by Nanofiltration from Groundwater

Mansi Sharma, Pragati Chauhan, Sapna Nehra, Rekha Sharma, and Dinesh Kumar

Abstract Groundwater has been used worldwide due to its ease of access and high quality. At present, groundwater quality has become a matter of concern because it is affected by multiple contaminants present in high concentrations such as nitrate, arsenic, fluoride, heavy metals, etc. Volatile organic compounds (VOCs) are the most prevalent hazardous chemicals that dissolve in water and vaporize in the air. Most of the VOCs are harmful to human health and the environment, such as trihalomethane, perchloroethylene, methyl tert-butyl ether, etc. Prolonged exposure causes dangerous diseases like damage liver, kidneys, nervous system, and some are carcinogenic. Agricultural runoff, septic tanks, landfill leachates, leaky sewage, industrial spillages, and agrochemicals release are the principal source of VOCs emission in groundwater. Oxidation, membrane, adsorption, air stripping, biological, and many other processes have been used to separate VOC. Despite all, nanofiltration (NF) is the newest and most advanced technology with high removal ratio of VOCs at trace level. This chapter begins by introducing different types of groundwater pollutants and NF. This chapter covers all the factors that affect the removal of VOCs. This chapter will cover the recent technologies and discuss the upcoming perspective, critical issues, applicability, and challenges in the presented evolving field.

Keywords Volatile organic compounds (VOCs) · Nanofiltration (NF) · Groundwater

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_7

Abbreviations

VOCs	Volatile organic compounds
NF	Nanofiltration
RO	Reverse osmosis
UF	Ultrafiltration
2D	Two-dimensional
MWCO	Molecular weight cut off

7.1 Introduction

Groundwater is the primary wellspring of freshwater everywhere in the world. According to the International Union of Hydrogeologists, about a third of the global population uses groundwater as drinking water, and it is used additionally for agricultural, domestic, and manufacturing uses. At present, the groundwater quality is affected by multiple contaminants in it. The term groundwater contaminants refer to the addition of unwanted substances present in groundwater. The contamination of ground as well as in surface water is different due to the fact the groundwater contamination stays odorless as well as colorless (De Toledo et al. 2019). There are many classes of contaminants found in groundwater. But mainly the groundwater contaminants are divided into three parts: (i) Biological (ii) Chemical (iii) Radioactive.

Over the last three decades, chemical contamination has been a consistent pattern in groundwater studies. The chemical contaminants include nitrogen contaminants (nitrate and nitrite), metals contaminants (chromium, lead, cadmium, mercury), metalloid contaminants (selenium, and arsenic), and the common organic contaminants (pesticides, halogenated compounds, hydrocarbons, plasticizers), etc. Among all volatile organic compounds (VOCs), hazardous chemicals dissolve in water and vaporize in the air under normal conditions. Since the 1980s, the consequences of VOCs in marine atmospheres have been studied notably. The surveys for VOC regulation from groundwater have been carried out in urban and rural regions. Due to their toxic and carcinogenic nature. At present, water quality has become a matter of concern due to these rapidly increasing contaminants (Li et al. 2021a, b).

At present, detection and the separation of evolving organic contaminants in water are getting a lot of concern. Several approaches have been established to eliminate organic pollutants from the ground and surface water, biological, chemical, and physical. The use of advanced oxidation processes is one available alternative, but high expenditure, operational expenses, and secondary pollution generation restrict their use in wastewater treatment. Additionally, adsorption can also be an effective physical treatment to remove volatile organic toxins. But most VOCs are toxic and prolonged exposure to them causes dangerous diseases such as damaged liver, kidney, nervous system, heart, mucous membrane, skin, and some are carcinogenic. For example, methyl palmitate exposure can lead to allergic skin reaction or skin irritation; toluene can damage the liver, nervous system, kidney, erythema, and vascular dilation. The International Agency for Research on Cancer (IARC) is characterized ethylbenzene as a carcinogen in class 1 and 2B because of its hazardous and carcinogenic nature to humans. The VOCs are produced via anthropogenic actions from domestic and industrial processes. For instance, chlorination, degreasing metal surface, food extraction, textile cleaning, applying fertilizers, pesticides, septic systems, fumigation, evaporating hydrocarbon fuel, landfill, pharmaceutical industries, petroleum storage, printing, traffic, and building materials. Oxidation, membrane, adsorption, air stripping, biological, and so many other processes have been used to separate VOC. Despite all, a separation system based on the membrane can lead to great attention due to its high efficacy, accessibility for up and downscaling, constant flow operation possibility, and low energy usage.

Recently, nanotechnology-based systems like nanofiltration have greater potential to eliminate charge particles, sediments, chemical effluents, hazardous chemicals, pathogens, bacteria, and impurities. Nanotechnology-based systems are the cost-effective and trending way to remediate contaminated water. There are several current methods to remove organic contaminants from water, including microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) (Rehan et al. 2020; Liao et al. 2021).

NF with pore size 0.001 micron (10^{-9} m) and the moderate pressure between 5 and 40 bars is generally used to remove hazardous or unwanted bivalent ions, toxic metals, solid dust, dyes, sugars, proteins, liquid droplets, multivalent ions, microorganisms like bacteria and viruses. Generally, NF is an intermediate process between ultrafiltration and reverse osmosis that eliminates a 1 nm size molecule. Nanofiltration act as a pressure-driven filtration with 300–500 Da molecular weight cut-off and displays characteristics between reverse osmosis and ultrafiltration. The term “NF” was first used in the 1970s, and this type of filtration was used for the first time in the second half of the 1980s. NF membranes have significant properties, such as being more permeable to monovalent ions than divalent ions and having a higher flux than RO films. There are many applications of NF membranes based on their significant properties, such as water treatment, pharmaceuticals, biotechnology, etc. The most important application of the NF membrane is water treatment. The remediation of wastewater is important because the demand for drinking water increases with the increasing population. Consequently, NF membranes provide more blessings than alternative membranes because of their improved consistency, integrity, generating large cycle times, and cost-effectiveness (Doménech et al. 2020; Bargeman 2021).

This section discusses how membranes are used to remove VOCs from groundwater, and NF explains which sources of contamination can result from these processes. Moreover, a discussion is also presented on volatile organic pollutants removal effectiveness. The removal of VOCs by dissimilar membrane modules and combined systems integrating membranes are also highlighted in this chapter.

7.2 Volatile Organic Compounds (VOCs)

Organic compounds with high vapor pressure and low water solubility are referred to as VOCs. VOCs mainly come from gasoline. The Environmental Protection Agency (EPA) states that VOCs are any carbon-based compound that participates in photochemical reactions in the atmosphere. VOCs have significant characteristics, such as higher mobility, volatility, and strong resistance to degradation. Because of these characteristics, VOCs travel long-distance once they release into the environment. VOCs can threaten the environment and human health. Aromatic and halogenated hydrocarbons including chloroethylene, ethylbenzene, benzene, toluene, xylene, trichloroethylene are the frequent VOCs detected in groundwater. Although, a huge number of VOCs are used to produce pharmaceuticals, refrigerants, and paints. VOCs are used as industrial solvents like trichloroethylene, methyl tert-butyl ether as fuel oxygenates in addition to the aid of merchandise produced thru chlorination in water treatment, which includes chloroform. There are frequent constituents like hydraulic fluids, petroleum fuels, dry-cleaning agents, and paint thinners. VOCs are the common and hazardous compounds for groundwater contaminants. They consist of various chemicals having short and long-term health effects (Lopes and Bender 1998; Li et al. 2019).

7.3 Types of Volatile Organic Compounds

According to their volatility, VOCs have been classified by the EPA, represented in Fig. 7.1. However, compounds in each group are considered toxic. The varying boiling point affects the adsorption of VOCs in the environment. Recently, The EPA renamed harmful outdoor emissions reactive organic compounds (ROGs) to Volatile Organic Compounds. Outdoor vapors aren't the only ones subject to VOC emission limits. Manufacturers must also pay close attention to the quality of indoor environments.

Irrespective of the environment, it is vital that manufacturers should understand what types of VOCs are being emitted, the location of the pollution, and the number of VOCs released. The following substances are not included in this classification: CO, CO_2, H_2CO_3, $(NH_4)_2CO_3$, and metallic carbides (MCs). According to the EPA, the VOCs are classified in the following:

7.3.1 *Very Volatile Organic Compounds (VVOCs)*

Organic compounds with boiling points between 0 and 50–100 °C are called very volatile organic compounds. These compounds frequently exist only as gas because

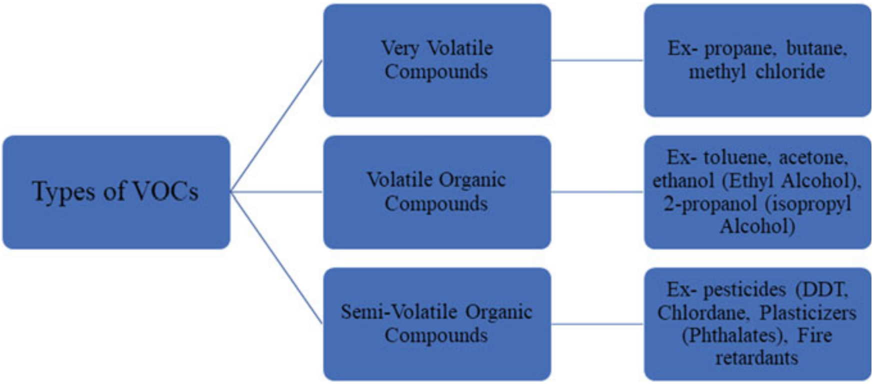

Fig. 7.1 The schematic diagram represents the types of VOCs

of their higher volatility. Propane, butane, methyl chloride are examples of very volatile organic compounds.

7.3.2 Volatile Organic Compounds (VOCs)

The term VOCs refers to those compounds with boiling points ranging from 50 to 260 °C. While the term volatile compound is frequently used for all volatile compounds, VOCs are defined as substances that vaporize at these temperatures. For example, d-limonene, formaldehyde, acetone, 2-propanol, ethanol, toluene, hexanal are standard volatile compounds.

7.3.3 Semi-volatile Organic Compounds (SVOCs)

Semi-volatile organic compounds have boiling points situated between 240–260 and 380–400 °C. The volatility of these chemicals is lower. A semi-volatile organic compound is an organic compound that is typically found in Phthalates (plasticizers), pesticides (chlordane, DDT, and fire retardants (Schieweck 2021; Wang et al. 2019; Xuet al. 2021).

7.4 VOCs in Groundwater: Sources and Effects

VOCs are natural and synthetic contaminants that can harm human health or the environment. VOC contaminants are produced by drug manufacturers, industrial

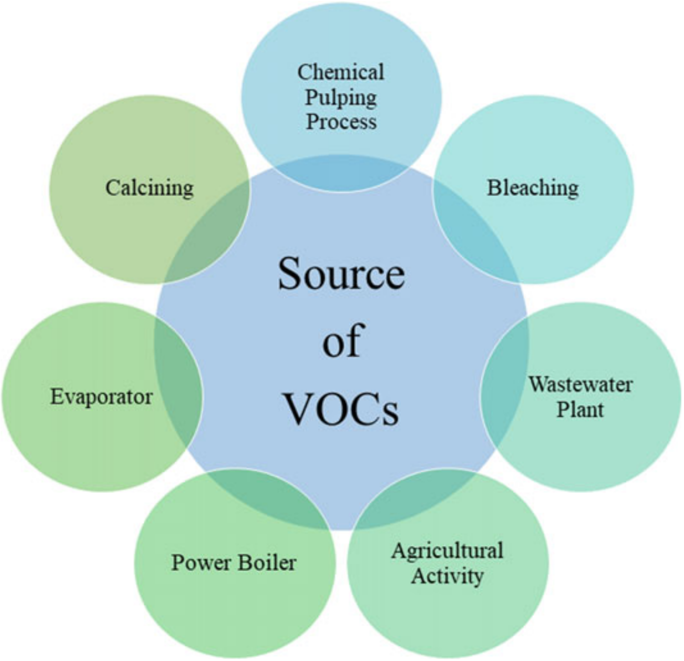

Fig. 7.2 The schematic diagram represents the groundwater source of VOCs

processes, agriculture, and everyday domestic actions. Pollutant sources are classified according to their origin. The groundwater sources of VOCs are shown in Fig. 7.2.

- Natural source and anthropogenetic source
- Point source and non-point source.

7.4.1 Natural and Anthropogenetic Sources

Groundwater defilement is a global problem to the increasing population. These VOCs originate mainly from natural and anthropogenic sources.

7.4.1.1 Natural Sources

Natural sources consist of natural causes, including discharge from vegetation, trees, forest fire, etc. The development of different contaminants in the environment is produced via biological processes, ecological actions, physical processes, and many natural marvels.

Natural processes such as floods and storms can also be assumed as the origin of organic contaminants in groundwater. Biological deposition, the transformation of dead plants and animal matter, is the biological process responsible for groundwater contamination. Agricultural sources are the extensive source of distribution of VOC's in the environment, such as the burning of agricultural waste, the fuels used in agriculture implements, and pesticide formulations, VOC's serve as completely inert constituents. Almost all plants can release VOCs through different organs such as fruits, flowers, leaves, stems, and roots (Singh et al. 2021).

Rock's weathering and further deposition activities in the atmosphere, such as rain, sleet, and hail, are examples of precipitation. In contrast, fog and aerosols from high to low altitudes are examples of physical activities. In groundwater, there are three main natural sources of organic matter:

- The organic matter deposits such as buried peat, kerogen, and coal
- Soil and sediment organic matter;
- Organic matter is present in waters infiltrating into the subsurface from rivers, lakes, and marine systems.

Several types of organic materials are produced during the biological decomposition of living matter. These materials are collectively referred to as organic natural materials. These natural organic materials are rich with hundreds of organic compounds, including fulvic and humic acids. When these compounds leach, they contaminate groundwater (Gautam et al. 2021). The source and the contaminants responsible for groundwater contamination are in Table 7.1.

7.4.1.2 Anthropogenic Sources

These sources include locations where pollutants are released due to human activity. Examples of such contaminants are synthetic and VOCs. There are many applications for synthetic organic compounds, such as industrial manufacturing, human and animal healthcare, food production, etc. The chemicals are synthesized from organic matter are pesticides, herbicides, or chemicals derived from industrial processes, urban stormwater runoff, and agricultural products. VOCs include chemicals such as cleaning agents, solvents, and by-products. Compounds, such as carbon tetrachloride, tetrachloroethylene, trichloroethylene, etc., are produced through industrial activities or found in petroleum products. Organic contaminants' nature and sources are always dependent on the activities and processes in the affiliated study region. For instance, organic contaminants in an urban area come from industrial actions, wastewater treatment plants, and sewage. Whereas agriculture and farming, as well as wasteland applications, take place in rural areas. As a result of these factors, human activities in rural areas produce different contaminants than those in urban areas. Natural phenomena occur in both urban–rural regions, illustrating that organic pollutants come from a similar source and nature (Cachada et al., 2013; Yan et al., 2021).

Table 7.1 The source of VOCs in the groundwater

Source	Contaminants	References
Agricultural activity	Diazinon, TCE and trichloromethane, malathion	Dehghani et al. (2019), Dehghani et al. (2017)
Bleaching	Acetone, chloroform, chloromethane, methylene chloride, trichloroethane	Zhao et al. (2014)
Calcining	Fine/coarse particulates	Ediz et al. (2010)
Chemical pulping	Alcohols, acetones, chloroform, terpenes, methanol, phenols, vinyl chloride, reduced sulphur compounds, Organo-chlorine compounds	Sjöström and Alén (1998)
Industrial activity	Benzene, carbon tetrachloride, para-dichlorobenzene, ortho dichlorobenzene, 1,1,2-Trichloroethane, 1,2-Dichloroethane	Li et al. (2021a, b)
Evaporator	Alcohol, phenols, terpenes	Mastelić et al. (1992)
Wastewater treatments	Acetones, chloroforms, methanol, phenols, spirits, terpenes	Hundža et al. (2019)
Power boilers	Coarse particulates, fly ash, NOx, SO_2	Shemwell et al. (2002)

7.4.2 Point and Non-point Source

Different routes are available to produce organic pollutants that enter the groundwater. They may be easily distinguished from each other if they are directly mixed into water bodies, while some can barely be distinguished from the rest. The following facts allow us to categorize contamination sources into points and non-points.

7.4.2.1 Point Sources

Pollution originating at discrete points is defined as point source pollution. An immobile site or fixed facility where pollutants are released or transferred through outfalls, pipes, or wastewater treatment facilities, and municipal wastewater treatment plants provide conveyance channels. A ‘point source’ is any identifiable, contained, and discrete conveyance that is discharged, including but not restricted to ditches, rolling stock, pipes, tunnels, well, conduits, discrete containers, boats, fissures, concentrated animal feeding operations, and, floating crafts. This definition does not include stormwater runoff from agriculture and return flows from irrigation agriculture (the United States Clean Water Act). Because the pollutants come from a specific and constrained location, point sources are easier to locate. Wastewater from homes, businesses, hospitals, waste disposal sites, oil refinery discharge pipes, and drainage ditches are examples of these sources (Lapworth et al. 2012).

7.4.2.2 Non-point Sources

A non-point source originates from multiple points rather than a single one. Although the site where pollutants are discharged is not defined or confined. The contamination from non-point sources is more difficult to recognize because the contaminants come from non-restricted regions, from multiple locations simultaneously. When the rain (or snowmelt) falls on the ground and mixes with contaminants that are natural and anthropogenic is the result of non-point source contamination. Consequently, those contaminants leach into the groundwater as pollutants move with the runoff. Agricultural activities are the significant leading source of pollution in general. Several fertilizers and agrochemicals, such as herbicides and pesticides, are generally applied to farmlands to improve productiveness during agricultural activities. These agrochemicals and fertilizers seep into the groundwater, contaminating it with organic matter. Correspondingly, discharge of harmful chemicals from urban regions, agricultural runoff, residues from poorly accomplished construction locations, forest lands, sewage system leakage, grease, oil, streambanks eroding, and energy production are all non-point sources (Trauth and Xanthopoulos 1997).

7.5 Processes of Groundwater Contamination by VOCs

The VOCs can evaporate in the air and easily dissolve in water. Once the hazardous VOCs discharge from their source, they enter the liquid phase. Dichloromethane is used to manufacture solvents. Trichloroethylene is used in drainage system cleaners. Tetrachloroethylene is used in the dry-cleaning industry. Significantly, the constituents' VOCs come in contact with the bottom of groundwater because they have a higher density than water at a concentration above residual saturation. Since the groundwater flow velocity is low or the contact area of the groundwater body is large, the downstream area has a low VOC concentration. The VOCs would be carried deep into the aquifers as a non-aqueous phase liquid, vaporizing at low concentrations as it was transported via the sub-surface. Hence, convection affects the movement of dissolved VOCs, hydrodynamic sub-stream-dependent absorption, dispersion, and transformation activities (Wiedemeier et al. 1999). The process of contamination by VOCs is shown in Fig. 7.3.

VOCs' relative solubility and volatility allow for widespread migration through the soil subsurface, where they are carried to groundwater and aquifer wells by dynamic hydrological cycles. The VOCs have been responsible for many negative health impacts, particularly in pregnant women and nursing. When these compounds are mixed into groundwater, they become extremely resolute. They can be transferred in soil vapors via unsaturated areas, rejuvenating as a nonaqueous-phase

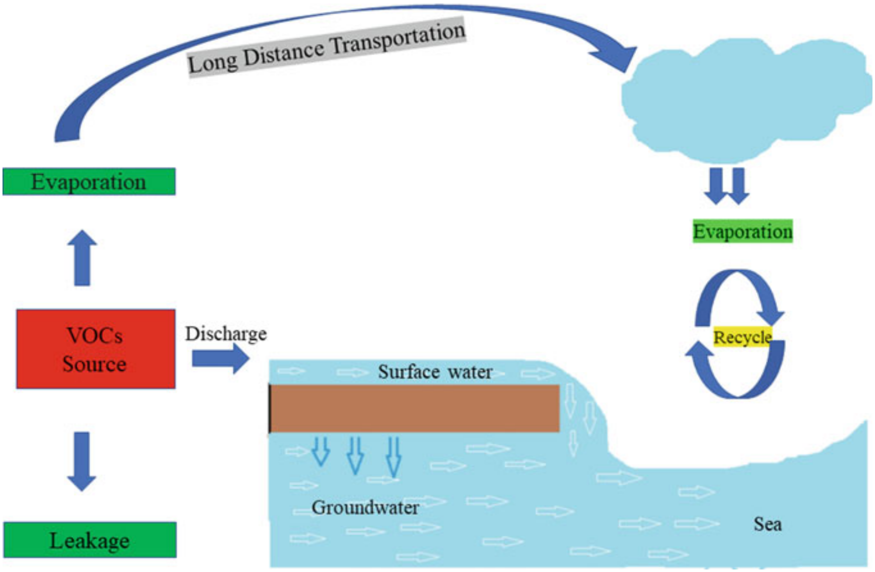

Fig. 7.3 The schematic diagram represents the process of groundwater contamination by VOCs

liquid. Bacteria tainted numerous VOCs in the aquifers, but others are resistant to the detriment and can be extended over a large area (Kim et al. 2019).

7.6 Factors Affecting Groundwater Contamination with VOCs

Factors that contribute to the contamination of groundwater with VOCs include.

- The concentration of VOCs in groundwater.
- Spilled or discharged many VOCs.
- The well's proximity to contaminant source.
- Well depth (deep wells suffer more damage from surface spills than shallow wells) (Pandey and Yadav 2018).

7.7 Impacts of VOCs

VOCs have several harmful impacts on the environment (global warming, acid rain) and human life. When the VOCs are exposed to the environment or sunlight, they react with carbon monoxide and nitrogen oxides to form tropospheric ozone, also known as ground-level smog. Ground-level smog is a term used to describe a type of smog that occurs at the earth's surface. The ozone present absorbs the harmful ultraviolet radiations coming from the sun in the stratosphere. But at ground level, VOCs can cause different diseases in plants, prevent fertilization, hinder seed production, and affect plants' growth (Abdul-Wahab et al. 2005).

VOCs can cause harmful health problems to humans when the VOCs are inhaled or absorbed by the skin. Health problems may include irritation in the nose, eyes, throat, coordination loss, headaches, impairment of kidney, liver, nervous system, heart, mucous membrane, skin, etc. Several VOCs act as carcinogens. They can cause cancer in humans. The proportion and nature of the health impacts will be determined by various factors, such as the level of exposure and the length of time spent in the environment. People have reported the following immediate symptoms after being exposed to certain organics: headaches, dizziness, memory impairment, visual disorder, allergic skin reaction, epistaxis, and irritation in the eye and respiratory tract described in Table 7.2.

Examples of some VOCs with their impact:

Benzene—Exposure to benzene can cause irritation in skin/eyes, CNS depression, impairments in the gastrointestinal, renal systems, cardiovascular, and neurological system, chromosomal abnormalities in bone marrow cells, and marginal lymphocytes. It also affects the immune system of humans, damaging antibody and leukocyte response.

Isoprene—At high concentrations, isoprene produces some toxicological effects such as CNS depression and respiratory effects. Here is some tentative animal research, along with neoplasms in the hematopoietic system, lung, and liver, in mice, which have provided some proof of carcinogenicity.

Trichloroethylene—Exposure to trichloroethylene caused eye inflammation, hypersensitivity, anorexia, immunosuppression, vomiting, neurological effects, cardiac arrhythmias, CNS depression, stroke, liver failure, coma, disturbances in the menstrual cycle, renal failure, reduced sperm quality, reduced prolificity, and death.

Phthalic acid—It causes hormone disturbance, immunotoxicity, genotoxicity, developmental toxicity, reproductive toxicity, and, neurotoxicity**.**

Isobutyl octyl ester—Isobutyl octyl ester affects or disturbs hormones that impair reproduction as well as development.

Nonanal—Nonanal is known as nonanaldehyde pelargonaldehyde or aldehyde C-9. It can cause severe diseases such as Ulcerative colitis, Celiac, Crohn's, Uremia, Autism.

m-fluoroanisol—m-fluoroanisol is a flammable liquid and vapor. It can cause eye irritation, skin inflammation, and respiratory irritation. Respiratory irritation can cause lung impairment.

1, 2 benzisothiazol-3-amine—Prolonged exposure to at least one, 2 benzisothiazol-3-amine can cause dermal ailments like skin sensitization and dermatitis due to allergic reactions. When inhaled, there have also been cases of asthma.

1, 6-octadien-3-ol,3,7, -dimethyl—1, 6-octadien-3-ol,3,7, -dimethyl can cause irritation in eye, nose, skin.

Table 7.2 The VOCs with their impact on human health

VOC	Health impact	References
Benzene	Dermal/ocular irritation, CNS depression, cardiovascular, gastrointestinal, neurological, and renal impairment, anemia decrease in blood platelets Increase risk of cancer	ATSDR T (2000)
Acrolein	Eye irritation	Keshava et al. (2020)
Tetrachloroethylene	Loss of color vision Neurobehavioral effects	Bari and Kindzierski (2018)
Xylene	Nervous system damage	Fay et al. (2007)
Trichloroethylene	Liver problems, increased risk of cancer	Todd et al. (2019)
Toluene	Nervous system, kidney, or liver problems	Davidson et al. 2021)
Cis-1,2-dichloroethylene (1,2-DCE), trans-1,2-dichloroethylene, (1,2- DCE) dichloromethane (DCM)	Liver problems	De Weerd et al. (1998)
Chlorobenzene ortho-dichlorobenzene	Liver problems, increased risk of cancer	Ifenna and Frank (2020)
Crotonaldehyde	Eye, skin, and respiratory irritation	Yang et al. (2013)
N, N-imethylformamide	Hepatic toxicity	Li and Zeng (2019)
1-Bromopropane	Oxidative stress, genotoxic effects	Stelljes et al. (2019)
Ethylbenzene	Hematological effects, chromosomal aberrations	Cakmak et al. (2020)
Acrylamide	Central nervous system (CNS) deficits	Tabeshpour et al. (2020)
Isoprene	Asphyxiant, CNS depressant	Li et al. (2021a, b)
Ethylene oxide	Reproductive damage	Gresie-Brusin et al. (2007)

2-octenal, (E)—2-octenal, (E) can harm or damage the eye's respiratory as well as cause skin problems.

IARC characterized acrylonitrile, benzene, isoprene, ethylbenzene, 1,3-butadiene, N, N-dimethylformamide, trichloroethylene, acrylamide, as well as styrene as cancer-causing agents (Koniecki et al. 2011; Francavilla et al. 2014; Odipe et al. 2020; Li et al. 2021a, b).

7.8 Membrane-Based Technology for VOCs Removal

Compared to surface waters, the frequency and pollutant concentration detected in groundwaters decreases. On the other hand, Polluted groundwater must be treated because it poses a serious health risk to humans. To eliminate organic pollutants, a variety of physical, chemical, thermal, biological, remediation methods can be used. While chemical methods, like advanced oxidation method and photochemical degradation, have some limitations such as low efficiency, degradation products, high expenditure, difficult operation, and by-product production. At the same time, adsorption and membrane treatment does not produce any by-products in the physical separation process. Despite physical adsorption, the membrane technology is efficient and cost-effective for excluding organic pollutants because physical adsorption methods have expensive steps to redevelop the adsorbent.

Membrane technology has gained much attention in the organic pollutant removal field due to its scalability, high effluent performance, modularity, efficiency, and versatility. The recent technologies used for the physical elimination of organic pollutants from water contain microfiltration, ultrafiltration, NF, reverse osmosis, and forward osmosis systems (Taheran et al. 2016; Zhang et al. 2020; Zainab et al. 2020).

7.8.1 Nanofiltration Technology for the Removal of VOCs

NF membranes have made great progress since their invention in the late 1980s. It is a hybrid of both UF and RO. NF membranes are gaining popularity as a separation tool due to their versatility. Their pores are typically one nm in diameter, and their molecular weight cut-off is about 100–5000 Da. NF membranes, for instance, consist of carboxylic and sulfonic acid components that ionize when they are in contact with an aqueous feed solution. Whether functional groups dissociate on their surfaces or if charged solutes adsorb, NF membranes have a medium level of charge. NF membranes offer a higher rejection of multivalent inorganic ions and tiny organic molecules because they do not undergo phase shifts at low pressure. Separations using this method are particularly modest in terms of selectivity and fee-effectiveness in evaluation to traditional separation methods (Oatley-Radcliffe et al. 2017).

NF membranes have separation performance among reverse osmosis and ultrafiltration membranes with molecular weight cut-offs (MWCO) 200–1000 Da and pore sizes ranging from 0.5 to 2 nm. NF membranes exhibit a greater permeation flux and simultaneously reject organic molecules and polyvalent salts. The operating pressure required by NF membranes is lower than that of RO membranes, thereby reducing both capital and operating costs. These membranes have high efficiency for personal care and therapeutic products removal. The exclusion mechanism of personal care and therapeutic products is generally determined via the membrane and the nature of the personal care and therapeutic products. Three mechanisms are involved in personal care and therapeutic products removal: (i) In polymeric membranes, size exclusion is the main mechanism, (ii) As membranes are hydrophobic, adsorption occurs by hydrophobic interaction. This latter mechanism is relatively permanent, (iii) A membrane's surface can be electrostatically excluded (Depending on the molecules and charges attached). Adsorption by hydrophobic molecules and the exclusion of sizes are the controlling mechanisms for the removal of therapeutic and personal care products that are neutral. Still, the electrostatic exclusion is the guiding mechanism for excluding charged personal care and therapeutic products. NF membrane can eliminate more organic pollutants than a UF membrane due to its wider molecular weight cut-off range, thus improving the water quality and yield.

Furthermore, at the same operating pressure, permeation flux and effectiveness of these membranes are higher than reverse osmosis. NF and RO use high pressures. It is resulting in scaling, fouling, and rising treatment costs. At the same time, forwarding osmosis gained more attention because a semipermeable membrane allows separation due to a draw solution causing an osmotic gradient. Despite the advantages of membranes, contaminants are isolated through membranes and not degraded, resulting in massive residues that must be stained or transformed. Otherwise, the resulting concentration polarisation will impact the execution of the membrane. The membrane bioreactor (MBR) is a creative innovation to tackle this problem. It often employs membrane technologies within the bioremediation process to supply high-quality effluent (Madsen et al. 2015; Gu et al. 2018; Delgado et al. 2019).

7.8.2 Membrane Selection

The feed water composition and the desired permeate quality largely influence membrane selection.

The performance of the process is determined not only by the performance of the membrane but also by the system design, which includes pre-and post-treatment (Pearce 2007).

7.8.3 Membrane Material and Module Type

Different types of materials used in NF membrane such as polyvinylidene fluoride, polysulfone, nylon, cellulose acetate, polyethersulfone, polytetrafluoroethylene, polyphenylsulfone, ceramic metals, carbon nanotubes, etc. The membrane types are mainly classified into the following:

- Tubular membrane
- Capillary membrane
- Membranes with a flat sheet
- Asymmetric membranes with a flat sheet

- Hollow fiber membrane modules
- Modules with spiral wounds.

Module with spiral wounds is commonly used for NF. It is more sensitive towards contamination and cost-effective. The surface area of the spiral membrane is larger than the tubular membrane and has greater capacity. The fouling potential of the water can be reduced by removing as many colloidal materials, suspended solids, and further components that can cause membrane fouling using spiral-wound modules. Chemical cleans are generally ineffective at removing colloids and particulates associated with membranes from spiral wound modules. Tubular membranes do not usually require pre-treatment because peripheral water velocity influences its formation during the membrane cake formation. Compared to spiral-wound modules, tubular modules are much easier to clean. The pre-treatment extends the membrane's lifespan, and installation takes longer to produce. It became easier to manage and was less expensive to work (Obotey Ezugbe and Rathilal 2020).

7.8.4 Nanofiltration Treatment Systems

The NF membrane system is divided into three parts: pre-treatment, membrane processing, and post-treatment, shown in Fig. 7.4. Significantly, a unique system with one influent (feed) and two effluent (permeate and concentrate) stream. Almost all water sources must be pre-treated before RO and NF membrane systems to prevent the precipitation of sparingly soluble salts. Several activities in the post-treatment process are usually prevalent in ordinary drinking water treatment, such as exposure to air, degasification, pH alteration, the addition of corrosion control chemicals, fluoridation, and disinfection (Deen 1987; Bergman 2007).

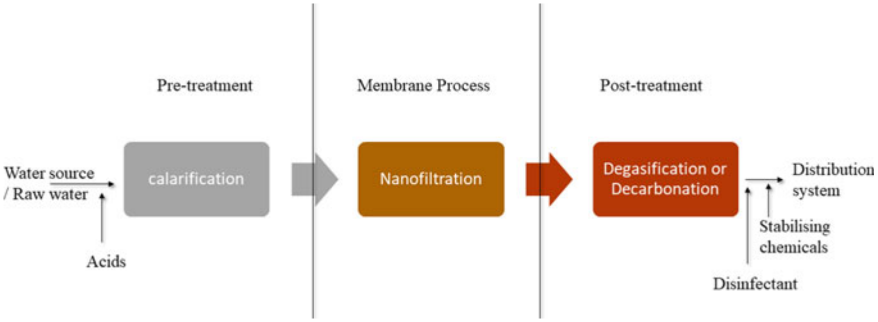

Fig. 7.4 Represents the flow chart of the NF membrane system

7.8.5 NF Separation Mechanisms

NF is a very complex method. This is ruled with the aid of micro hydrodynamic and interfacial tactics that arise on the membrane's surface and within its pores. Several effects like Donnan effects, steric, dielectric, as well as transport effects are significant in the pollutant's separation via NF. The Donnan effect explains the membrane potential and equilibria during the interaction between a membrane interface and charged solute. The membrane acquires the charge state due to the dissociation of ionizable groups at the membrane's surface and in its pore morphology. According to the membrane composition, the ionizable groups can be acidic, basic, or a mixture of both. Their dissociation from the membrane's surface is heavily influenced by the surrounding solution's amphoteric nature and pH. It implies that an amphoteric membrane will also have an isoelectric point at a specific pH level. In addition to the process described previously, the NF membrane may undergo weak ion interchange. However, a small variation in the membrane charge is due to the ion's adsorption of the containing solutions on the surface membrane. As a result, electrostatic forces are affected by the membrane charge and ion valence. These factors can vary due to the factors listed above. Subsequently, a lesser-known effect is a dielectric effect, though several hypotheses have been proposed to explain it.

Consequently, the interaction between the pores and the solution passing through them significantly impacts the solute's movement via NF membranes. As a result, solutes' free movement is believed to be impeded. Besides, it is classified as a transport effect. This mode of transportation is made up of both convective and diffuse components. It affects the complete passage outcome. The NF membranes have been difficult to study due to the near-atomic sizes of the active layer membrane. Therefore, the separation mechanism has been ambiguous and debated, with the dielectric exclusion precept posing the most challenges.

Although evaluating the efficiency of NF/RO membranes in refusing volatile organic chemicals, it is important to examine membrane permeate flux as a function of filtration time for samples obtained from numerous locations. As per the conclusions, the NF membrane can effectively remove various VOCs found in groundwater. In comparison to volatile hydrophobic compounds, volatile hydrophilic compounds are easily eliminated by NF membrane, according to the performance of NF. Hydrophilic mixtures can be adequately discharged thru reverse osmosis and NF films utilizing the steric block (size exclusion component). In contrast, RO NF layers can be adsorbed hydrophobic mixture afterward, and the thick polymeric framework will diffuse throughout. These mixtures have a lesser expulsion ratio compared to the hydrophilic mixture. According to the study, membrane fouling in NF-90 has a significant impact on eliminating VOCs (Donnan 1995; Ernst et al. 2000; Bowen and Welfoot 2002; Oatley et al. 2012; Mohammad et al. 2015; Roy and Warsinger 2017).

The solution diffusion model is divided into the following phases:

- Feed side absorption,
- Membrane facilitates diffusion,
- Permeate side desorption.

Additionally, It can be used to explain the flow of the fluid across the NF membrane. The solution-diffusion concept has garnered greater attention in recent decades as a viable alternative to the existing concepts. It requires fewer observable characteristics than a NF membrane, such as membrane charge and pore radius. These are not easily determined. The model is based on the premise that the chemical potential gradient is continuous. At the membrane interface, adsorption and desorption occur at a higher rate than diffusion. Absorption–desorption doesn't affect the overall transport rate of molecules. Therefore, the permeation rate depends on the diffusion process, in response to the concentration gradient and preferably without any pressure gradient within the membrane. There is no difference in the mechanisms operating on 2D nanomaterials compared to other membrane types, but their relative importance remains a topic of discussion among researchers (Fierro et al. 2012; Qian et al. 2020a, b).

7.9 Conclusion and Future Outlook

In the twenty-first century, one of the greatest problems facing today is environmental contamination. The contamination in the water increases gradually due to a fast expansion in population, industrialization, urbanization in arid and coastal regions. Groundwater infiltrated with volatile organic contaminants has serious health effects on humans and damages the environment due to its specific properties such as low biodegradability and hydrophobicity. As a result, there is an instant necessity to find effective solutions. NF's efficacy in water and wastewater treatment has become one of the most reliable standard techniques for obtaining high-quality drinking water. NF is a cost-effective and efficient way to eliminate contaminants from water such as chemical effluents, pathogens, sediments, organic pollutants, and arsenic. Over the last few years, there has been substantial advancement in the growth of innovative materials and methods in the field of NF. As a result, adsorption, advanced oxidation methods, and membrane technologies are proposed as advanced treatment processes. Advanced oxidation and photochemical degradation methods have limitations like lower efficacy, greater cost, arduous process, defecation products, and the production of by-products. For organic pollutant removal, technologies based membranes are a more efficient, feasible, affordable method that produces no waste. As a result of its lower energy consumption, enhanced water permeability, and high removal efficiency, the NF membranes are the better choice for removing organic pollutants than the reverse osmosis membrane. NF technology has limitations like insufficient separation, chemical resistance, membrane lifetime, insufficient rejection for individual compounds, treatment of concentrate. In preparing a new generation of NF, advanced 2D nanomaterials like graphene oxide, boron nitride, and graphene will be used.

Acknowledgements Rekha Sharma gratefully acknowledges the support from the Ministry of Human Resource Development Department of Higher Education, Government of India under the scheme of Establishment of Centre of Excellence for Training and Research in Frontier Areas of Science and Technology (FAST), for providing the necessary financial support to perform this study vide letter No. F. No. 5–5/201 4–TS. Vll.

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Chapter 8
Desalination Through Nanofiltration Technique

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Abstract Seawater or saline water is desalinated by removing salt. Desalination also explains the process of elimination of inorganic ions from a solution to generate safe and potable water. Within this category of desalination, nanofiltration (NF) plays an important role as a subset of membrane processes. A decent prediction model for NF membrane growth can be used for membrane characterization, process modeling, optimization, membrane design and application. As a result of the integrated modeling work, researchers and developers have been able to study different aspects of the phenomenon of separation, formation, adaptation of desalination processes, to smaller extensions and applications possible in the real world. The future of NF membrane development must revolve around solving existing industrial barriers to its development. Consequently, strong academic-industry collaboration should be emphasized. This chapter begins with introducing the desalination and application of various membrane technologies for desalination. This chapter discusses the latest advances in NF membrane technology combined with the fouling of membranes and seawater desalination.

Keywords Ultrafiltration · Reverse osmosis · Nanofiltration · Seawater · Diffusion

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_8

Abbreviations

NF	Nanofiltration
RO	Reverse osmosis
UF	Ultrafiltration
TDS	Total dissolved solids
DSPM	Donnan-Steric-Pore model
FO-NF	Forward osmosis nanofiltration
NF-SWRO	Nanofiltration-sea water reverse osmosis
NF-SWRO-MD	Nanofiltration-sea water reverse osmosis membrane distillation
NF-MSF	Nanofiltration multi-stage flash

8.1 Introduction

Nanofiltration membranes are hybrid pressurized membranes with ultrafiltration membranes and reverse osmosis properties. High flux, comparatively low investment, high maintenance of polyvalent anion salts, minimal operation pressure, and maintenance expenses are just a few of the benefits of nanofiltration. Due to these benefits, the usage of nanofiltration has expanded over the world (Lu et al. 2002). This Nanofiltration (NF) technology was developed in the 1970s, a decade that saw the first RO membranes with a decent water flux and low pressure. Therefore, RO was associated with significant energy costs due to the high pressure utilized in the past. It would be significant for separation technology to develop membranes with greater permeability and fewer rejections of dissolved components. Nanofiltration membranes are a type of low-pressure reverse osmosis membrane (Bruggen and Vandecasteele 2003). First applications were documented in the second half of the 1980s when NF was already established (Conlon and McClellan 1989; Schaep et al. 1998). The method of eliminating salt from brackish and seawater is referred to as desalination. Similarly, desalination is the process of removing different types of inorganic ions from the solution by end goal producing clean and potable water in a wider context. NF, a subset of membrane techniques, has gained widespread usage in the desalination field. For instance, NF was employed as a pretreatment for dual RO and thermal processes in a detoxification plant. It leads to lower expenses and more desalted seawater production. Despite this, the method is still environmentally beneficial (Al-Sofi et al. 1998). Nanofiltration pretreatment of seawater feed to RO/thermal tactics avoids scaling through casting off scale-forming hardness ions membrane fouling in RO procedures via putting off turbidity and microorganism. It is projected to minimize the necessary pressure to behavior a RO plant via lowering the saltwater input total dissolved solids (TDS) (Al-Sofi 2001). Researchers intend to investigate a large yet innovative way to improve the role of NF in detoxification method. The foremost topic of the research is the advancement of NF membrane modeling with its simultaneous application for characterization, technique modeling, optimization, membrane design, and packages. Incorporating modeling work into several areas of research and development leads to this effort, ranging from the fundamental understanding of separation phenomena to the design and optimization of desalination processes. This field has one of the highest scientific papers worldwide (ISI citation report 2007). Significantly, this research aims to findings from previous studies in NF. Recent research has focused on fundamental knowledge of separation mechanisms and linked that understanding to targeted applications. The global need for clean water has risen steadily and rapidly because of the rising population, enhanced living conditions and requirements, and the growth of agricultural or industrial operations. Pure water scarcity is acknowledged as a universal hazard to agricultural, manufacturing, domestic activities, as well as to society's fundamental existence. To avert this threat, immediate action is necessary. Desalination methods, which convert large, available, but useless water resources, such as brackish or seawater, into a useable form, have been extensively researched to address these rising demands for clean water. The relatively high manufacturing costs of seawater desalination technologies (thermal or membrane-based) are a key hurdle to widespread usage. Conversely, several recent improvements in seawater detoxification technology have led to substantial cost reductions in water production. The use of NF as a preliminary treatment technology for thermal and membrane-based processes is one of the examples of such progress. The elimination of scale-forming substances (mostly sulfates) that impede desalting procedures is the goal of NF. Divalent ion rejection is typically 75–99% for NF membranes, while monovalent ion denial is usually 30–50% (Hilal et al. 2003). The use of nanofiltration is insufficient on its own to bring the TDS content down to the legal edge of 150 mg/L. The presence and quantities of divalent ions rely on brine temperature constraints in thermal seawater detoxification procedures, for example, MED and MSF, as illustrated in Fig. 8.1. Scaling begins with crystal development, nucleation, and precipitation under supersaturation circumstances (Wang et al. 2008). The pace of the scale manufacturing process is influenced by ion concentrations, ph, temperature, and TDS. In thermal seawater desalination plants, NF could eradicate the scaling species, which enhances the top brine temperature (TBT). Although, in MED or MSF technologies, the number of phases increased, resulting in a higher gain output ratio (GOR) (World Health Organization 1996). Now, anti-scaling chemicals are used to prevent scaling. In MSF and MED method, the scalants are divided into two categories in MED or MSF methodologies:

- Alkaline scales—Calcium carbonate and magnesium hydroxide cause alkaline scale.
- Non-alkaline scales—calcium sulfate causes a non-alkaline scale (Voutchkov 2012).

In MSF, the TBT is often less than 112 °C, while in MED, it is less than 66 °C. The utilization of nanofiltration membrane softening to eliminate bivalent ions as a feasible preliminary treatment for purification methods has been investigated. The

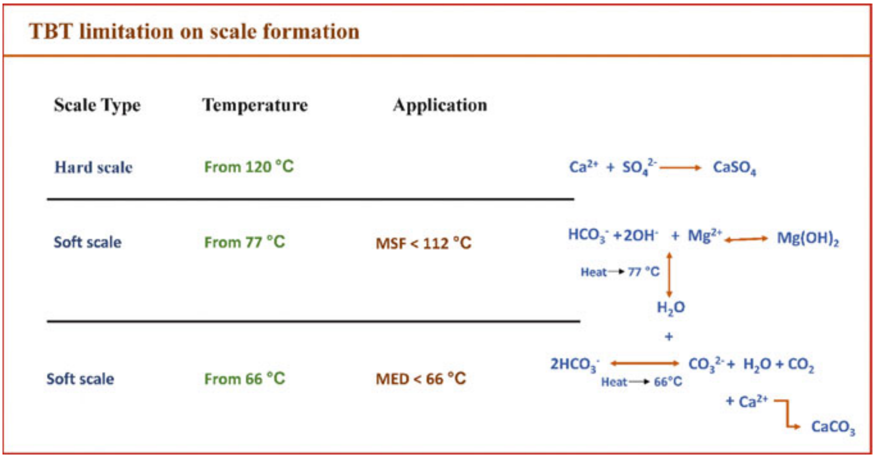

Fig. 8.1 Represents the Scale deposition and its chemical relation in thermal desalination of seawater

current segment would permit a thermal desalination plant to operate at a higher TBT of one hundred seventy degrees Celsius.

NF membranes have been the subject of several literature reviews (Hilal et al. 2004; Van der Bruggen et al. 2008; Cotruvo et al. 2010; Altaee et al. 2013; Mohammad et al. 2015). Several studies reported using membranes of NF as a pretreatment in desalination processes. The pore size and roughness, as well as their performance, have been studied. Nanofiltration membrane was used as the initial treatment step in the desalination of brackish water (Hilal et al. 2004). According to the authors, NF membranes eliminated turbidity, dissolved salts in a portion, and bacteria. Fouling is a problem with NF membranes, which results in excessive energy consumption and short lifespan. The advent of NF membranes through interfacial polymerization and the shipping of ionic ions via NF membranes had been defined using the Nernst–Planck equation (Mohammad et al. 2015). The authors also discussed how to prevent and mitigate NF membrane fouling. NF's drawbacks were examined, i.e., membrane fouling difficulties and mitigation, and simulations of solute transport models (Bruggen et al. 2008). The flow, rejection, and fouling of NF membranes, were investigated (Luo and Wan 2013). A rise in pH occurs due to a rise in the membrane's pore size. Besides swelling, charge shift, and electrostatic action, pH may alter membrane performance for various reasons. NF can be used as a preliminary treatment stage for seawater desalination. It begins with an examination of the NF membrane's performance, including the elimination of ions, membrane characterization, and permeation flux. The efficiency of NF as a seawater desalination pretreatment method is then highlighted and compared to other pretreatment approaches. The concept of transportation of ions via nanofiltration is next considered, surveyed through membrane fouling, which is the most significant operational obstacle. The broad extent of this study demonstrates the possibility for future research employing NF.

8.2 Process Modelling for Nanofiltration Membrane

A desirable predictive model will allow customers to obtain membrane characteristics, expect procedure presentation, and optimize the process. The capability to increase such modeling strategies efficiently will result in fewer experimentations and ultimately store time and money inside the advanced degree of a procedure (Bruggen et al. 2008). The model's framework was first proposed in more than one study in the overdue 1990s, primarily based on the extended Nernst-Planck equation and Donnan equilibrium. (Hilal et al. 2003; Luo and Wan 2013). The Donnan-Steric-Pore model (DSPM) was developed and is widely acknowledged as one of the maximum successful fashions for forecasting ionic rejection behavior in nanofiltration membranes. The work has been prolonged through a modified DSPM to predict the rejection of aggregates of charged ions in NF membrane. This is based on the extended Nernst-Planck equation with the incorporation of price and steric effects for the shipping of ions in the membrane and incorporation of attention polarization effect for the aggregate of charged ions (Bowen et al. 1997; Bowen and Mohammad 1998). The permeate flux can be decided using this technique primarily based on the concentration and solutes at the membrane floor. The DSPM-DE model has recently been modified to include the osmotic impact caused by high salt concentrations in desalination applications (Bowen and Mohammad 1998). The improved model was discovered to be able to predict the rejection and go with the flow of unmarried salt answers, which includes NaCl, Na_2SO_4, and $MgCl_2$ at concentrations starting from 5000 to 2000 mg/L, which might be ordinary values in marine waters. The salt concentrations employed in the study were often higher than those reported in earlier investigations. The concentrations have been selected to mimic common ions concentrations in seawater. The osmotic pressure distinction brought on a flux drop at this kind of excessive awareness, which turned into fairly sizable compared to natural water flux. The Pitzer and Vant Hoff equations were used to compute the osmotic pressure. In this investigation, the concentration range was used; both equations could estimate the difference in osmotic pressure with negligible deviations. The DSPM-DE model and the Vant Hoff equation can be utilized to forecast permeate flux and salt rejection. DSPM-DE changed into capable of estimating reaction fluxes and rejections moderately properly for diverse salts clearly via using the suitable parameters derived from the NaCl rejection information. Researchers used simulated and actual saltwater to test six commercial NF membranes to find the best membranes and operating parameters for removing several ionic species that cause scale formation in SWRO, including, $CaSO_4$, $Mg(OH)_2$, and $CaCO_3$ (Mohammad 2002; Mohammad et al. 2007; Llenas et al. 2013). The authors measured the membrane's roughness and size of the pores. Neutral solutes like glycerin, glucose, and 2-propanol as control solutes, pore sizes of membranes were determined. In this case, the membrane roughness was determined by AFM. Inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography, and total carbon analysis was utilized to determine anion and cation concentrations and boron, strontium, and inorganic carbon. The working pressure ranged from 2 to 20 bar. The elimination of divalent ions that cause scale was found to be high in all membranes examined. Further, monovalent ions were rejected in actual saltwater more than synthetic seawater, although scale-forming ions were rejected essentially the same way across all membranes. A surface texture or the difference between the membrane's real surface topography and a smooth atomically flat surface is measured by its roughness. As a result, the effective surface area of the membrane is defined by its surface roughness. Membrane water permeability is determined by surface shapes, such as surface area and protuberance thickness. A membrane with a larger floor vicinity or smaller thickness has higher water permeability, while morphologies of membranes with numerous water permeabilities are compared (Llenas et al. 2013). The NF membranes' performance in seawater and brackish water was investigated (Hilal et al. 2005; Kurihara et al. 2015). They used three industrial NF membranes to handle (sodium chloride) salt solution at concentrations of up to twenty-five thousand ppm (NF30, NF90, and NF270). Using AFM, they could decide the membranes' pore size and their distribution. The smallest pore size, porosity, and maximum roughness are found in NF90. The average pore size with a normal variation of NF30 is 0.61 and 0.12 nm. The pore size varies between 0.43 and 0.90 nm. NF30 has the largest pore size and the smallest porosity and roughness. Finally, the pore size of NF270 is the largest, as well as these, have moderate unpleasantness and porosity. The applied strain differed somewhere between 2 and 9 bar in the layer tests. Salt dismissal and penetration motion expanded with expanding pressure and diminishing salt fixation for every tried layer. Because of its smallest pore size, the NF90 membrane is the best choice. It has a maximum rejection rate of 95%. NF30 exhibited the lowermost refusal at only 6%. The NF90 membrane rejects salt 40% at twenty-five thousand ppm salinities, while the NF30 membranes dropped to 3%. The NF270 membrane had a salt rejection rate of 11–29%. The membrane with the lowest porosity and flux was the NF30, whereas the NF270 membrane had the highest flux rate. Three distinct NF films, such as SR90, NF90, and ERN were examined in seawater detoxification applying an across-stream course of action (Van Bruggen et al. 2008; Ryabchikov et al. 2012). The operating pressures ranged from 8 to 18 atm. Cl^-, SO_4^{2-}, Ca^{2+}, and Mg^{2+} concentrations, pH, and the solution's temperature were all monitored. With increasing pressure, the applied flux, as well as salt rejection, increased. A total of 30–40% of the salt was rejected, while salts that influence water hardness (Ca^{2+} and Mg^{2+}) were rejected 90–95%. Hilal et al. (2005) and González et al. (2015) used NF270 membranes to examine the rejection of sulfates and chlorides in extremely saturated saline water. Scanning electron microscopy determined the membrane's effective layer, 0.70 and 0.27 m thick. The rejection rate for sulfate was 96%, but it was only 11% for chloride. With increasing chloride content, the scientists found that sulfate rejection decreased.

The efficacy of NF membranes (NE40-90) to eliminate ions from diluted seawater at four to eight bar working pressures turned into tested (Izadpanah and Javidnia 2012;

Ryabchikov et al. 2012). TDS levels of 9750, 7220, and 4970 mg/L were measured in three diluted seawater samples. Calcium, magnesium, and total hardness were all rejected in the 96–98% range, whereas TDS was rejected at 79–89%. Nevertheless, at much higher pressures, the rejection dropped slightly. The NF membranes permeate flux and salt refusal increased. Diffusion and convection play a role in NF membrane transport (Pérez-González et al. 2015). As pressure rises, convection defeats diffusion because of increased water flux and refusal. Nevertheless, the rejection rate reduces as pressure rises (Izadpanah and Javidnia 2012). With increasing pressure, the flux and polarisation modulus both increased. Increased polarisation modulus overcomes the high flux impact, resulting in much less rejection at extraordinarily high pressures (e.g., 34 bar).

The effects of different ion compositions on NF rejection have been studied (Kaewsuk et al. 2012; Liu et al. 2014). The rejection of anions increases as the salt concentration rises, but the rejection of cations decreases. At high cation concentrations, total ion rejection is extensive. As cation and anion concentrations accelerated, the flux decreased. The rejection of magnesium ions was inspired extra by chloride ions than the rejection of calcium ions. At low quantities, sulfate and bicarbonate ions had a high electrostatic repulsion with the NF membrane. The diffusion of water and ions, in addition to the polymer separation layer, suffered from temperature modifications in the membrane (Mänttäri et al. 2002; Harrison et al. 2007; Nilsson et al. 2008).

The polymer chain inside the separation layer grows and becomes more effective at excessive temperatures, resulting in large membrane pore diameters. Water and ion diffusion improve as nicely at excessive temperatures, as shown in Fig. 8.2. As a result, the permeate flux rises as nicely as the temperature rises. In the interim, maximum ions' rejection will increase, but Na^+ and Cl^- ions' rejection lowers slightly. Because Na^+ and Cl^- ions are smaller than other ions, they can effortlessly pass thru the NF membrane.

The efficacy of dual-degree NF-NF membranes has been the concern of numerous investigations (Awerbuch 2006; Nilsson et al. 2008; Song et al. 2013). An NF system operating with two stages, with the first stage using 35 bar and the second stage using 20 bar, was tested. Permeate flux, ion rejection, and TDS all increase as the pressure

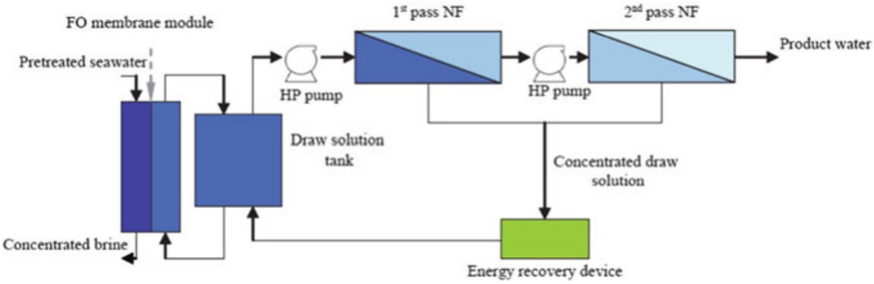

Fig. 8.2 An illustration of a hybrid FO-NF system for desalinating seawater

increases. Pressure had a stronger effect than temperature and feed go with the flow amount. Because most of the scaling ions were eliminated inside the first stage, the scaling index becomes decreases inside the second stage. A study was conducted on NF membranes (dual-stage) for desalinating saltwater (Nilsson et al. 2008). Three types of membranes such as TS80, NF90, and NE90 were used to examine water flux, ion rejection, and fouling. The working pressure ranged between 10 and 40 bar. The consequences validated that the seawater became desalinated using dual-stage NF membranes. A two-stage NF system was studied for seawater desalination (Vuong 2006; Awerbuch 2006). The permeation from the first stage was used to feed the second stage. The first and second levels had working pressures of 36 and 20 bar, respectively. Divalent ions had been rejected more strongly than monovalent ions.

8.3 NF Membrane Performance in Integrated Systems

8.3.1 NF-UF

An incorporated film framework (UF-NF) was used for five hundred hours to evaluate the presence of nanofiltration layers in saltwater purification preliminary treatment (Al-Rawajfeh 2011; Song et al. 2012). Two cleaning sessions were held (after 280 and 440 h). The working pressure becomes, to begin with, 20.3 bar; however, extended to 20.5 bar at some stage in the second period (after the primary cleaning). The pressure increased to 20.6 bar in the third period (after the second cleaning). Fouling had occurred, as evidenced by the higher operating pressure. Chemically cleansing membrane fouling is difficult. Before and after the chemical washing, salt refusal and permeate flux declined with time. A UF-dual-stage, combined system's performance was assessed (Kaya et al. 2015; Su et al. 2015). The turbidity of the UF filtrate was virtually nil. The permeate flux of the dual-stage NF reduced as the feed temperature dropped. The amount of salt rejected and the amount of electricity fed on grew because the running temperature rose. Divalent ions were rejected more than 95 times.

8.3.2 Ion Exchange and NF

Scale formation was examined in the MSF and RO desalination processes by using Preliminary treatment with salt precipitation (Al-Rawajfeh 2011; Song et al. 2013; Abdelkader et al. 2018). They experimented with four alternative setups. Sulfate scaling was shown to be considered in the MSF process, while carbonate scaling was found to be important in the RO process. NF was also shown to eliminate sulfate ions effectively. There have also been studies examining the effectiveness of ion exchange with a mixed approach (IX) and NF processes in detoxifying brackish as

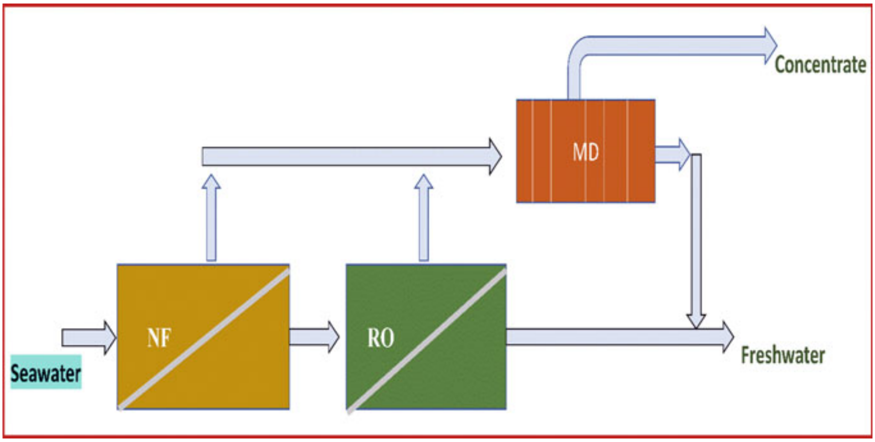

Fig. 8.3 A flow diagram of the hybrid NF-RO-MD desalination process

well as seawater (Al-Sofi et al. 1998; Hassan et al. 1998; Hamed et al. 2005, 2009; Hamed 2005; Hassan 2006). The supply for the NF membrane was ion-exchange treated water. Over 95% of the chloride ions were transformed to sulfate ions by (IX). Sulfate refusal was excellent in the NF procedure (more than 99%). Exhausted IX resin might be restored with NF retentate, a sulfate-rich derivative.

8.3.3 FO-NF

A complex (FO-NF) system was proposed for seawater detoxification (Tan and Ng 2010). As shown in Fig. 8.3, high pressures of 43 bar were applied to the FO draw solution before being circulated through the two-stage NF membrane. In step with the findings, the second-stage NF became required to desalinate the seawater. For brackish water, a complex FO-NF system was investigated. A decrease in hydraulic pressure was required for this system than RO, low flux declining was generated via fouling of membrane, and no additional pretreatment was required. For brackish water, a multistage NF-FO-RO gadget was investigated (Altaee and Hilal 2015). The recovery rate of the system approached 90%.

8.3.4 NF-SWRO

NF has been employed as a pretreatment step before reverse osmosis in saltwater distillation. NF270 and NF90 were compared in seawater reverse osmosis or a combined system (NF + RO). A closed-loop was established with an NF membrane at thirty bars. The NF permeate was used as the feed for the SWRO membrane in the integrated system study. The NF270 membrane has a higher permeate recovery than NF90. NF90 membrane rejected salt more efficiently than the NF270 membrane. The effectiveness of nanofiltration membranes in SWRO preliminary treatment operations in terms of conductivity and feed pressure during 8 years (Al-Hajouri et al. 2013). The permeability was initially quite high. Fouling leads to a reduction in NF salt refusal. After every 9 months, chemical cleaning was carried out. The effectiveness of nanofiltration membranes to estimate the scaling potential of nanofiltration-seawater reverse osmosis (Song et al. 2013). At 10–15 bar, NF membranes reject sulfate ions while producing desalinates with lower scaling potential (Ryabchikov et al. 2012; Altaee and Hilal 2015). Compared performances, exact power consumption, energy necessities, complete costs of dual-stage NF-RO, NF16, as well as single-stage RO membrane procedures using ROSA software (Su et al. 2015). The lowest cost and specific energy consumption have been discovered in NF-NF, while RO had the highest.

8.3.5 NF-SWRO-MD

The efficiency of combined membrane systems was evaluated, and it was discovered that combined organizations had greater retrieval features than RO units (Al-Rawajfeh 2012). The output was roughly twice that of the RO unit. The overall performance of an NFSWRO-MD membrane system that is incorporated. The RO system's pretreatment stage included the use of NF (El-Zanati and El-Khatib 2007; Al-Rawajfeh et al. 2012). The MD process that can be utilized to reject brine from the SWRO and NF systems as an input. The permeate flow rate was 43 m^3/d. Correspondingly, NF and RO had brine flow rates of 30 and 28 m^3/d. At 35 °C, the MD feed proportion was 58 m^3/d.

8.3.6 NF-MSF

A series of simulations and experiments compared the performance in a solar-powered MSF pilot plant, NF membranes were used as a preliminary treatment stage (Mabrouk and Fath 2013; Hilal 2015a, b, c). A series of modules of four solar concentrators were connected to systems for tracking. Shell and tube heat exchangers acted as a thermal heater for the oil passing over the NF permeate. The system was put to the test at 100 °C. The GOR was established at 15 °C. NF was incorporated into MSF treatment to increase TBT (Awerbuch 2006; Richard and Wahab 1998). The effectiveness of SR90 membrane was investigated. The use of NF reduced fouling and expanded the percentage of NF permeate within the MSF, resulting in a better TBT. Another SWCC research group investigated the effectiveness of the nanofiltration membrane as a preliminary treatment for MSF and RO detoxification procedures. (Mänttäri et al. 2002; Vuong 2006; Nilsson et al. 2008; AlTaee and Sharif 2011;

Al-Rawajfeh 2011; Song et al. 2012; Liu et al. 2013). Figure 8.4 demonstrates the preparation and testing of three integrated systems: NF-RO, NF-MSF, and NF-RO. The MSF contained NF permeate from 20 to 40 bar of feed. The MSF was run without antiscalants for the first 34 days at 120 °C. There was no evidence of scale formation, according to the findings. Nevertheless, fouling increased with increasing retrieval proportion. Afterward, the MSF was operated for 50 days at 130 °C and 35 ppm acids. There were no scalability issues discovered. The SWRO was fed NF permeate, while SWRO retentate provided the feed for the MSF in the trihybrid system. Calcium and sulfate ions were in comparatively low amounts in the NF permeate, and the MSF has been operated at 130 °C due to their low concentrations. The temperature of the nanofiltration feed was diverse between 24 and 34 °C, while the pressure was varied between 24 and 28 kg/m^2. With rising temperature and pressure, the proportion of NF recovery accelerated.

In multistage flash detoxification systems, the effect of nanofiltration pretreatment on scale formation was investigated (Llenas et al. 2013; Hilal et al. 2015a, b, c; Al-Rawajfeh 2016). Using IMS software, Hydronautics Nitto Denko Company simulated NF rejections and permeated flows. The MSF received NF permeate as a feed. As the percentage of NF-treated feed increased, the scaling potential decreased. The rates of $CaSO_4$ and $CaCO_3$ deposition reduced dramatically as the stages progressed. The Skillman index measures the relationship between the actual concentration of $CaSO_4$, $CaCO_3$, and the solubility at various temperatures. When concentration is greater than solubility, the scale does not form.

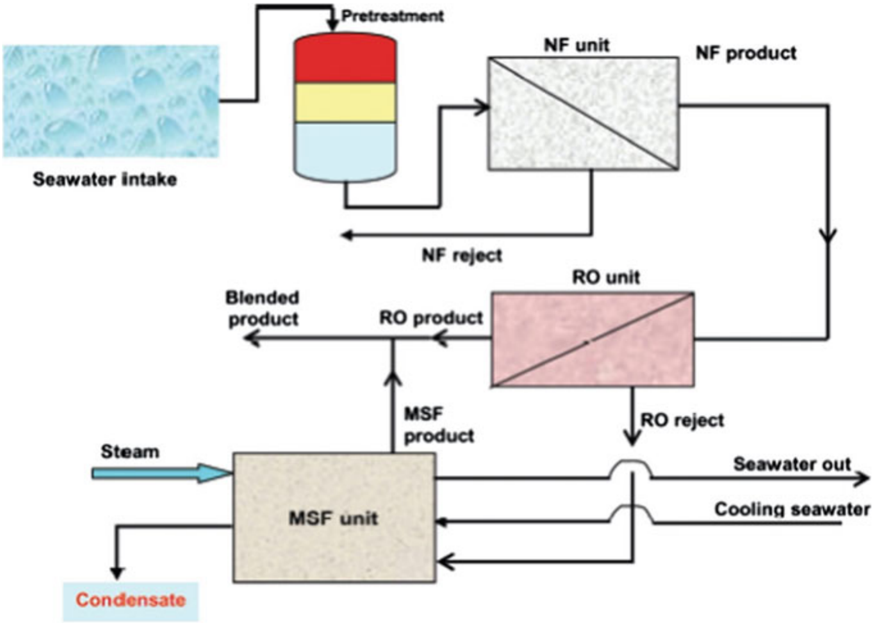

Fig. 8.4 Schematic diagram represents the trihybrid NF/RO/MSF desalination system

8.3.7 NF and Salt Production

NF270, NF200, and TFC-SR2 KOCH are the three types of NF membranes that were tested in a combined ultrafiltration-nanofiltration-reverse osmosis-multiple effect distillation-salt crystallization method (Hilal et al. 2015a, b, c; Turek and Chorążewska 2009). According to 20 pieces of research, salt crystallization led to lowered costs and decreased waste products in NF, a high-water recovery rate of 78.2%, and a low water unit cost of \$0.5/m^3, which is less than RO and MED systems. A combined NF membrane crystallization method was studied for its performance (Sarkar and Sen Gupta 2008; Curcio et al. 2010).

Three-quarters of a bar was applied to an NF90 membrane. The sulfate rejection rate was greater than 95%, and the recovery factor was 50%. A crystallization system based on MF-NF-RO-MD was studied (Drioli et al. 1999; Sarkar and SenGupta 2009). The recovery factor for water was 92.8%. A reduction in freshwater costs and brine concentrations was achieved by adding MC to an integrated membrane.

8.4 Conclusions and Future Perspectives

Both $CaSO_4$ and $CaCO_3$ can be rejected using NF. Scaling species in seawater desalination plants can be eliminated using this method. Thermal desalination can be improved by this elimination, which allows for more steps in the MSF and MED processes and thus improves GOR. Several technologies have been tested for desalination, including NF, ion exchange, forward osmosis, membrane distillation, MSF, and RO. Operating pressures were lower than many of the most common reverse osmosis processes between 2 and 20 bar. Fouling was a serious issue with these systems, resulting in increased energy consumption, higher operating costs, and lower membrane lifetime. Due to the participation of convection, salt rejection, at high pressure induced through an increase in high water flow, the penetration of flow and the increase in operating pressure.

However, due to the large degree of supersaturation at extremely high pressures (e.g., 34 bar), the nucleation phase is quite small. Due to the increase in membrane polarization, the rejection of some salts decreases with increasing pressure. As a result, rejection decreases at high pressures for these salts. Ion rejection is only slightly affected by temperature. The permeate flux and ion rejection increase as temperature rises (though the chlorine and sodium ion elimination slowly reduces). The production of scales on membrane surfaces is influenced by temperature. The 35 thermodynamic solubility products for a given precipitate varies with temperature. The solubility product constants of $CaCO_3$ and $CaSO_4$ drop as the temperature rises, resulting in homogeneous crystallization. Because of the high supersaturation at high temperatures, calcium carbonate precipitates on membrane surfaces in the bulk concentration. Permeate flux, and salt rejection decreases with time before chemical cleaning and dramatically decrease after chemical cleaning. The nucleation stage's duration is significantly lower at high operating pressures because of the larger degree of supersaturation, which enhances membrane fouling. Surface crystallization is the primary process where the feed rate is decreased. Bulk crystallization is the major membrane fouling process when the feed rate is increased. The linear connection between flow and deposited mass loss suggests that flux decreases are caused by membrane fouling. Calcium sulfate and calcium carbonate are the primary sources of surface foulants. Increased surface roughness leads to increased fouling of the membrane. Future research would concentrate on producing more durable membranes or approaches for controlling as well as reducing fouling. More comprehensive and rigorous studies of NF applications are essential to enhance the effectiveness of complex detoxification facilities. Furthermore, ongoing NF membrane research would be critical in advancing saltwater detoxification technology NF-based pretreatments that can provide optimal feed water quality, making the desalting process more energy-efficient and resulting in lower freshwater costs.

Acknowledgements Rekha Sharma gratefully acknowledges the support from the Ministry of Human Resource Development Department of Higher Education, Government of India under the scheme of Establishment of Centre of Excellence for Training and Research in Frontier Areas of Science and Technology (FAST), for providing the necessary financial support to perform this study vide letter No, F. No. 5–5/201 4–TS. Vll.

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Chapter 9
Modified Nanofiltration Membrane for Wastewater Treatment

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Abstract Because of the globe's expanding community and industrialization, there is a greater need for fresh water supplies worldwide. Coatings serve an important part in wastewater purification operations, with innovative applications, continual technological advancements, or cost savings. The much more popular approach to producing biomaterials is stage reversal. Nevertheless, many industrial films are composed of aquaphobic substances, making these highly sensitive to chemical deposition or adsorption on their interface from within their holes. This condition, known colloquially as clogging, is among the most serious operating risks in surface technology. Membrane technology, multiple surface transformation approaches to reduce fouling and increasing porosity at the film interface, application of nanofiltration (NF) membranes, and future potentials are discussed in this chapter. This chapter also covers the advanced modifications and crosslinking techniques to enhance the porosity and longevity of the films used in pressure-driven isolation.

Keywords Wastewater · Biomaterial · Deposition · Adsorption · Nanofiltration membrane · Moulding

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_9

Abbreviations

AEM	Anion exchange membranes
BSA	Bovine serum albumin
CA	Cellulose acetate
CEM	Cation exchange membranes
CF6	Fluorinated carbon chains
CIP	Clean-in-place
CMC	Critical micellar concentration
EC	Epoxy-containing coumarin moieties
ED	Electrodialysis
EIPS	Evaporation-induced phase separation
EO	Ethylene oxide
EPS	Extracellular polymeric substance
FO	Forward osmosis
GO	Graphene oxide
HBPs	Hyperbranched polymers
HNTs	Halloysite nanotubes
LM	Liquid membrane
MD	Membrane distillation
MEUF	Micellar enhanced ultrafiltration
MF	Microfiltration
MMMs	Mixed matrix membranes
MOFs	Metal–organic frameworks
MSPs	Mesoporous silica particles
NF	Nanofiltration
NIPS	Non-solvent-induced phase separation
NPs	Nanoparticles
PA	Polyamides
PAA	Poly (acrylic acid)
PAMAM	Poly (amido amine)
PAN	Polyacrylonitrile
PD	Polydopamine
PE	Polyelectrolytes
PEA	Poly (ether amine)
PEG	Poly (ethylene glycol)
PEI	Poly (ether imide)
PES	Poly (ether sulfone)
PET	Poly (ethylene terephtlate)
PEUF	Polymer enhanced ultrafiltration
PO	Propylene oxide
PP	Polypropylene
PSU	Polysulfone
PVA	Poly (vinyl alcohol)

PVDF	Poly (vinylidene fuoride)
PVP	Poly (vinyl pyrrolidone)
QS	Quorum sensing
RO	Reverse osmosis
SDS	Sodium dodecyl sulphate
TIPS	Thermally induced phase separation
TMP	Transmembrane operative pressures
UF	Ultrafiltration
UV	Ultraviolet
VIPS	Vapour-induced phase separation

9.1 Introduction

Water is the most significant requirement for humankind's nourishment, and its cleansing and supply are now key concerns. The present global freshwater crisis results from global expansion and dramatic environmental degradation. The planet's population is predicted to reach billion by 2050, considerably increasing the demand for economic goods. Water usage increases due to urbanization (Gehrk et al. 2015). As a result, water consumption, especially from food supplies, is increasing significantly, as 70% of the planet's freshwater resources are being used for irrigated agriculture each year. Even though the world is mainly surrounded by groundwater, only a small part of such an ocean is available to humans. Different parts of the planet have different access but lack access to safe and pure water. As a result, a good plan is important to deal with the water problem. Membrane filtration is a reliable alternative to water purification due to its strong financial and ecological benefits (Yin and Deng 2015). The surface technique has been proven widespread use during wastewater cleaning methods like industrial and municipal waste cleaning, saltwater distillation, membrane filtration, and ultrafiltration (UF) generation. Compared to traditional techniques such as oxidation, adsorption, cryogenic distillation and chemical coagulation, it has many advantages such as a small area, good quality control, low capital cost, simple servicing simplicity of handling and monitoring (Tul Munthaet et al. 2017).

Nanofiltration (NF) films, as reverse osmosis (RO) film surface, can effectively eliminate small organic compounds and inorganic salts. Nevertheless, the fundamental difference between the NF and RO films includes the most denial of ionic species, a decreased denial of the multivalent ionic species, and an increase in flow. Because of these qualities, the NF film may be used in various activities, including treating wastewater, biotechnology, pharmaceuticals, and food engineering (Mukherjee et al. 2013). Particles are generated on the surface of the membrane and in the porous membrane as ionizable functional groups dissociate. Depending on the individual material used in the synthesis method, these units may be basic, acidic, or a mix of both (Minjing et al. 2008). Because the chemical nature of the film is basic, the pH of the interacting water has a large effect on surface chemical dispersion.

Nevertheless, the film may see an isoelectric range during certain pH levels. Electrostatic interaction or repulsive might arise depending on the membrane's fixed ions and neutral atoms. Two conflicting hypotheses describe the type of encounter: (i) the solubilization power restriction process and (ii) the visual dynamics phenomenon (Vignati et al. 2005). The NF membrane is a tension film with features similar to UF and RO membranes. NF membranes have many advantages, including high flow, minimum maintenance, low operating cost, low operating stress, and significant ionic salt retention. Such benefits have extended the global use of NF films. Many materials have already been used and produced in various separation processes. Commercial exploitation of membrane technology has been achieved in Japan and the United States. The nanocomposite film approach is the best efficient way to make NF film. To form a nanocomposite, an extremely narrow layer is produced on a permeable layer.

Nevertheless, a variety of additional approaches might be used to create an NF nanocomposite (Raoufi et al. 2014). Many investigations have been conducted in the latest days to investigate contamination's management and causation. On the other hand, coating clogging became a severe issue in an array of applicants. As a result, the physical and chemical factors driving fouling should be investigated. The latest research has found that geometry and interface appearance determine their specific function membrane interface characteristics such as hardness, average pore diameter, electrokinetic properties, geometry, and chemical characteristics, all studied to see how they affect membrane performance. On the other hand, the stiffness of the interface of the film has a considerable impact on the degree and speed of contamination (Peng et al. 2011). The main purpose of this chapter is to provide a critical evaluation of NF film studies. The first section of the chapter includes a variety of membranes and NF membrane modification methods. NF film has been used in biotechnology, pharmacology, food sector and water treatment. In addition, the future perspective is also discussed in this chapter.

9.2 Membrane Technology

Membrane technology accounts for more than half of the global treatment of wastewater potential. The emphasis is placed on the elimination of pollutants in water purification, including such organic, chemical and biological contaminants, and in addition to obtaining sufficiently pure and good tasting water, also the dispersed particles contained in the water (Razmjou et al. 2011). In recent times, membrane technology has been increasingly employed in wastewater and desalination treatment in biotechnology, manufacturing and food processing industries, due to its specific and cost-efficiency. A membrane can be defined as “a selected protective boundary that places undesirable substances at the interface, while allowing certain chemicals to flow based on their physical and chemical characteristics when a driving factor is

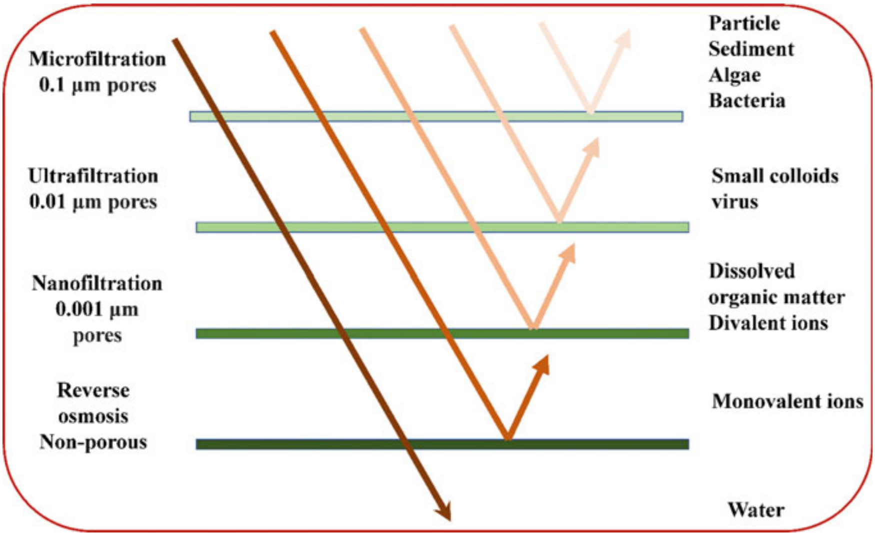

Fig. 9.1 Division of membranes for water purification regarding retained species and pore size

provided on the film" (Díez and Rosal 2020). The different types of membranes for water cleaning in terms of intact species and pore size are shown below in Fig. 9.1.

9.3 Membrane-Based Filtration and Separation

9.3.1 Ultrafiltration

At limited transmembrane operative pressures (TMP), UF is employed. Since the UF film holes may be bigger for the heavy metals, chemicals may be attached to ionic species to increase their size. So, polymer enhanced ultrafiltration (PEUF) and enhanced micellar ultrafiltration (MEUF) are presented as a result (Zahid et al. 2018). MEUF is created by combining a surfactant as well as for UF. MEUF has resulted in minimal energy consumption, large flow and specificity, a small footprint, and high removal efficiency. MEUF is best suited for sewage with low amounts of heavy metals. In MEUF, a surfactant with a proportion greater than the critical micellar concentration (CMC) is combined with wastewater. In addition to CMC, emulsifier molecules enhance and combine the formation of certain microspheres in the liquid. A watery cap and a polar end are included in the surfactants (Daufin et al. 2001). The interior wet center of the microspheres can dissolve organic materials (with a small chemical mass) as a solubilizate. At the same time, the interface activated carbon opposing metals on its surfaces owing to electrical interactions. Surfactants, whose electric current is diametrically opposed to metallic ions, often have the greatest average rates. Ionic surfactants (e.g., sodium dodecyl sulfate (SDS)) and polyelectrolytes (PE) are employed to remove heavy metals (Qasem et al. 2021) effectively.

MEUF efficiency is affected by a numeral of parameters, such as the kind of membranes utilized, the solute molecules supplied the operational parameters, and the type of surfactants employed. PEUF is created by combining UF with attaching materials. Bridging polymeric' organic molecules might be phosphonic, sulfonate, amine, or carboxylated, and chelating or electrical bonds will join them. PEUFs are also called polymer-assisted, polymer-supported, size improved, and complexation enhanced UF (Zeng et al. 2020).

9.3.2 Nanofiltration

NF is utilized to extract components with an atomic mass of more than 1000 Da and to eliminate melted materials with particle sizes more than 200 Da. Consequently, the NF working frequency is among RO and UF processes. The NF films are made of polymeric materials with numerous layers of negatively charged chemical structures (Abdullah et al. 2019).

9.3.3 Microfiltration

Microfiltration (MF) is a technique that utilizes a micro-porous film to remove bacteria, micrometers materials, protozoa, viruses, contaminants, and other micron-sized particles from a solution. The MF process is similarly a lower pressure-driven membrane method, with film pits extending from 0.1 to 10 m. Ceramics, silica, alumina, zirconia, polysulfone, PVC, polypropylene, PTFE, polyamides, PVDF, cellulose acetate, polycarbonate, composite materials, or cellulose esters are used in the manufacture of certain MF films. Furthermore, the MF method may be used in particle separation from wash water in the electronics sector, clarity of various cider and juices, sterilization of wine and beer, and effluent treatment (Huang et al. 2017). Due to its limited elimination capabilities, the use of MF in reducing heavy metals has received insufficient consideration. It has, nevertheless, been employed by altering the membranes or chemically pre-treating the concentrated solution. The MF method is accessible in two major variants, based on the manner of usage: dead-end and crossflow (Tanhaei et al. 2014).

9.3.4 Reverse Osmosis

RO is a pressure-driven separating method that uses a semi-permeable film (pore size 0.5–1.5 nm) to enable only tiny particles to flow through. The RO method replicates the typical filtration method by adding pressure (20–70 bar) to the source solution's osmosis tension. The inhibited solute molecules' particle mass is typically in the 0.00025–0.003 m range. The RO technique could extract 95–99% of charged organic and inorganic salts. The RO method is minor and has a remarkable refusal rate. The main drawback of the RO process, however, is film contamination and degradation (Baharuddin et al. 2015).

9.3.5 Forward Osmosis

Forward osmosis (FO) is a type of filtration that uses a substrate to combine specificity and penetrated liquid flux. A semi-permeable film divides a feed-in FO. The solvent has a higher concentration of solutes than the feed water. Fluid crosses from the feedstuff water to the draw solution because of the osmosis pressure gradient between the feeding and draw situations, retaining rejecting dissolved substances on the feed solution and purified liquid on the drew solution. FO does not need mechanical power and hence saves fuel. Because the FO method is also simple to wash, ecologically safe, and has minimal clogging, it is extensively employed in effluent treatment. Nonetheless, FO has film selection problems, drawing solution re-concentration and external and internal intensity polarization (Abdelkader et al. 2018).

9.3.6 Electrodialysis

Electrodialysis (ED) is a technique for separating ions based on electrical differences. ED employs a sequence of cation exchange membranes (CEM) and anion exchange membranes (AEM) that are interchangeably stacked in parallel to divide electrical substance molecules. Anions flow via AEM during the ED procedure, whereas metal ions move via CEM. The processed flow is generated through one of the ED towers tubes, whereas the concentrate flow is discharged from another half (Jamil et al. 2018). ED has a minimal stage shift, rising water return rate, no molecular involvement, and no reactivity, and thus can function across the pH range. Nevertheless, ED suffers from foulants, a large need for electromotive force, and expensive membrane costs.

9.3.7 Other Membrane-Based Methods

Liquid membrane (LM) and membrane distillation (MD) are also utilized for sewage remediation. MD is a dual heat-driven pore division technology that uses a permeable carbon wet film to divide cold and warm chambers. Only vapor can pass through MD's holes, whereas other particles are blocked. MD may be classified into four types: direct contact MD, air gap MD, sweeping gas MD, and vacuum MD (Samaei et al. 2020). On the other hand, LM is composed of a water form organic layer that serves as a wall among two water phases. LM is insoluble with both the feed water and the recirculated solution, and the peeling procedures may be completed in one stage. LM is extremely efficient, selective, and capable of achieving precise molecule recognition. However, the membrane's lengthy durability is a concern (Al-Amshawee et al. 2020).

9.4 Membrane Fouling

Polysulfone (PSU), polyethersulfone (PES), polyacrylonitrile (PAN), cellulose acetate (CA), polyamides (PA), polyvinylidene fluoride (PVDF) are the most often utilized polymer resources for creating UF, MF, RO, and NF films due to which great chemical, mechanical and thermal stability. However, one downside of such polymeric is that they are susceptible to settling certain chemicals on their uppermost layer or within their permeable assembly, resulting in a reduction in infuse fluidity (Zaheri et al. 2015). This condition is known as fouling. It necessitates costly cleaning and periodic regeneration methods to minimise membrane performance loss and alleviate the requirement for increased energy and pressure consumption that would be essential to preserve steady fux. Membrane emmeshing also shortens their valuable provision life. Fouling is described by the International Union of Pure and Applied Chemistry as "the process that results in a deterioration in membrane performance caused by the deposition of suspended or dissolved particles on the external membrane surface, on the membrane pores, or within the membrane pores" (Díez and Rosal 2020).

As a result, there are four forms of membrane fouling:

9.4.1 Inorganic Fouling

Inorganic fouling, often known as precipitated pollution, is caused by the precipitation or deposition of inorganic materials in the intake and the crystallization of trace minerals, hydroxide ions, and oxide (Padaki et al. 2015).

9.4.2 Organic Fouling

Organic fouling is mostly composed of natural organic materials. Organic matter contains proteins, polysaccharides, humic compounds, nucleic acids, and fatty acids produced by the bacterial decomposition of vegetables and plants; such substances aid in forming a coating of chemical hydrogel over the surfaces, as well as within their holes. Adsorption is the first precursor of such a layer (Alvarado et al. 2016).

9.4.3 Colloid/Particulate Fouling

Colloids range from a few nanometres to a few micrometers in dimensions. The classification of particle substance in usual waterways and effluents is as follows. Supra-colloidal solids >100 μm, settleable solids 1–100 μm, colloidal objects 0.001–1 μm. Materials that are near in dimension to film holes might obstruct them. Still, larger particles can aggregate on the membrane surface, forming a solid coating that provides additional mechanical susceptibility to water flow (Ly et al. 2019).

Five clogging types could be detected based on the kind of blockage:

1. Total porosity refers to the full closing of apertures with materials. May include dimensions greater than film holes are required for this blockage.
2. Pore-blocking relates to the occlusion of the porous membrane caused by the adhesion and accumulation of tiny particles on the porous interior structure.
3. Transitional pores obstructing is a hybrid of the previous two. Materials obstruct pores and adhere to certain other materials on the substrate, forming porosity bridged.
4. Cakes coating is the exterior membrane leading to creating a filter cakes coating.
5. Bacterial pollution or membrane fouling is the growth of biofilm communities on undesired surfaces.

The term “biofilm” refers to a kind of microorganism that forms an “aggregate of microorganisms in which cells that are typically embedded inside a self-produced matrix of extracellular polymeric substance (EPS) attach to one other and/or to a surface” (Cui and Choo 2014). Maturation, adhesion, and dispersion are the three stages of bacterial development. The adhesive method can be divided into two stages: irreversible adhesion and reversible adhesion. It starts with the movement of planktonic cells and minerals from the source to the interface. Cells are originally lightly applied to the top due to physicochemical factors. Flagella and Fimbriae could also be used to give physical adhesion to the surfaces. Then, over seconds to several hours, cells produce EPS, which aids microbial adhesion to the interface, resulting in irreparable bacterial adhesion to the ground (Guo et al. 2012). Bacteria that have matured have a higher diversity and cell density. There seem to be routed for nutrient and water flow inside the bacterial membrane that keep cells alive. As a result, cross-species microorganisms may communicate with one another while understanding the different types of resources. Eventually, certain biofilm and bacteria clumps can be freed from the framework, enabling the biofilm to grow and colonise habitats on the surfaces. EPS is a term used to describe a group of people that work together to achieve the same goal "polymeric conglomeration generally composed of extracellular biopolymers such as polysaccharides and proteins, in various structural forms" (Amosa 2017). Microbe organisms benefit from EPS formation because it provides physical stability for the microbial population and insulation from climate factors such as salt and dryness. Biofilm generation and microbial quorum sensing (QS) are two phenomena that are intimately linked. This mechanism is guided by tiny genic particles known as autoinducers. The quantity of such signaling particles controls the declaration of a numeral of genes, letting cells control superficial adherence, EPS generation, biofilm, and maturation dissolution. QS is a complicated communication mechanism that can sense cell bulk in a given microbial communal and control gene transcription in response to environmental stimuli (Iritani 2013). Membrane surface chemistry and membrane-solute connections are widely known to be significant inconsiderate snarling. Membrane snarling is a complicated phenomenon caused by various factors, which may be categorized into three groups:

1. Physical and chemical configuration of the feed water: Due to specific connections between both the membrane and the foulants revealed in the liquid, physical and chemical characteristics of personal graze particles like concentration, morphology, hydrophobic interactions, and start charging have an effect on the production of layer clogging (Matin et al. 2011).
2. Operating conditions: Operating factors like feed crossbow velocity, transmembrane pressure (TMP), feed concentration, pH influence membrane performance or temperature and have a consequence on membrane snarling. A concise overview of the many aspects is provided somewhere else (Vert et al. 2012).
3. Membrane properties: Membrane properties such as hydrophobicity or surface roughness or hydrophilicity, surface charge, and pore size have a significant impact on Film clogging is caused by dissolved exchanges. Hydrogel films are thought to be less susceptible to clogging than dry films. Rough textured surfaces also make biofouling easier Surface protuberances contribute to membrane fouling by trapping adjourned inorganic and organic resources, whereas smoother surfaces are less sensitive to fouling (Crozet et al. 2014).

9.5 Strategies for Reducing Fouling and Biofouling

Since their initial discovery in the 1960s, several changes have been suggested to improve phase transition coating fouling and biofouling behavior. The first successful method was to use PVP as an addition in the molding mixture of PES UF films, which was shown to alter pore size (Rabin et al. 2015). Following are summaries and comments on recently suggested coating, grafting or blending procedures targeted at refining membrane biofouling or fouling behavior (Solano et al. 2014). Antifouling

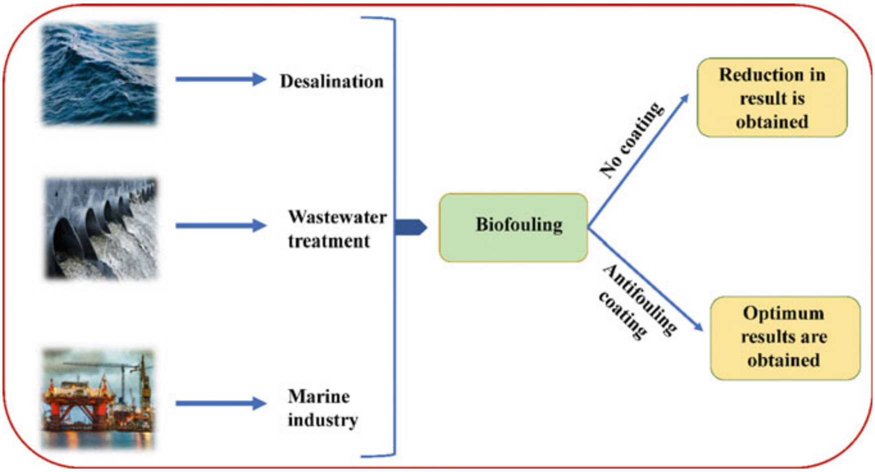

Fig. 9.2 Antifouling strategies in desalination, marine environment, and wastewater treatment

strategies in desalination, marine environment and wastewater treatment are shown below in Fig. 9.2.

9.5.1 Surface Grafting

The adding of functional moieties, hydrophilic chains or electrostatically charged groups to the film exterior. Interface grafted continuously modifies the interface by forming a chemical bond between the grafted chains and the membrane. This method offers several advantages, including the ease with which it may be modified that allows for spatial control and substantially higher chemical stability of grafting onto the required surface (Toyofuku et al. 2016). Current research using surface-grafting modification approaches is shown below in Table 9.1.

However, it has the drawback of necessitating energy-intensive processes, raising membrane costs, and making scaling-up difficult. Table 9.1 provides a review of the current surface grafting research. Different approaches can be used to stimulate the membrane surface for grafting.

9.5.1.1 Plasma-Induced Grafting

Plasma is the fourth phase of the material, consisting of a partly ionized electrical semi gas. The liquid is formed whenever atoms are stimulated into an explosive state by radiofrequency radiation or microwaves (Jaleh et al. 2019). Multiple operational groups can be defined on the surface of a polypropylene material once it is subjected

Table 9.1 Current research that has used surface-grafting modification approaches

Base membrane	Modification	Results	References
Polypropylene (PP)	UV grafting of polyacrylic acid (PAA) as the photoinitiator with benzophenone	Rejection rate and increased water use	Bokhary et al. (2018)
Polyvinylidene fuoride (PVDF)	Argon–plasma therapy + deposition of polystyrene sulfonate	Divalent anions are preferred The average pore radius shrank. Good Cr(VI) stability and elimination	Cassano et al. (2018)
Polyethersulfone (PES)	Acrylic acid molecules are UV-grafted	Reduce salt diffusion increased water permeability	Pichardo-Romero et al. (2020)
Polysulfone (PSU)	NH_3–O_2 plasma treatment	Bovine serum albumin (BSA) is used to improve the antifouling qualities of membranes increased hydrophilicity and permeability	Díez and Rosal (2020)
Polyvinylidene fuoride (PVDF)	UV-grafting of graphene oxide by benzophenone-initiated crosslinking	Extensive antibacterial activity qualities of rejection no effect on membrane permeability or solute transport	Kumar and Ismail (2015)
Polypropylene (PP)	Deposition of TiO_2 NPs + O_2 plasma treatment	Important development of the membrane hydrophilicity	Gude (2018)
Polysulfone (PSU)	Natural seed basil gum NPs + Argon–oxygen plasma therapy	Membrane fouling is reduced Increased permeability of clean water. Higher rate of BSA rejection	Lee et al. (2018)

to it, which can then be exploited for future grafted or bridging processes. Plasma therapy may be divided into two types in this fashion.

1. Plasma Activation or Functionalization:

Surfaces charges are generated when ions and electrons form the plasma phase collide with the surface. The adhesion of ligands is determined by the kind of mixture of gases utilized, which might be reactive or inert (Wang et al. 2018). When ionized is activated with gaseous products like hydroxyl, oxygen, or peroxide, functional groups are presented. Atmospheric plasma therapy to engage the surfaces of polypropylene (PP) films allowed the insertion of oxygen supply organic compounds and promoted nanocrystals' coating by soak. Plasma generated from carbon monoxide or carbon dioxide contains carboxylic acid units and aldehyde, hydroxyl, ketone, and ester groups. Surface primary, secondary, and tertiary amides, and amines are produced by ammonia and nitrogen plasmas (Garcia-Ivars et al. 2016). While inert gas particles like argon or helium do not produce functional groups on the surface, they are less aggressive, resulting in more stable membranes.

2. Plasma Polymerization or plasma Deposition:

Plasma polymerization, also known as plasma deposition, involves using a plasma discharge to fragment monomers and generate radical sites on the membrane surface. In the gaseous state, reacting particles can reunite to make monomers, yielding a polymeric particle covering the surface. As a result, rather than attaching free radicals, functional groups on the surface might induce graft polymerization (Rahman and Seman 2018).

9.5.1.2 UV-Induce Grafting

Because of its simplicity, adaptability, photochemical-initiated graft polymerization, and cheap cost, one of the greatest commonly utilized methods for surface morphology alteration is UV grafting. This method modifies the surface layer by introducing functional groups while retaining the bulk properties. Even without or with the use of a photo activator, photo-initiated grafting polymer could be performed. If illuminated, polyarylsulfone films are inherently sensitive, which means they may create active sites or free radicals without the need for photoinitiators (Igbinigun et al. 2016). Owing to the combination of phenoxy–phenyl chromophores in the framework of the PES polymer network, UV light absorbance has been observed, leading to the heterolytic breakdown of the C–S bond at the position of a sulfonate group. This reaction produces two radical positions: a sulfonyl radical and an aryl radical that sheds its sulfonic label, leading to the development of an additional aryl radical, which induces grafting. Using an acrylic acid monomer solution, UV photo-grafting was used to modify polyacrylic–polyethersulfone NF membranes, resulting in decreased reverse salt diffusion and better water permeability (Kaneda et al. 2019). UV light of Fuse allylamine monomer to the surface of PES membranes, then transplant graphene nanofibers on top. Increased hydrophilicity, smooth surfaces, higher water flux, and decreased fouling attachment were seen in functionalized membranes. To begin the grafting procedure, some composite membranes require the addition of a photo activator or photocatalyst and an additional step called the photo-activation stage. PVDF membranes are permanently grafting graphene oxide (GO) nanosheets under UV irradiation through a benzophenone-initiated crosslinking process. Enhanced antimicrobial property over *Escherichia coli* was achieved without affecting solvent storage or permeability. Acrylate polymer on the interface of PP cylindrical strand surfaces during UV irradiation using benzophenone as a photographic activator to produce membranes with higher flux and reduced rejection rates (Yang et al. 2016).

9.5.2 Surface Covering of a Membrane

Surface coating is a cost-effective, straightforward, and ecologically acceptable surface modification approach that includes a film deposited on the membrane's interface. This method aims to reinforce surface qualities while generating minimum structural impacts. The main drawback of this approach is that the covering layer might be uneven (Capozzi et al. 2017). In this way, coating materials having a high covalent bond at the potting medium contact increase efficiency and durability. A high-molecular-weight polymer is also used to keep the covered film from penetrating the micropores. The following are recent research of films that various coating materials have changed in Table 9.2.

1. Coating with polydopamine

Polydopamine is a biomaterial influenced by mussels' good adhesion capability. It can quickly conscience in basic conditions (pH typically between 7.5 and 8.5) with oxygen as an oxidizing, resulting in a quite fine layer on a range of surfaces. The experiment consisted of coating's anti-organic fouling, and surface hydrophilicity properties are outstanding. Polydopamine also possesses many functional groups that may react with a wide range of biological compounds, giving it an excellent framework for forming chemically grafted active coatings over a substrate (Kumar and Jaafar 2018).

2. Electrospun nanofiber layer

It is a technology that provides certain distinct advantages owing to the nanofibers' better qualities, including tunable porosity, high interconnectivity, a high surface area to volume ratio, and tunable functionalization. Electrospun films can also contain antimicrobic compounds such as carbon nanomaterials, metallic nanoparticles, or antimicrobial biopolymers, which help to minimize biofilm development (Mujtaba et al. 2018). Electroplating seems to be the only technology that can produce fibers with extremely small dimensions. A higher potential supply, a spinneret, as well as a capturing screen, which is typically a metallic screening slab or spinning gadget, make up an electrospun device. A large power generator is being utilized to infuse charge into a polymeric mixture of a specific orientation, which is then pushed toward that goal (Bokhary et al. 2018).

9.5.3 Blending Method

The process of manually combining two or so more chemicals into the colloidal solution using the same solvents is known as polymeric mixing. Inorganic nanofillers or polymeric materials are commonly used as solid dispersion method additions to

Table 9.2 Current researches of membranes modified by diverse surface coatings

Base membrane	Modification	Results	References
PVDF	Electrospun PVDF nanofibers holding SiO_2 NPs	Additional steady flux than uncoated films superhydrophobic membranes	Ding et al. (2016)
PSU	Polydopamine (PD)-layer	Excessive deposition reduces membrane permeability owing to pore size reduction and pore blockage. Greater surface absorption of membranes. Concentration optimum 2 mg/mL–15 min time for deposition	Dolez (2019)
PSU	PAA-PVA electrospun coating	Less organic fouling (BSA) Improved membrane hydrophilicity	Amarieiet et al. (2017)
PSU	Ag-PD layer	Increased protein-fouling resistance. Enhanced water flux while keeping BSA rejection constant. Excellent antimicrobial activity	Sandoval-Olvera et al. (2019)
PVDF	TiO_2 electrospun nanofiber coating	Improved antifouling performance and a greater rate of glucose rejection greater hydrophilicity	Tafreshi and Fashandi (2019)
PSU + PVDF	PD-layer	greater retention, lower water flow aged membranes' performance and characteristics were restored polysaccharide and Protein adsorption buildup is reduced	Zhang et al. (2018)
PVDF	In situ immobilized CuNPs + Dopamine coating	Improved antibacterial action. Improved surface hydrophilicity	Trachevskyi et al. (2018)
Poly(ether imide) (PEI)	Immobilized AgNPs + PD layer	Anti-biofouling protection against both Gram-positive and Gram-negative bacteria enhanced leakage and dissociation	Laohaprapanon et al. (2017)

change film properties. This method is regarded as the simplest way to avoid contamination and increase membranes solubility because the bulk of such compounds is highly hydrophilic. The limitations of this technology are the restricted compatibility of hydrophobic polymers and hydrophilic additives and the leaching of blended components after long-term usage.

9.5.3.1 Blending Inorganic Materials

MMMs are films that mix the qualities of filler particles with the characteristics of polymer composites. MMMs attempt to make use of polymers' durability, processability, selectivity and permeability, by providing a unique surface chemistry. Introducing inorganic additives to the polymer matrices increases the heat (e.g., thermal conductivity or thermal stability) and physical (e.g., young's modulus, tensile strength, hardness, and stiffness) characteristics of the polymeric membrane when compared to the pure membrane materials. Moreover, the homogeneous dispersion of inorganic materials in the matrix material increases material characteristics, including crystallinity, viscoelasticity, conductivity, density, morphology, and structure (Zeng et al. 2020). Current research on composite and blended polymeric membranes is shown above in Table 9.3.

Nanocomposite membranes have higher viscoelastic characteristics than virgin membranes. The polymeric substrate of MMMs screens has been infused with a variety of solid elements, including metallic nanoparticles (inorganic NPs) are a potential addition that may increase membrane fluidity and characteristics. Several kinds of inorganic materials, such as GO, TiO_2, Ag or Al_2O_3, and CuNPs, have indeed been directly embedded into the suitable solvent throughout film formation (Abdullah et al. 2019). TiO_2 is an excellent choice because of its low toxicity, chemical and thermal stability, super hydrophilicity, self-cleaning capability, and photocatalytic activity, all of which may be employed to prevent fouling. To manufacture UF porous material by phase inversion, TiO_2 NPs are added into the PVDF/PAN colloidal solution. Better purified water flux, Greater hydrophilic nature, and better antifouling capabilities were found in mixed films. AgNPs have sparked a lot of attention due to their broad range of antibiotic action and low toxicity. AgNPs operate as a local supply of Ag^+ ions, which prevents reduced solute adhesion and bacteria growth to film surfaces (Tanhaei et al. 2014). PES films were combined with AgNPs utilizing the splash precipitate method to develop films with strong anti-biofouling and antibacterial properties. However, there are two major drawbacks to using inorganic compounds. On one side, nanomaterials prefer to clump together during the drug production step. Nevertheless, NP leaks into the ecosystem are a concern. Several porosity nanomaterials, such as silica nanoparticles and nano-minerals (sepiolite, halloysite nanotubes), have been developed to solve these difficulties (Jamil et al. 2018).

Mesoporous silica particles have grown in popularity in recent years owing to their beneficial properties such as consistent pore size between 2 and 50 nm, high

Table 9.3 Current researches of composite and blended polymeric membranes

Base Membrane	Modification	Results	References
PVDF	HPG	Greater hydrophilicity. Pore generating agent with increased pore size. Enhanced pure water flux	Cassano et al. (2018)
PES	TiO_2 NPs	Porous structure with enhanced macrovoids. Membrane fouling reduced. Flux for improving membrane permeability	Pichardo-Romero et al. (2020)
PSU	GO-PEG-PAMAM-Dendrimers	Effective in terms of CO_2 permeation. Greater porosity	Lee et al. (2018)
PVDF/PAN	TiO_2 NPs (PVDF/PAN/TiO_2)	Antifouling and clean water flux characteristics are improved. Improved membrane hydrophilicity	Jaleh et al. (2019)
CA	PEG	Improved hydrophilicity. Increased pure water flux and improved pore dispersion	Garcia-Ivars et al. (2016)
PSU	GO	Improved mechanical characteristics at low GO concentrations and greater ion rejection porosity. Hydrophilicity, pure water flow, and permeability are all improved	Igbinigun et al. (2016)
PSU	Polyvinylpyrrolidone (PVP)	Enhanced pure water flux, antifouling performance and surface hydrophilicity	Kaneda et al. (2019)
PES	AgNPs	Increased porosity. Properties that are anti-biofouling and antibacterial	Dolez (2019)
Thin-film composite (TFC)	GO-Ag-MOF	Anti-biofouling and antifouling characteristics improved. Greater water permeability and hydrophilicity	Amarie et al. (2017)
PSU	Ag-GO NPs	BSA-fouling reduction	Zhang et al. (2018)

specific surface area and ease of functionalization. Mesoporous silica may be manufactured in basic and acidic conditions and is typically generated using a surfactant template. Santa Barbara Amorphous and Mobil crystalline material (MCM-41) are the two most frequent forms of mesoporous nanoparticles (SBA-15). PES membranes are synthesized using titanium and zirconium nanoparticles on functionalized SBA-15 material to increase membrane hydrophilicity and permeability. An attentiveness of as little as 0.6 wt% SBA-15 was used to achieve antifouling behavior (Samaei et al. 2020). A co-condensation approach was used to increase the surface porosity, functionalize SBA-15 with carboxylic groups and amine, the permeability of PES membranes and hydrophilicity. Composite membrane antifouling capabilities have improved, particularly against irreversible fouling. Halloysite nanotubes (HNT) are natural zeolite found alumina naturally—silicate nanoparticle material with the chemical equation $Al_2Si_2O_5(OH)_4H_2O$. Its crystal lattice is a multi-walled inorganic nanotube with a long tubular form and consistent wide pores of octahedral (Al–OH) and tetrahedral (Si–O) sheets. It has a tubular shape, large surface area, excellent dispersity, and a well-crystallized structure; it is often utilized as a filler in polymeric matrices (Zaheri et al. 2015). PES UF films with HNTs supplied using copper ions (Cu^{2+}) as an antibacterial agent were produced via a phase inversion approach. Cu^{2+}-HNTs/PES membrane was much more porosity and hydrophilic was greater. $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_{48}$ H_2O is the equation for zeolite, a hydrated silicate. Adjacent layers split a base unit configuration of bricks in its layout.

As a consequence of this structure, a syringe particle form with excellent athletic properties and a huge surface area emerges. After magnesium lixiviation in acid, sepiolite was utilized as a substrate to incorporate nanomaterial into the silicate matrix. Phase inversion is also used to create composite PSU/PVP UF membranes with sepiolite-supported nanometals. No nanoparticles moved to the filtrate, confirming NP stability. Antimicrobial activity inhibited bacterial colonization in both gram-negative and gram-positive microorganisms. Zeolites are hydrating aluminosilicate crystals having the general formula $M_{x/m}[(AlO_2)_x(SiO_2)_y]$, wherein $M_{x/m}$ denotes an ion that can be exchanged (Padaki et al. 2015). The addition of zeolites to a polymeric substrate improved membrane fluidity as well as heat resistance, chemical stability, and good mechanical. NPs can also be included in zeolites for antibacterial purposes.

To eliminate heavy metals from water, PSU films were produced impregnated with zeolite particles. PVDF UF membranes with Ag-loaded zeolite nanoparticles were also produced with a longer antibacterial activity. MOFs are crystallized microporous substances formed by a periodic matrix of metallic ions connected through versatile organic compounds (Alvarado et al. 2016). They offer some, including a large surface area, distinguishing features, high pore volumes, high metal content, and tunable pore size, which all offer useful active sites. The GO NPs are used in a silver-based MOF to create a fine nanocomposite barrier with improved antifouling properties. PES NF films were created via a phase inversion method and subsequently altered with nanocrystalline Ce (III) MOFs.

Composite membranes demonstrated better permeability, antifouling behaviour, and dye rejection capability during wastewater treatment and hydrophilicity. A composite CA UF membrane by MOF-GO and incorporating GO into the matrix was created. CA/MOF-GO hybrid membranes with modified pores have smoother surfaces and bigger pores. The water flux and hydrophilicity were also enhanced, resulting in a good performance in the water purification process (Cui and Choo 2014).

9.5.3.2 Blending Organic Molecules

PEG or PVP, for example, are often used as aqueous polymeric additions to make membrane manufacture or improve membranes performance easier. PVP is an efficient pore generating chemical due to its hydrophilic nature. It serves as a phase separation booster in terms of expediting phase inversion and thermodynamics, resulting in better membrane flow, contributing to creating a homogenous finger-like porous structure. Furthermore, raising PVP content decreases highly diffused development, lowering permeability. PEG is a fluid chemical that may be utilised to increase pore formation and improve porosity in polymer films. PEG comes in a range of molecular weights and has the general formula $H(OCH_2CH_2)_nOH$, where n is the average of repeated oxyethylene groups (Guo et al. 2012). PEG also reduces the thermodynamic stability of the casting solution, causing finger-like porous structures to emerge. The membranes form changed from needle pore porosity to ellipsoids or spheres when the PEG molecular mass in the foundry liquids was increased from 200–10,000 Da. This resulted in inferior physical efficiency. Dendritic polymers, including random hyperbranched polymers (HBPs) and dendrimers, have sparked a great deal of interest in developing a variety of nanostructured materials. A dendrimer is a polymer with a set of nodes that is extremely branched and contains many terminating functional groups. Aptamers are made in a controlled and repetitive production process, beginning with a core structure and continuing to a new “generation” of dendrimers for every step. The amount and dimension (generation) of terminating organic compounds might affect their quality. The very first group of dendrimers to be commercialized was main ending polyamidoamine (PAMAM). The phase inversion approach created PSU hybrid films with diverse semi constituents. In gas separation procedures, PAMAM-dendrimers (G0) were added directly into the polymer solutions, generating a selected surface for CO_2 absorption (Vert et al. 2012). Dendrimers can also be used as a pattern to enclose or attach to other materials in their internal vacant areas.

In-situ manufactured PAMAM (G1) dendrimers as containers and hosts for platinum NPs were used to develop a simple approach for manufacturing catalytic PVDF membranes. PAMAM dendrimers were used to make dendrimer encased AgNPs, which were then transplanted onto the interface of PVDF membranes through an interfacial process and showed permeability, good solubility, and antibacterial properties. Hyperbranched polymers (HBPs) are extremely twisted polymers with many terminating organic compounds, spatially gaps, and unique physicochemical characteristics, similar to dendrimers. Despite dendrimers, HBPs can be easily synthesized in one-step polymerization methods, giving them a limited alternative to dendrimers with promising uses on a wide scale. PVDF films containing polymerized polyglycerol as an additive were made via phase inversion. Coatings with surface pore size and a larger water-soluble characteristic were created using increased water flux. By combining epoxy/amine click chemistry with fluorinated carbon chains and epoxy-containing coumarin moieties (EC) Ji et al. produced a novel amphiphilic hyperbranched poly (ether amine) (hPEA) (CF6). PVDF was dissolved, and the resulting copolymer (hPEA-EC-CF6) was used to make the mixed solutions. Disbanding PVDF and the associated copolymers (hPEA-EC-CF6) produced the blending liquid, and phase transition films displayed significant properties to aqueous dyes in aqueous systems.

9.6 Nanofiltration Membrane Applications

NF films are a newer invention that bridges the space among two well-known separation techniques: UF and RO. The ability of NF films to allow soluble ions over the membranes yet refuse multivalent and divalent particles, including such sodium sulfate, is one of the most remarkable features. This versatility opens up many possibilities for customizing method uses across a wide range of industries. Because filtration is typically utilized in processing systems, adding NF films to an already diverse technology line of MF and UF membranes was a logical fit. NF film methods are used in various segments, such as the food, chemical industry, metal finishing, textiles, pharmaceutical, biotechnology and pharmaceutical applications, power generation, and pulp and paper. The following are some of the most commonly cited applications:

1. Use in the petrochemical sector
2. Purification of food businesses [juice processing, dairy, sugar industry, soft drinks, beverage products, baker's yeast, fish meal, olive processing, and meat processing], and use in pharmaceutical manufacturing.
3. Whey dehydration in part,
4. Optical brighteners and textile dyes desalination
5. Nickel, Metal, and chrome plating in the metal fin fishing, including leather sectors, are being phased out.
6. Wastages clean-in-place (CIP) solvents are purified.
7. Applications in biotechnology and pharmaceuticals

9.6.1 NF Application by Industry

9.6.1.1 Dairy, Food, Plant Extracts and Beverage

1. Lactose demineralization and concentration: Lactose may be demineralized and concentrated concurrently using NF films, with various levels of cleanliness depending on the procedure.

2. Sugar Syrup Intensity: NF Can Be Utilized to Reduce Both Processing Time and Costs Compared to Standard Boiling Reduction Techniques for Thick Maple Syrup.

Gibberellins [pharma /plant]: Gibberellins are plant enzymes promoting development and plant growth. NF is a reliable approach to increase total product outputs by focusing on phytohormones such as gibberellins (Rahimpour et al. 2010).

9.6.1.2 Dyes and Textiles

1. Dye absorption: By enabling salts water and to flow over an NF film, NF can be a viable option for the desalination and concentration of textile colors.
2. Removal of dye penetration: NF is commonly used in dye recovery to fulfill discharge requirements following penetration challenges with fluorescent dyes.
3. Concentration of desalination and optical brightening agents: Optical improving mediators can improve the look of colors. To decrease operational expenses, NF can be utilized to enhance the concentration of agent brightening that can be reused (Mohammad et al. 2007).

9.6.1.3 Wastewater and Industrial Processes

1. Removal of liquified natural organic materials to assist manufacture for industrial process water or natural organic matter—enriched water natural organic matter may be removed from groundwater using NF superficial water:
2. Treatment of Leachate from landfills: NF can be used to remediate some landfills as a low-energy option. Leachate can be improved by lowering COD and TOC levels, eliminating contaminants, and lowering turbidity.
3. Brine retrieval: NF films may contain large castoff volumes of sulfate while allowing sodium chloride ions to flow over, making brine recovery in industrial processes a feasible option (Misdan et al. 2013).

9.6.1.4 Pharmaceutical/Biotech

1. Production of antibiotics: NF membranes have shown to be an appealing separation process technique, with applications in the concentration, separation, and synthesis of antibiotics and hormones.
2. Fluid from the Plasma: After Separating Blood Plasma and Serum, NF Can Be Employed to Collect Fibrinogen and Other Clotting Components.

9.6.2 *New NF Applications*

9.6.2.1 Water Softening Systems

Ions of magnesium (Mg^{2+}), calcium (Ca^{2+}), and bicarbonate (HCO_3^-) create stiffness. Hardness minerals or ions promote gauge development in equipment and potable water pipelines and systems that utilise water processes such as heat exchangers. To remove scale-forming ions from water, softening units can be used.

9.6.2.2 Municipal Effluent Action

An innovative action combination for cleaning community wastewater in order to replenish safe groundwater was studied. Biofouling on the NF membrane (De a greater speed of crossflow of roughly 1 m/s can regulate the surface. It is necessary to perform proper pretreatment, such as gradual sand filtration (Dražević et al. 2013).

9.6.2.3 Water Purification

Membrane cleansing innovation is commonly used in the food sector, especially for the treatment of effluents. Effluent from the food sector causes fouling and fast concentration of the membrane layer, especially when operating at high pressure.

Tiny beverage and food industry organizations develop cost-effective technology to collect water using effluents due to the increasing price of water. One typical method for adequately cleaning and recovering water is to use a fermenter in combination with an NF unit. COD in the effluent is reduced by roughly 95% in the reactor. As per German drinking water, the produced water is similar to potable water. The reclaimed groundwater can be utilized to satisfy some of the company's needs. In addition to treating wastewater, NF may be employed in process water or lower MW salt extraction. Consequently, NF can be employed to retain sulfate during seawater filtration and the processing of petroleum products (Amarie et al. 2017).

9.6.2.4 Parting Methods

NF may play a significant part in unraveling valued compounds or undesired components or removing harmful after fluid watercourses that could improve the industry's environmental effect and save money to replace liquids, NF could be used. Material concentration and pH are two main factors that may influence efficiency improvement. With such membrane production materials, barrier specificity cannot be preserved. Dye manufacturing wastewater must be cleaned before even being released to minimize the negative effect on aquatic life and human. Adsorption, oxidation, coagulation, and biological treatment are conventional color removal methods. Reversing microemulsion extraction is a relatively new method of decolorization.

On the other hand, older methods of elimination have proven to be highly effective. Different elimination processes can be utilized to obtain a satisfactory dye removal rate considering its adverse effect on all organisms. To improve the integrity of sewage, the scientific industry has the right to identify cost-effective and more effective removal solutions (Zhang et al. 2018).

9.7 Conclusion and Future Prospective

Creating nanocomposite membranes is vital for the fabrication of UF, MF, RO, NF, and FO membranes for desalination and wastewater treatment. It has recently received a lot of attention. The inclusion of nanoparticles profoundly affects the physical and chemical properties of the outer layer of the membrane (porosity, hydrophilicity, membrane durability, charge density, chemical, thermal, and mechanical stability). Compared to a normal membrane, and also has the wonderful possibility of fixing the permeability-selectivity barter's situation. The techniques for reducing film biofouling and fouling are discussed in this chapter. The concentration is on phase-inverted membranes that incorporate a variety of inorganic and organic additives and methods for modifying the surface layer. The purpose of the research covered in the chapter is to see if adding new chemicals with functional groups, either on the membrane surface or in the mass, may help reduce the amount of flux produced by inorganic and organic substrate coating. Comparable arguments have been made to support changing films to make them resistant to biofouling and bacterial adhesion. PEG and PVP are well-known polymeric additions for enhancing the asymmetric structure and causing pore growth of phase-inverted films. Various organic and inorganic mixed substances have been recommended to modify pore structure, enhance hydrophilicity, most notably metals with antibacterial activity, or produce a reservoir of different chemicals, all with the same purpose in mind. Surface treatment can be accomplished by coating or grafting reply procedures to introduce specific compounds. The interface of the comparatively inert films used in the bulk of industrial expulsion is activated using irradiation and plasma.

The bulk of the studies inside this chapter is still in the field, providing little information into realistic difficulties such as behavior under real-world operating conditions, long-term stability, or cost restrictions related to complicated membranes. Further research should stress continuous quasi-size film monitoring over timeframes at a minimum comparable to the average lifespan of commercialized films. Operations in applicable contexts include the use of authentic streams or effluents and the evaluation of clean-up systems. Nanofiber films for wastewater purification are in the early stages of commercialization. There are several pilot-scale research and laboratory efforts on polymeric membrane applications, but fewer publications on huge manufacturing and commercial use are available. So much study is required to create manufacturing nanofiber membrane development and processing, like effective practices for nanoscience inclusion, the synthesizing and producing appropriate nanoparticles, and assessing the long-term stabilization of fabricated membrane surface under different scenarios. In the twenty-first century, major challenges, including water, energy, and a clean and safe ecosystem, will have to be overcome. Membrane filtration and advancements are vital to effectively overcoming such challenges via innovative development and research and internal transaction advancements.

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Chapter 10
Performance of Ceramic Nanofiltration Membranes in Water Purification

S. Lakshmi Sandhya Rani and R. Vinoth Kumar

Abstract Water scarcity is one of the significant issues many countries face due to the increased demand for freshwater and exhaustion of water resources. Therefore, developing efficient technologies for water purification is anticipated. Nowadays, nanofiltration (NF) separation processes are gaining importance in water purification and pre-treatment for desalination due to their capability in eliminating hardness, salts, and multivalent ions. In addition, NF can be operated under relatively lower pressure than reverse osmosis (RO), where its membrane pore size lies between ultrafiltration (UF) and RO membrane. Polymeric membranes such as polyamide, cellulose acetate, and polyethersulfone are generally used in NF. Many polymeric membranes offer flexibility in the fabrication process and are relatively inexpensive. However, the application of ceramic membranes in water purification has increased hastily due to their beneficial characteristics such as longer life span, fouling resistance, high stability towards corrosive media, and greater mechanical strength. Hence, this chapter discusses the recent signs of progress in ceramic NF membranes for water purification. Various kinds of composite ceramic NF membranes were elaborated in detail, including ceramic-ceramic, ceramic membranes incorporated with nanoparticles and metal–organic frameworks, and ceramic-polymeric membranes. In addition, the implementation of ceramic NF membranes for various water purification methods such as desalination, heavy metal ion removal, removal of dyes, etc., were discussed.

Keywords Ceramic membrane · Nanofiltration · Water purification · Desalination

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_10

10.1 Introduction

The increasing population continuously raises the demand for purified water worldwide. Water shortage increases day by day in many regions due to unnecessary utilization of freshwater resources and severe water pollution. Therefore, obtaining water with high-grade purity is becoming a significant concern. Nowadays, membrane technology is being extensively used in water purification due to its numerous advantages, including high efficiency, low energy requirement, and smaller footprint. It is becoming a promising alternative to traditional techniques, adsorption, distillation, flocculation and chlorination, etc. Various pressure-driven membrane separation processes exist, including micro, ultra, nanofiltration, and reverse osmosis. Nanofiltration (NF) is an efficient filtration method for water purification and desalination to remove heavy metal ions and other organic matter with high flux at relatively low operating pressure. The pore size of the NF membrane ranges between 0.2 and 2.0 nm. As the operating pressure of NF lies between ultrafiltration and reverse osmosis, it provides good solute rejection and less energy consumption. In addition, NF can efficiently separate multivalent salts and organic molecules possessing various sizes.

Various polymeric materials, including cellulose acetate, polyvinyl alcohol, chitosan, polyethersulfone, polyimide, etc., are vigorously used in NF applications. Polymeric membranes are often flexible and can be prepared by simple procedures at a low cost. However, they are not much resistant to harsh operating conditions such as high temperature and pressure. On the other hand, ceramic NF membranes have numerous advantages over polymeric membranes, thus fetching research interest. They are highly stable in extreme acidic and basic conditions. As a result, they can be efficiently cleaned by acids and alkalis for membrane regeneration. They possess high mechanical strength and does not deform under relatively high pressures. Therefore, they also allow regeneration of membrane by backflushing. Ceramic membranes are corrosion and erosion resistant also. In addition, they are thermally very stable and can be operated at high temperatures up to 800 °C. As a result, they offer a relatively much longer life span. Furthermore, they show good anti-microbial and antibacterial properties, thus fitting for medical and biological applications. They are often less toxic and also apt for food and drug applications.

Hence, this chapter focuses on the NF membranes made from ceramic materials. Various kinds of composite ceramic NF membranes, including ceramic-ceramic, nanoparticles embedded ceramic membranes, ceramic membranes coated with metal–organic frameworks, and composites made of the ceramic-polymer combination, are discussed. In addition, the performance of ceramic NF membranes in various water purification applications, including desalination, dye-removal, and heavy metal ion removal, are discussed in detail.

10.2 Ceramic Membranes

Ceramic membranes are often made up of pure oxides of various minerals, including TiO_2, SiO_2, Al_2O_3, ZrO_2, SiC, etc. Usually, ceramic membranes are applied for water purification, and water treatment is a composite of asymmetric membranes that contain more than one layer, as shown in Fig. 10.1. The bottom layer provides mechanical support to the membrane. Intermediate layer act as a bridge layer between the bottom and top layers. It prevents infiltration of the top layer into porous bottom support and provides a smooth surface for the deposition of the top layer. The top layer can be considered a functional or active layer that plays an essential role in the separation. This layer only decides which components will pass through the membrane and retain on the membrane surface. Dip coating, sol–gel method, casting are a few standard methods for the deposition of a selective layer.

Ceramic membranes can be classified based on different aspects. Based on the average pore size of the top layer, they can be classified into micro, ultra, nanofiltration and reverse osmosis membranes (Fig. 10.2). Furthermore, they can be differentiated into tubular, flat, and hollow fiber membranes based on the geometry. Flat membranes are useful in the laboratory and small-scale applications. Tubular and hollow fiber membranes provide a high surface to volume ratio and can be applied in a continuous mode of operation. However, membranes with both configurations are being applied for various applications, including removing dye molecules, heavy metal ions from water, and desalination. Though ceramic membranes made from alumina, zirconia, titania, and silica are commonly used, composite ceramic membranes are gaining interest over common ceramic membranes in water purification and treatment due to the enhanced performance and functionality of the presence of an active separating layer. In this aspect, various kinds of existing composite ceramic NF membranes used for water purification were discussed in detail in the subsequent sections.

10.2.1 Various Kinds of Composite Ceramic NF Membranes

Composite ceramic NF membranes can be of several types, including ceramic-ceramic combination, nanoparticle incorporated ceramic membranes, ceramic membranes containing metal–organic frameworks (MOFs), and composites made from ceramic and polymeric materials (He et al. 2019).

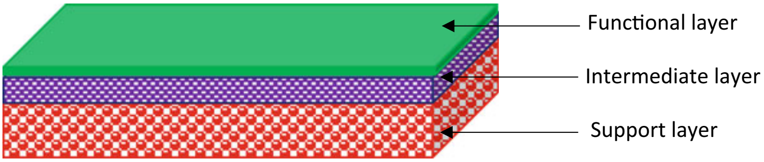

Fig. 10.1 Basic representation of a multi-layer ceramic membrane

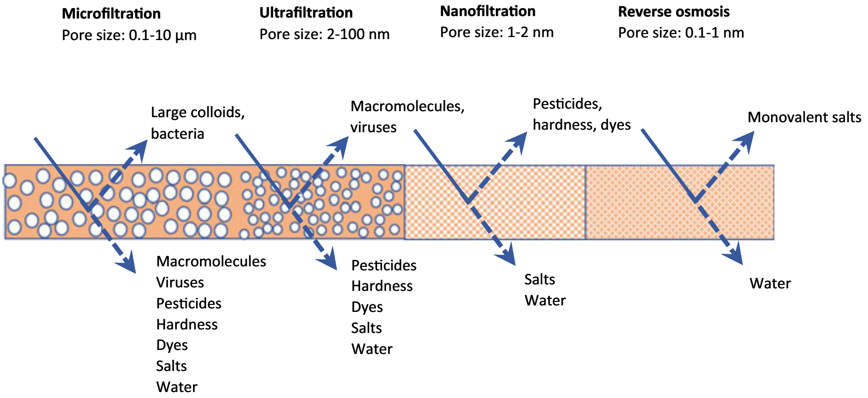

Fig. 10.2 Ceramic membrane classification based on the pore size of the membrane and rejected components

10.2.1.1 Combination of Ceramic-Ceramic

The composite comprises two or more than two ceramic materials in this type. The top functional layer will be made up of a combination of ceramic materials. Compared to monolithic ceramic membranes, these composites perform better in water purification due to the added active layer. For example, Tsuru et al. (2001) has prepared silica-zirconia membranes by sol–gel process and used them for NF applications (Tsuru et al. 2001). Furthermore, Lin et al. (2012) fabricated cobalt oxide silica membranes via a sol–gel process, and prepared membranes were applied for the desalination of seawater. The membranes have shown excellent salt rejection of nearly 99% (Lin et al. 2012). In another study, Zhang et al. (2006) prepared silica/titania composite nanotubes using a sol–gel process and coated them on alumina support by the dip-coating method. As a result, the composite membrane attained more hydrophilicity and photocatalytic activity. The pore size of the fabricated membrane was in the range of 1.4–10 nm. Finally, the membrane was applied to remove Direct Black 168 and achieved an enhanced rejection of 85%. This retention value was comparatively higher than the rejection obtained by membrane separation and photocatalysis alone (Zhang et al. 2006).

10.2.1.2 Ceramic Membranes Incorporated with Nanoparticles

Nowadays, nanotechnology is being employed with membranes for water purification applications. Nanoparticles are embedded on the outer/inner surface of the ceramic membranes, and the resulting layer acts as a functional layer. Due to the incorporation of nanoparticles, the structural properties, including pore size and porosity, can be modified. In addition, functional properties such as hydrophilicity also can be altered. Furthermore, composite membranes may attain additional features such as photoactive nature and antibacterial properties due to the various properties of incorporated nanoparticles. The resulting membranes with improved functionality can efficiently perform in water purification applications.

Various types of nanoparticles have been incorporated into ceramic membranes in several studies. A few of them includes titania, iron oxide, silver, and iron oxide nanoparticles. In a study, iron oxide nanoparticles were coated on alumina–zirconia-titania ceramic membrane via a layer-by-layer method to improve the permeate water quality. After sintering the membrane at 900 °C, the modified membrane has shown a uniform surface structure with interconnected pores of nano size. In membrane separation combined with ozonation, the modified membrane has efficiently reduced the disinfection by-product precursors and thus improved water quality (Karnik et al. 2006). Silver nanoparticles offered antifouling properties and were thus incorporated into ceramic membranes by a few researchers. Accordingly, in a study, Lv et al. (2009) coated silver nanoparticles on the inner side of a porous ceramic substrate. In their study, amino silane was used as a coupling agent. The fabricated composite membrane has shown strong antibacterial properties, and thus they reported that the membrane was suitable for water purification applications (Lv et al. 2009). Furthermore, Chen et al. (2012) incorporated carbon nanotubes on a ceramic substrate using the chemical vapour deposition method. The fabricated composite NF membrane treated oil–water emulsion and obtained 100% oil rejection for the membrane fabricated at optimum conditions (Chen et al. 2012).

10.2.1.3 Ceramic–Metal Organic Frameworks (MOFs)

MOFs are recently developing porous materials and are attracting research interest. Organic linkers and metal nodes make them. The surface properties, including pore size, porosity, pore shape, can be easily tuned according to the application. Therefore, they are widely used in various applications, including water purification and gas separation. For example, a study reported that the Zr-MOFs membrane was synthesized on ceramic alumina substrate via an in-situ solvothermal synthesis technique. The membrane was applied to remove fluoride from drinking water and obtained a rejection of 98% (He et al. 2016). Similarly, in another study, Zr-MOFs were synthesized on ceramic alumina hollow fibers by in-situ solvothermal synthesis. The fabricated membrane was applied for desalination experiments and showed outstanding rejection efficiencies for multivalent ions (Ca^{2+}, Mg^{2+}, and Al^{3+}) with a decent permeability (Liu et al. 2015).

10.2.1.4 Combination of Ceramic and Polymer

In this kind of membrane, an active polymer layer is deposited on the ceramic substrate/support surface. Ceramic support provides enough strength to the selective layer, whereas the active polymeric layer does actual separation. Due to polymers' simplicity and flexibility, this kind of composite membrane is gaining enormous interest in water purification and water treatment applications. In addition, they can combine advantages of inorganic membranes, including low-permeation resistance towards water and simplicity in preparing polymeric selective layers.

In a study, ceramic monoliths were coated with polydiallyldimethylammonium chloride (PDADMAC) and polysodium 4-styrene sulfonate (PSS) by layer-by-layer film assembly. The fabricated composite NF membrane was stated as regenerative and also has shown remarkable chemical stability (Menne et al. 2016). Furthermore, a polyamide-TiO_2 NF membrane was coated on ceramic TiO_2 hollow fiber substrate by interfacial polymerization method. Before coating, the rough surface of the substrate was modified with TiO_2 interlayer by the sol–gel process to mitigate negative effects during adhesion of the selective layer. They reported that the membrane obtained at optimized conditions exhibited high water flux of 105.5 L/m^2 h applied for salt rejection (Li et al. 2018).

10.3 Fabrication Methods

The quality of ceramic membranes depends on the fabrication method and vigilant tuning of processing parameters. Various fabrication methods exist for ceramic substrates and top layers. Generally, ceramic supports are available in flat and tubular forms. Flat sheet ceramic membranes have limited applications due to their low packing density. On the other hand, tubular and hollow-fiber membranes provide a wide range of applications due to their high packing density and surface to volume ratio. In general, the fabrication of ceramic membrane involves three primary steps, including preparation of raw material mixture/slurry, shaping, and thermal treatment (Sandhya Rani and Kumar 2021). The porous membrane is generally prepared from these methods, which can be used as a support layer to fabricate the nanofiltration membrane. Dry pressing, slip casting, paste casting, freeze casting are a few methods used to manufacture flat ceramic membranes, whereas extrusion is used to prepare tubular membranes.

Several methods, including dip-coating, sol–gel, CVD method, and interfacial polymerization were used to deposit a selective separation layer on the porous support to get ultra and nanofiltration membranes. In recent times, various other methods are also reported in several studies. They include atomic layer deposition (ALD), molecular layer deposition (MLD), in-situ hydrolysis, and atmospheric pressure atomic layer deposition (APALD). Each fabrication method has its own merits and demerits. In the case of in-situ hydrolysis, the pore size of the layer can be efficiently adjusted by controlling precursor deposition. Tuning in the ALD method can be done by adjusting the membrane layer thickness with cycle times. Uniform layers can be obtained by using this method. MLD is also a gas phase deposition technique like ALD. On the other hand, APALD does not need a vacuum to deposit a functional layer on ceramic membranes as in ALD. Several research studies on the preparation of composite ceramic NF membranes by various fabrication methods as shown in Table 10.1.

Table 10.1 Various methods used for the fabrication of ceramic NF membranes

S. No.	Fabrication method	Ceramic support	NF layer	References
1	Dip-coating + sintering	α-Al$_2$O$_3$	ϒ-Al$_2$O$_3$	Wang et al. (2016a, b)
2	Sol–gel + sintering	Alumina	ZrO$_2$	Da et al. (2016)
3	Layer-by-layer deposition + sintering	Alumina–zirconia-titania	Iron oxide nanoparticles	Karnik et al. (2006)
4	Atomic layer deposition + calcination	α-alumina porous support and TiO$_2$ inner layers	Titanicone	Chen et al. (2017)
5	Direct growth using a coupling agent	Clay and diatomite-based ceramic	Silver nanoparticles	Lv et al. (2009)
6	In-situ solvothermal synthesis	Alumina	Zr-MOF	He et al. (2016)
7	Chemical vapor deposition	Yttria stabilized zirconia	Carbon nanotubes	Chen et al. (2012)

10.3.1 Challenges in the Preparation of Ceramic NF Membranes

Fabrication of thin membranes with a thickness of less than 50 nm is very sensitive and needs a cleanroom facility. In addition, membrane fabrication requires organic solvents. Using organic solvents involve some technical precautions. Furthermore, the mechanical supports and intermediate layers should be prepared to deposit the selective NF layer without any minor defects. The sintering temperature should be carefully adjusted to get defect-free membranes. And this sintering temperature usually lies above 1100 °C. In addition, the standard raw materials used in ceramic membrane fabrication, such as alumina, are costly. These specifications lead to the high cost of ceramic membranes. However, the high permeation flux and longer lifetimes make ceramic NF membranes favourable over polymeric membranes.

Nevertheless, to overcome these challenges, research is being focused on preparing ceramic supports from inexpensive precursors. Various studies reported ceramic membranes based on natural clays such as bentonite, kaolin, and ball clay (Monash and Pugazhenthi 2011; Almandoz et al. 2015; Vinoth Kumar et al. 2015). Along with natural clay materials, various kinds of waste materials such as sugarcane bagasse, rice husk ash, stone dust, fly ash, etc. also has been used in ceramic membrane fabrication (Suresh and Pugazhenthi 2016; Hubadillah et al. 2018; Saikia et al. 2019). These materials efficiently reduced ceramic membranes' cost and sintering temperature (Sandhya Rani and Kumar 2021). In addition, research studies suggest that the membranes prepared from these materials can be used as efficient porous supports to deposit UF and NF layers (Saffaj et al. 2006; Jedidi et al. 2009).

10.4 Applications of Ceramic NF Membranes

Microfiltration (MF) and ultrafiltration (UF) membranes have been widely used in water treatment applications. However, they show low removal efficiency for micropollutants and organic matter. In this aspect, various studies focused on integrating nanomaterials into MF and UF membranes. Different nanomaterials, including zeolites, nano Al_2O_3 and TiO_2, carbon nanotubes, etc., have been applied to ceramic MF and UF membranes. Ceramic NF membranes are comparatively less industrialized than ceramic MF and UF membranes. However, NF membranes can efficiently mitigate hardness, organic matter, and particulate pollutants from the water. Here, a few studies on water purification applications using ceramic NF membranes are discussed.

10.4.1 Desalination (as a Pre-treatment for Desalination)

Seawater desalination is becoming an important method to overcome the scarcity of fresh water. Usually, freshwater should possess total dissolved solids (TDS) below 1000 mg/L for most human needs. Several thermal-based processes exist for seawater desalination, such as multi-effect distillation. But in recent times, membrane-based processes such as reverse osmosis (RO) are gaining importance due to their energy efficiency, lower operating and capital costs. However, NF can be performed under lower pressure than RO and thus can further reduce the operating cost. In addition, it provides higher flux, low investment, and high rejection rates of bivalent ions. Accordingly, NF is becoming an attractive pressure-driven separation process for the pre-treatment of desalination application. In addition, NF membranes can efficiently separate low-molecular-weight compounds and some parts of NaCl from seawater (Zhou et al. 2015). Therefore, sometimes it can be regarded as a desalination process instead of pre-treatment. For example, Perez-Moreno et al. (2012) modified ceramic membranes with the impregnation of platinum and silver and achieved a salt rejection near 30% from seawater (Perez-Moreno et al. 2012).

In a study, the TiO_2 NF membrane was fabricated by the molecular layer deposition method with an approximate pore size of 1 nm. The water purification performance of the prepared membrane was tested by the filtration of aqueous solutions of salts including NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ (Song et al. 2016). Zhao et al. (2021) prepared composite ceramic NF membranes by depositing polydopamine/polyethyleneimine and crosslinking glutaraldehyde on tubular UF ceramic support. The fabricated membrane was tested to remove $MgCl_2$ and $MgSO_4$ solutions at high temperatures (60 °C). A decent rejection of divalent ions of more than 91%

was observed for the NF membrane (Zhao et al. 2021). Furthermore, a study developed TiO_2/ZrO_2 composite NF membranes using the sol–gel route and dip-coating method. The prepared membranes possessed pore sizes between 1.2 and 1.5 nm. They have used the membranes to reject different salts including Na_2SO_4, NaCl, $CaCl_2$, $MgCl_2$, and observed that Donnan exclusion is the primary transport mechanism involved in the separation (Guo et al. 2018). Wang et al. (2016a, b) developed γ-Al_2O_3/α-Al_2O_3 with a dip-coating method applied for salt rejection experiments. The obtained NF membrane has a pore size of 1.6 nm and exhibited a water permeability of 17.4 L/m^2 h bar. Furthermore, it was stated that the membrane showed a high rejection for multivalent ions including Ca^{2+}, Mg^{2+}, Al^{3+} and relatively low retention for monovalent ions including Na^+ and NH_4^+ (Wang et al. 2016a, b).

10.4.2 Heavy Metal Ion Removal

The heavy metal ion is a generalized term that indicates metals and metalloids. In general, heavy metal ions refer to mercury, chromium, copper, lead, cadmium, and arsenic, which cause harmful effects on human health and the environment. The worldwide industrial revolution resulted in the widespread heavy metal ions in the aquatic environment. In most cases, these heavy metal ions are not degradable and periodically accumulate in human beings and other living organisms, which leads to severe health disorders. For example, high doses of copper and zinc cause hazardous health problems such as anaemia and kidney-related diseases. Therefore, they need to be removed to minimize their impact on human health and the environment (Liu et al. 2018).

As ceramic membranes have superior chemical resistance, they have been widely used to remove heavy metal ions. In a study, a thin film nanocomposite NF membrane made of polyamide with graphene oxide was deposited on ceramic hollow fiber support. The fabricated membrane removed heavy metal ions from simulated tap water. A rejection rate of 93.33% and 92.73% were obtained for Zn^{2+} and Cu^{2+}, respectively (Li et al. 2021).

10.4.3 Dye Removal

Wastewater containing dyes is more complex to treat due to their intense color and the presence of high organic content. Furthermore, often dyes are toxic, mutagenic, and carcinogenic. Therefore, efficient removal of dyes from water is necessary. In addition, most of the dyes are resistant to acidic and alkali conditions and oxidation. Thus, traditional water purification methods, including adsorption and chemical oxidation, may not eliminate dyes. In this aspect, membrane technology can efficiently recover dyes and salts from wastewater without causing secondary pollution.

A study used alumina as a substrate material, and a layer-by-layer self-assembly method was used to fabricate a metal organic framework (MOF) membrane. It was applied to remove methylene blue (MB) dye from water. They have rejected 98.6% of dye from water under optimum conditions (Wang et al. 2016a, b). Chen et al. (2018) have used tubular configured ceramic UF membranes possessing approximately 5 nm pore size as support to fabricate nanofiltration membrane. First, layers of TiO_2 were coated on this substrate by atomic layer deposition. Then, the fabricated membrane possessed a 5 nm pore size and was used to remove dyes from water. It was observed that the membrane had shown higher removal efficiency for negatively charged dyes due to electrostatic repulsion (Chen et al. 2018).

10.5 Conclusion and Future Perspective

The present chapter presented an overview of ceramic-based nanofiltration membranes for water purification applications. Ceramic membranes possess more advantages than polymeric membranes due to their high stability, less fouling, and longer life span. Furthermore, ceramic composite NF membranes perform well over common ceramic membranes in water purification and water treatment. They exist in various kinds, including ceramic-ceramic, ceramic membranes incorporated with nanoparticles, ceramics combined with MOFs, and ceramic-polymer membranes.

Different fabrication methods were presented to fabricate ceramic support and deposit selective NF layers on the support. Standard ways to fabricate NF layers, including sol–gel processing, dip coating, CVD, etc., were highlighted. In addition, a few emerging technologies, including ALD, MLD, and APALD, are also being efficiently used to prepare selective layers. The type of fabrication method plays a vital role in the structural properties and thus the performance of the membrane.

Due to the superior properties of composite ceramic NF membranes, they are being applied in various aqueous and gaseous applications. Specifically, they have shown excellent performance in water purification applications, including desalination, dye removal, and heavy metal ion removal. However, despite these advantages of ceramic NF membranes, the future direction must be towards applying low-cost ceramic membranes to reduce the high cost of commercial ceramic membranes.

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Chapter 11
Fouling Mechanisms in Nanofiltration Membranes

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Abstract Nanofiltration (NF) membranes have been attaining research interest since the late 1980s, especially in water purification applications; they are very efficient and can selectively remove undesired ions and other organic substances. Various applications of nanofiltration such as treatment of surface and groundwater, removal of organic contaminants and pathogens from water for its reuse are discussed in this chapter. However, a significant disadvantage of any membrane separation process is the fouling phenomenon, adversely affecting membrane efficiency. The fouling phenomenon is majorly dependent on the properties of the membrane and interactions between the solutes and membranes. The present chapter discusses various fouling phenomena such as gel formation, adsorption, deposition, pore blocking, and cake formation in NF membranes. To better understand the fouling, mechanisms involved and various mathematical models to describe fouling are necessary. Therefore, Hermia's models to describe fouling, such as standard pore blocking, complete pore blocking, intermediate pore blocking, and cake filtration models, are discussed in detail. In addition, many researchers are working on fouling mitigation of nanofiltration membranes to avoid fouling. Consequently, this chapter described the various fouling mitigation methods.

Keywords Nanofiltration · Fouling mechanism · Fouling mitigation · Water purification

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_11

11.1 Introduction

Nanofiltration (NF) is a pressure-driven membrane separation process used to separate nano-sized molecules. The pore size of the nanofiltration membrane ranges from 0.2 to 2 nm, which lies between ultrafiltration and reverse osmosis membranes. NF membranes can selectively reject different dissolved salts possessing low molecular weight. Therefore, they are being efficiently used in desalination applications. NF processes are usually operated between 5 and 30 bar trans membrane pressure to attain strong divalent ion rejection. Nanofiltration membranes are neither fully dense nor fully porous, so their retention mechanism can be defined by size exclusion, sorption, and diffusion. Usually, NF membranes have a high charge density and possess pore diameters in the nanometer range. The surface charge is generally negative and has the most significant impact on the membrane's selectivity. New investigations are being conducted, and new membranes with distinct properties such as a wide range of hardness rejection and fouling resistance are being developed (Broeckmann et al. 2005; Bartels et al. 2008).

However, the fouling phenomenon limits a large scale utilization of the nanofiltration membrane processes, which gradually reduces the permeate flux. Fouling can be caused by multiple reasons that are intricately related. First, it is a time-dependent phenomenon caused by membrane features and the interactions between solute and membrane, solute and solute, which results in an irreparable decrease in permeate flux. Process variables can also impact fouling, including feed concentration, flow rate, equipment design, temperature, and pressure. A few common types of fouling include particulate, biological, organic and inorganic fouling. Nevertheless, the membrane can regain its performance (permeability and selectivity) if fouling is removed by proper cleaning methods (Ogawa et al. 2010).

The present chapter discusses the applications of nanofiltration membranes. Furthermore, various kinds of fouling and mechanisms involved in the fouling phenomenon are discussed in detail. Consequently, this chapter highlights the different fouling mitigation methods.

11.2 Applications of Nanofiltration

Nanofiltration membranes were commonly utilized to partially soften potable water by permitting few minerals to flow through the membrane, boosting the water's steadiness and preventing them from becoming aggressive to the piping material. Furthermore, they are being widely used to cleanse industrial effluents and reduce waste disposal. The membrane material is generally designed/chosen according to the required application. Nanofiltration could be used in various ways in various industries. For example, membrane processing looks to be a viable alternative to traditional processing in a wide range of industrial processes. These membranes were also increasingly used to filter effluents at the industrial level and reduce waste disposal. The ability to process waste, preserve essential substances derived from it, reduce energy consumption, and eliminate other additives are just a few of the main advantages of NF membranes (Silva 2018). A few promising applications of nanofiltration are elaborated as follows.

11.2.1 Surface-Water Treatment

Surface water is the primary source of drinking water. It is available in various forms, including streams, rivers, lakes, and reservoirs. Generally, the surface water offers superior quality with the TDS (total dissolved solids) less than 1000 mg/L. Nevertheless, surface water properties vary from one season to another in terms of its composition. Moreover, the composition of surface water may also change when rainwater dilutes it. The traditional method involving coagulation-sedimentation followed by filtration and disinfection exists to treat surface water. But, disinfectants in this process may react with precursors and form undesired disinfection byproducts.

On the other hand, nanofiltration membranes can efficiently reject most organic matter. Hence, it is becoming an efficient option for treating surface water (Al-Qadami et al. 2020). A study developed a hollow-fibre membrane that operates at relatively low pressures to soften the surface water. This particular membrane has a thin film layer, and positive charges have permeability and molecular weight cut off of 17.1 L/m^2 h bar and 500 Da, respectively. While operating at a pressure of about 2 bar, Donnan exclusion and steric hindrance's separation mechanisms showed rejection of magnesium chloride and magnesium sulphate around 96.7% and 80.6%, respectively. In addition, at a water flow of 20 L/m^2 h with 3000 ppm of total dissolved solids and salt mixtures, membrane rejection was around 90% of Mg^{2+} and Ca^{2+} ions (Fang et al. 2013).

11.2.2 Groundwater Treatment

Groundwater is majorly used for drinking water supply and agriculture irrigation. In most cases, groundwater possesses ions such as Ca and Mg, which leads to the hardness of the water. These hardness ions should be removed to get safe drinking water. In addition, the water is being continuously polluted by the disposal of industrial wastes. These pollutants may cause adverse health effects in humans. Therefore, efficient technologies such as NF must treat polluted groundwater into potable water. NF is gaining priority over RO as it can be operated under less pressure comparatively. In addition, the permeate obtained from NF does not require remineralization.

Arsenic (As) is one of the toxic pollutants that can be identified in groundwater. It can cause severe health hazards such as skin cancer and lung cancer. As is usually occur in its trivalent (As (III)) and pentavalent (As (V)) forms. A study has used the pre-oxidation step before nanofiltration to convert trivalent arsenic into a pentavalent format for better removal. A 97–100% rejection percentage was obtained by size exclusion and electrostatic repulsion (Sen et al. 2010).

11.2.3 Removal of Organic Contaminants and Pathogens for Water Reuse

The effluents produced from the wastewater treatment plants are generally used as feed water for membrane-based separation processes to get water ready for reuse. The effluents contain a more complex composition when compared to surface and groundwater. This complexity will remain even after necessary treatments have been carried out. This will pose a difficulty in the separation performance of nanofiltration membranes. Removal of organic contaminants from the effluent of wastewater treatment plants is one of the main challenges associated with health and water safety (Guo et al. 2022).

The removal of organic contaminants by NF membrane may occur by several mechanisms, including size exclusion, electrostatic interactions, polar effects, and hydrophobic interactions. NF membranes can easily remove hydrophilic organic contaminants and possess higher molecular weight due to the size exclusion effect. Besides, NF is negatively charged at the pH range of 6–9, which is advantageous for rejecting contaminants with a negative charge because of electrostatic repulsion. At the same time, organic contaminants with positive charges might not be entirely removed because of the Donnan effect. Furthermore, organic pollutants that are highly hydrophobic and polar are also poorly permeated through the membrane. Accelerating the water transport is one of the ways to increase the rejection of organic contaminants due to dilution effects on the side of permeate. Other than this, strategies like porous nanofillers, preparation of selective nanochannels and introduction of interlayers can improve the water permeance through a membrane, thereby increasing the rejection of contaminants.

Removal of pathogens has utmost priority in the membrane-based water reuse and wastewater treatment chain. It has become severe after the pandemic of covid-19. In general, the average size of pathogens ranges from 220 to 300 nm, which is appreciably larger than that of the effective pore size of NF membranes. Hence, there is a scope for completely removing pathogens by NF membranes. But several studies have reported incomplete removal of the virus and bacteria by reverse osmosis membranes. For instance, Mi et al. (2004) reported the poor rejection of bacteriophage MS2 using spiral-wound RO elements. This improper rejection might be because the virus may permeate through the imperfections in the elements (Mi et al. 2004).

In addition to this, one of the recent studies reported the possible formation of intrinsic defects nano-size during the fabrication of polyamide NF membranes by interfacial polymerization (IP) (Guo et al. 2022). These may function as hot spots for virus transportation, resulting in incomplete virus rejection. To maintain the safety of reused water from pathogens, hugely sensitive methods are required to check the integrity of membranes and elements. Polishing is also considered one of the methods to improve membrane integrity to achieve satisfactory virus removal.

11.3 Definition and Types of Membrane Fouling

Fouling can be defined as the accumulation of non-dissolved matter on the surface of the membrane. The accumulation can be found on the walls of the membrane, at the pore mouths, or a combination of both. Membrane fouling can be classified into the following types: organic fouling, biofouling, and inorganic fouling (Al-Qadami et al. 2020) (refer Table 11.1). Fouling also can be differentiated into reversible and irreversible fouling. These various kinds of fouling are briefly explained in the following sections.

11.3.1 Organic Fouling

Organic fouling refers to the adsorption of dissolved organic compounds on the membrane surface. Various organic foulants such as proteins, humic acids, polysaccharides, etc., can adhere and form a gel layer on the membrane surface. Consequently, the permeate flux significantly reduces, and concentration polarization increases. This will provide nutrients that may further promote the formation of biofilm.

Table 11.1 Different types of fouling with an explanation

Fouling type	Foulant	Explanation
Biofouling	Bacteria and fungi	The development of bacteria on the surface of the membrane as well as the excretion of the extracellular polymers
Colloidal fouling	Clay minerals, silica, suspended matter, salt precipitates and metal oxides	Deposition of colloidal matter takes place on the surface of the membrane
Organic fouling	Polysaccharides, effluent organic matter (EOM) and proteins	Deposition of organic matter or colloidal matter takes place on the surface of the membrane
Scaling	Calcium carbonate, barium sulphate, calcium sulphate and silica	On the membrane surface, the ionic product of the sparsely soluble salt lags behind the equilibrium solubility product, forming a scale layer because of the precipitation

11.3.2 Inorganic Fouling

Inorganic fouling can be defined as the formation of precipitation/scaling on the membrane surface due to inorganic foulants such as Ca, Mg, Mn, and Fe. A study investigated $CaCO_3$ Fouling on ceramic ultrafiltration membrane (Ognier et al. 2002). In that report, Ognier et al. (2002) prepared wastewater using hard tap water (with 8 mg/L of Mg^{2+} and 120 mg/L of Ca^{2+}). The alkalinity of activated sludge increased with the precipitation of $CaCO_3$. In another study, Lyko et al. (2007) investigated the presence of metal substances (Lyko et al. 2007). Inorganic fouling is harder to remove, even with the chemical cleaning process. Inorganic fouling usually takes place by two kinds of precipitations. That is of chemical and biological precipitations. Ions such as Al^{3+}, Ca^{2+}, Fe^{3+}, PO_4^{3-}, Mg^{2+}, OH^-, CO_3^{2-} are present. Chemical precipitation occurs when anion and cation bond to form an insoluble salt. Ions such as PO_4^{3-}, OH^-, SO_4^{2-}, CO_3^{2-} are present in biological precipitation. In some cases, acidic functional groups containing ions and calcium ions may form gel layers, decreasing flux (Muntha et al. 2017).

11.3.3 Biofouling

It is a type of fouling caused by the accumulation of microorganisms such as bacteria and their secretions on the membrane surface. It starts to accompany the precipitation of bacterial cells, and it multiplies to form bio cake. Yun et al. (2006) studied and analyzed cake's arrangement and membrane permeability for wastewater treatment (Yun et al. 2006). It was found that the membrane filterability depends on the biovolume and porosity of bio cake. Furthermore, bacterial cells' affinity toward the membrane also affects the deposition on the surface (Kirschner et al. 2018).

11.3.4 Reversible and Irreversible Fouling

If foulants cannot be removed by physical cleaning methods such as backflushing and surface cleaning, fouling is irreversible. Therefore, the study of irreversible fouling is important for defendable and far usage of membranes. Solutes that are very small such as colloids and microbial cells are the main reason for irreversible fouling since they can go via the membrane and precipitate inside it. Therefore, chemical cleaning methods are required to remove the irreversible fouling.

Loosely attached foulants cause reversible fouling, which can be removed using physical methods. In general, reversible fouling causes cake layer formation on the surface and irreversible fouling cause pore blockage. Membrane fouling is an inevitable occurrence that occurs in membrane filtration. Therefore, membrane selection, operating conditions and membrane cleaning must be appropriately selected to decrease the membrane fouling. Various membrane cleaning methods include biological, chemical and physical processes. Biocides, specifical microorganisms, are used in biological cleaning to remove foulants. Physical cleaning methods to remove foulants include water jets, sponges and backflushing. Acids and bases are used in chemical cleaning to remove impurities (Muntha et al. 2017).

11.4 Fouling Mechanism

In membrane separation processes, permeate flux, and thus membrane performance gradually decreases with time. Therefore, it is important to know the reasons for the reduction in permeate flux. In general, the reduction of permeate flux occurs in more than one step. Firstly, as the membrane is selective, it permeates desired components and stops undesired components from passing through, resulting in concentration polarization. This causes the solutes or the particles to accumulate in a mass transfer boundary layer next to the surface of the membrane. The activity of the solvent deteriorates as dissolved molecules accumulate at the surface, reducing the flow of solvent through the membrane. Because of this reason, an osmotic pressure difference between the filtrate and the feed solution directly next to the surface of the membrane rises, and the effective transmembrane pressure (TMP) driving force is reduced. Though this effect is unavoidable, it can be reversed by reducing TMP and hence flux. Fouling, or accumulation of material, is the second issue. Fouling can be observed in various forms such as adsorption, pore blockage, layer-by-layer deposition, and gel formation. Adsorption happens as a result of interactions between membrane and solute particles. Even in the absence of permeate flux, a single layer of particles and solutes could find, resulting in increased hydraulic resistance. Concentration polarisation will exacerbate adsorption quantity if the adsorption's degree depends on the concentration. Pore blocking can occur during filtration, resulting in flux decline due to complete or partial closure of pores. Also, solutes may deposit layer-by-layer on the membrane surface, reducing the flux significantly due to extra hydraulic resistance. In some cases, such as the concentration of proteins, the level of concentration polarization can cause gel formation in the immediate proximity of the surface of the membrane (Field 2010).

In the present chapter, the focus will be on porous membranes at first to grasp the foundations of fouling, an understanding of transportation to the surface of the membrane, and the physical rules that control transportation across the membrane, along with a suitable model. Fouling increases resistance, resulting in less flux for a given TMP or a higher TMP is needed for a constant flux which can be employed with the help of external devices such as a metering pump. As discussed earlier, concentration polarization decreases the driving force across the membrane, whereas fouling adds additional resistance. Therefore, the concept of concentration polarisation is explained in detail, followed by fouling models.

11.4.1 Concentration Boundary Layer

Membrane separation processes including MF, UF, and RO are used to separate oil droplets, salt, and proteins. In any membrane separation process, the rejected component (oil in oil–water emulsion, salt in desalination, etc.) would be in higher composition in the concentration boundary layer. This higher-concentration layer is a mass transfer boundary layer over which the concentration alters, and the total procedure is known as concentration polarisation. This entire process is unavoidable as it is a result of membrane selectivity. Moreover, as rejected components' concentration is higher at the concentration boundary layer, it may diffuse back into the bulk solution. The equations described below can be used to determine the extent of deposition in this layer and its thickness. The relevant fluxes (in kmol/m^2 s) are described by the following relations under steady-state circumstances. These equations are given based on Fig. 11.1.

Component 1:

$$j_{1,con} = j_1 \tag{11.1}$$

Component 2:

$$j_{2,con} = j_{2,diff} + j_2 \tag{11.2}$$

To get the mass balance, some assumptions have been taken into consideration. First, the concentration gradient parallel to the membrane is insignificant; Fickian diffusion, steady-state, no chemical reaction, constant density, and the diffusion coefficient are independent of the solute's concentration.

For general component i, with the incorporation of volumetric flux J, the equation becomes:

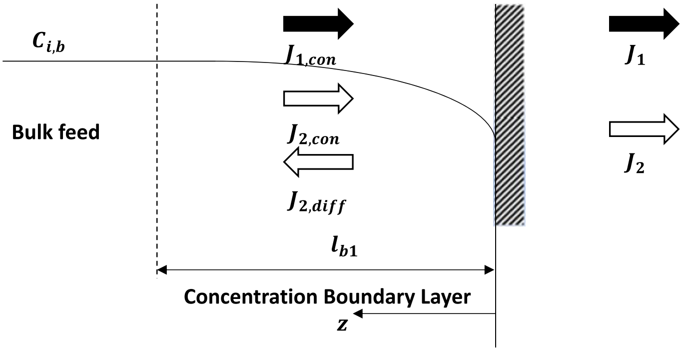


Fig. 11.1 Concentration polarization

$$\mathrm{J}.C_i = \mathrm{J}.C_{i,P} - D_{ji}\frac{dC_i}{dz} \tag{11.3}$$

The following boundary conditions are considered for the integration of the Eq. (11.3)

$$\mathrm{z} = 0 \quad C_i = C_{i,M}$$

$$\mathrm{z} = l_{bl} \quad C_i = C_{i,b}$$

Post integration of the Eq. (11.3) results in the following equation by considering the above conditions

$$J = \left(\frac{D_{ji}}{l_{bl}}\right).\ln\left(\frac{C_{i,M} - C_{i,P}}{C_{i,b} - C_{i,P}}\right) \tag{11.4}$$

where l_{bl} is the mass transfer boundary layer's thickness, subscript M denotes the membrane surface, and subscript P denotes the permeate.

According to Eq. (11.4), the concentration at the surface of each component i is exponential to the flux:

$$C_{i,M} = (C_{i,b} - C_{i,P}).\exp\left(\frac{J.l_{bl}}{D_{ji}}\right) \tag{11.5}$$

The mass transfer coefficient $k_{i,b}$ can be described as (D_{ji}/l_b) in Eqs. (11.4) and (11.5). Because of the exponential relationship from Eq. (11.5), the average concentration within the mass transfer boundary layer is much higher than in bulk; it is also known as the concentration polarization layer. Because the concentration profile curve is affected by flux, the relation among the mass transfer coefficient $k_{i,b}$ ($=D_{ji}/l_b$) and those derived from the conventional correlations in chemical engineering must be considered with caution. As the flux through the membrane tends to 0 ($J \to 0$), it could be proved that $k_{i,b}$ approaches a typical mass transfer coefficient. The correlations between Reynolds number, Schmidt number and Sherwood number, which employs the mass transfer coefficient, can be employed in systems with low fluxes, such as electrodialysis, reverse osmosis, and ultrafiltration. However, conventional correlations must be utilized with much care when there is moderate to high concentration polarization, which could be related to the boundary layer Peclet number's ($J/k_{i,b}$) value. Usually, the mass transfer coefficient is determined from the experimental way by using Eq. (11.4).

In case of complete rejection of the solution, the equation becomes Eq. (11.6)

$$J = k_{i,b}.\ln\left(\frac{C_{i,M}}{C_{i,b}}\right) \tag{11.6}$$

Now that $C_{i,M}$ has been determined to be almost constant, a plot of flux versus $\ln(C_{i,b})$ frequently yields a straight line with a negative slope, referred to as $k_{i,b}$. In a broad sense, the Peclet number of the boundary layer is a significant process variable on the feed side in liquid membrane processes. In contrast, the polarization effect in gas phases is much less significant due to the larger (about 10^5 higher) diffusion coefficient in gas phases compared to liquid phases. The mass transfer boundary layer is thin, as was indicated in passing; its thickness is determined by $D_{ji}/k_{i,b}$. The boundary layer is thin when D_{ji} is merely small, but D_{ji} is extremely small for macromolecules, and the boundary layer is skinny. Fouling is related to the highly localized high concentrations that arise.

11.4.2 Overview of Fouling: Its Causes and Effects

Fouling of the membrane is described as a reduction in the active area, resulting in a flux that is less than the membrane's theoretical capacity for a particular driving force. This is true if the pores are partially blocked or restricted, but sometimes a cake layer on a membrane's surface becomes a resistance in series with the membrane resistance. Two types of substances cause problems: those that destroy the membrane and foul it. Because a fouled membrane must be cleaned, harm to the membrane may occur if precautions are not taken during the cleaning process. Fouling during filtering has a clear detrimental impact on the economy of any membrane process. Thus it should be recognized, and countermeasures should be taken to limit the impacts.

The fouling rate is influenced by various factors, including the nature of the membrane module's hydrodynamics, characteristics of the membrane's surface, the material of the membrane, concentration of the solvents and the solutes. For a few applications, such as wastewater treatment, biofilms are becoming a challenging issue as they form from the ingredients of feed itself instead of foulants. The effect of concentration polarisation exacerbates the negative impact of all of these foulants; as previously stated, surface concentration is projected to grow exponentially with flux Eq. (11.5). As a result, less fluxes will reduce fouling, with a non-linear effect. Also, Eq. (11.5) shows that improved mass transfer would result in low surface concentrations, which is the reason the membrane module's hydrodynamics were stated to influence the rate of fouling. Therefore, the mass transfer will be improved, and fouling will be reduced with a higher crossflow velocity. An electrostatic term could be included in the mass balance Eq. (11.3). Under these conditions, the critical flux is the flux at which the electrostatic convective term equals the convective term; Fouling will be high beyond this flux. In general, the net flux of material towards the membrane could be considered a mix of fluxes, a few of which tend to transport material away from the surface of the membrane while others, such as the convective flux, move the material towards it.

The overall material flux, which is denoted by N, is:

$$N = JC - D\frac{dC}{dz} + p(\varsigma) + q(\tau) \tag{11.7}$$

where D denotes the diffusion coefficient of the Brownian. $p(\varsigma)$ denotes the term for solute/particle migration caused by surface interactions between the membrane and the solute/particle. $q(\tau)$ represents the influence of local hydrodynamics on the mass flux. The possibility of non-buoyant particles settling on the membrane's surface had not been considered.

11.4.3 Fouling Mechanism Assessment

A couple of models are being utilized to understand the concept of fouling process. The foremost one is based on the total membrane resistance (Chang et al. 2011). Resistance in series is denoted by R_t (cm^{-1}), and this is further divided into reversible cake formation (R_c) and irreversible Fouling (R_i). The resistance in the series model can be represented by Eq. (11.8), which was obtained using Darcy's law considering a constant transmembrane pressure (ΔP).

$$J_v = \frac{\Delta P}{(R_m + R_t)\mu} = \frac{\Delta P}{(R_i + R_m + R_c)\mu} \tag{11.8}$$

where J_v, R_m, ΔP, μ are the water flux, membrane resistance, transmembrane pressure and dynamic viscosity, respectively.

The other approach uses semi-empirical fouling models to fit the experimental fouling data to recognize the corresponding fouling mechanisms. A general equation (Eq. 11.9) was developed for dead-end filtration by modifying the Hermia empirical model for the crossflow filtration given by Vincent Vela et al. (2009).

$$-\frac{dJ_p}{dt} = K_{CF}\left(J_P - J_{pss}\right)J_p^{2-n} \tag{11.9}$$

where J_{pss}, J_p, K_{CF} and t are the steady-state permeate flux, permeate flux, the coefficient for the phenomenological dependent on the specific mechanism, and time-taken for the filtration. According to Vincent Vela et al. (2009), n represents the fouling mechanisms. The value of n is 0, 1, 1.5, and 2, which implies gel formation, standard blocking, intermediate blocking and complete blocking, respectively (Vincent Vela et al. 2009).

11.4.4 Hermia's Fouling Models

Hermia developed four fouling models: complete pore blocking, intermediate pore blocking, cake filtration, and standard pore blocking (Fig. 11.2). These models are derived considering dead-end filtration under constant pressure.

The following assumptions were taken in developing the models:

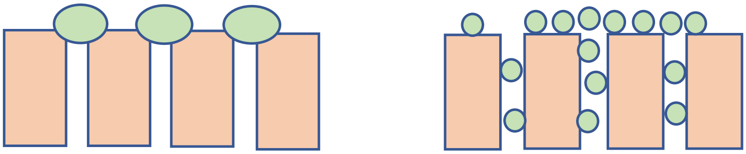
1. Pores are symmetrical and parallel to each other
2. Foulants are uniform spheres
3. Overall filter resistance is constant.

In cross flow filtration, the flow rate of the feed can detach some of the foulants from the surface, so a term of foulant removal has been added in the derivation. This term comes for all mechanisms except standard pore filtration since it is not a surface phenomenon. Constant flux can be maintained by increasing the pressure drop ΔP across the membrane since the membrane area decreases due to fouling. A study developed models for fouling in the case of cross flow filtration and constant flux as follows (Kirschner et al. 2018).

11.4.4.1 Complete Pore Blocking

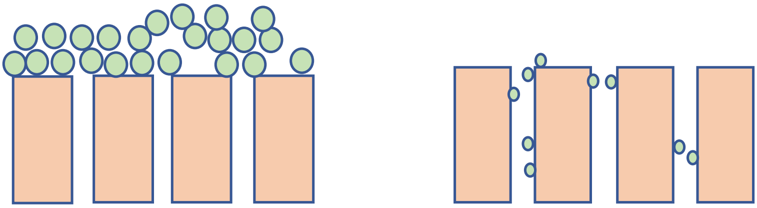
This model assumes that the foulants occupy all the pores and do not occupy the space on the top of other foulants (single layer fouling).

According to Darcy's law for flow through a membrane



Complete pore blocking

Intermediate pore blocking



Cake filtration

Standard pore blocking

Fig. 11.2 Different types of Hermia fouling models

$$Q = \frac{\Delta P a}{\mu R} \tag{11.10}$$

where a, μ, ΔP, Q and R represent the free surface area, viscosity, transmembrane pressure, flow rate and overall resistance, respectively.

Since Q, μ, R are constant, we can write

$$\Delta P_{\mathrm{t}} = \frac{\Delta P_0 a_0}{a_{\mathrm{t}}} \tag{11.11}$$

0—initially at time = 0 s, t—at time = t s.

From Hermia,

$$a_{\mathrm{t}} = a_0 - \sigma V \tag{11.12}$$

σ and V have occupied surface area per filtrate volume is filtrate volume, respectively.

As the permeation rate is constant,

$$V = Q_0 t = a_0 J t \tag{11.13}$$

Here, J is the permeation flux

Substituting Eq. (11.13) in Eq. (11.12), we get

$$-\frac{da}{dt} = \sigma a_0 J \tag{11.14}$$

Foulant removal term is added,

$$-\frac{da}{dt} = \sigma a_0 J - B(a_0 - a) \tag{11.15}$$

B is the particle resuspension rate.

On integrating Eq. (11.15) we get,

$$a_{\mathrm{t}} = a_0\left(1 - \frac{\sigma J}{B}(1 - \exp(-Bt))\right) \tag{11.16}$$

Substituting Eq. (11.16) in Eq. (11.11) we get,

$$\Delta P_{\mathrm{t}} = \frac{\boldsymbol{\Delta P_0}}{\left(\mathbf{1} - \frac{\boldsymbol{\sigma J}}{\boldsymbol{B}}(\mathbf{1} - \mathbf{exp}(-\boldsymbol{Bt}))\right)} \tag{11.17}$$

The second term in the parentheses always lies between 0 and 1, which indicates that ΔP increases with time.

11.4.4.2 Intermediate Pore Blocking

Intermediate pore blocking is similar to complete pore blocking, but particles are allowed to deposit on top of previously accumulated particles.

$$-\frac{da}{dt} = \sigma a J \tag{11.18}$$

Since the probability of occupying new pore decreases in intermediate pore blocking, we consider a in place of a_0 Eq. (11.14).

Foulant removal term is added,

$$-\frac{da}{dt} = \sigma a J - B(a_0 - a) \tag{11.19}$$

On integration, we get,

$$a_{\mathrm{t}} = a_0\left(\frac{1}{K_i} + \left(1 - \frac{1}{K_i}\right)\exp(-K_i B t)\right) \tag{11.20}$$

$\mathrm{K_i}$—intermediate pore blocking constant.

$$K_i = \frac{B + \sigma J}{B} \tag{11.21}$$

$$\boldsymbol{\Delta P_{\mathrm{t}}} = \frac{\boldsymbol{\Delta P_0}}{\left(\frac{\mathbf{1}}{\boldsymbol{K_i}} + \left(\mathbf{1} - \frac{\mathbf{1}}{\boldsymbol{K_i}}\right)\mathbf{exp}(-\boldsymbol{K_i B t})\right)} \tag{11.22}$$

The denominator of this equation is always positive and varies from ($1/\mathrm{K_i}$) to 1.

The ΔP initially increases and reaches constant since the foulant removal and deposition balance each other.

11.4.4.3 Cake Filtration

In cake filtration, foulants cover the membrane surface in multiple layers, forming a cake of foulants. The overall mass transfer resistance increases with an increase in cake thickness. Therefore, overall resistance is the sum of membrane resistance, cake resistance, and the foulant removal term.

$$R_{\mathrm{t}} = R_0 + \frac{\alpha W}{a_0} - \alpha S t \tag{11.23}$$

α, W and S are specific cake resistance, cake mass and rate of erosion of cake per unit area, respectively.

From a mass balance on the cake,

$$W = \frac{V\gamma s}{(1 - ms)} \tag{11.24}$$

γ, s and m are filtrate density, mass fraction of solid in fouling solution, and the mass ratio of wet to dry cake.

Substituting Eqs. (11.13) and (11.24) in Eq. (11.23) we get,

$$R_{\mathrm{t}} = R_0(1 + K_c Jt) \tag{11.25}$$

K_c is cake filtration constant for crossflow filtration (m^{-1})

$$K_c = \frac{\alpha\gamma s}{R_0(1 - ms)} - \frac{\alpha s}{JR_0} \tag{11.26}$$

Substituting Eq. (11.25) in Eq. (11.10) we get,

$$\varDelta P_{\mathrm{t}} = \varDelta P_0(1 + K_c Jt) \tag{11.27}$$

This equation shows that $\varDelta P$ increases linearly with filtration time. Therefore, cake filtration is the dominant fouling mechanism for long filtration times.

11.4.4.4 Standard Pore Blocking

In this mechanism, it is assumed that foulants occupy only inside the pores, i.e. reducing the pore diameter and pores are assumed to be straight and parallel.

Laminar flow through a straight cylindrical pore,

Hagen-Poiseuille equation

$$Q = N\left(\frac{\pi r^4 \varDelta P}{8\mu L}\right) \tag{11.28}$$

N, r and L are the number of membrane pores, pore radius and pore length, respectively.

Since the initial and final flow rates are equal, we get

$$\varDelta P_{\mathrm{t}} = \varDelta P_0\left(\frac{r_0}{r_t}\right)^4 \tag{11.29}$$

Following Hermia, a solid mass balance gives,

$$N\pi\left({r_0}^2 - r_t^2\right)L = CV \tag{11.30}$$

C—volume of particles deposited per unit volume of filtrate.

Rearranging Eq. (11.30), we get,

$$\left(\frac{r_t}{r_0}\right)^4 = \left(1 - \frac{CV}{N\pi L{r_0}^2}\right)^2 \tag{11.31}$$

K_s is the standard pore-blocking constant.

Where

$$K_s = \frac{C}{N\pi L{r_0}^2} \tag{11.32}$$

Substituting Eq. (11.31) in Eq. (11.29) we get,

$$\Delta P_t = \frac{\Delta P_0}{(1 - K_s a_0 J t)^2} \tag{11.33}$$

From the above equation, it can be observed that the ΔP increases with an increase in time.

11.5 Cleaning Methods to Remove Fouling

Fouling is unavoidable, but its effects can be reduced by efficient cleaning and regeneration of membranes. Cleaning of the membrane is defined as removing the unwanted material and recovering the lost membrane efficiency. The membrane, after cleaning, should approximately act as the original membrane. The most recent development in membrane separation processes is carbon nanotubes (CNT) (Kramer et al. 2020). These tubes offer much less fouling potential than ceramic and polymeric membranes, but further research must be carried out to develop them to the industrial-scale level of wastewater treatment. Moreover, their potential toxicological effect on the environment is not yet studied (Wei 2015).

However, membrane cleaning is critical once the membrane is used for specific applications. Hence many researchers have focused on developing and modifying the mechanisms and cleaning techniques in the most economical and environmentally friendly way. Two cleaning methods exist to remove fouling, namely physical and chemical cleaning. In the following sections, these methods are described in detail.

11.5.1 Physical Cleaning

This cleaning method includes hydraulic permeate backwash, forward flush, electrical methods, and ultrasonic methods. Of these, backflushing is more advantageous

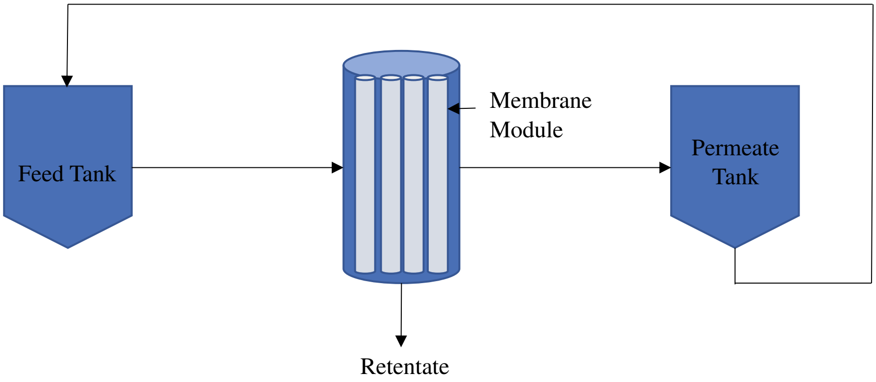


Fig. 11.3 Schematic representation of permeate backwash cleaning

compared to others. Many researchers worked out backwash efficiency and manipulated many parameters to obtain better output. Kramer et al. (2020) highlighted the disadvantages of chemical cleaning and employed hydraulic backwash, which failed in their case because backwash strength is not attained. Backwash strength is the ratio of backwash pressure to the permeate pressure (Kramer et al. 2020). Usually, backwash strength should reach 2.1 to avoid damage to the membrane. So, they employed precoating methods. Chang et al. (2011) studied irreversible fouling of ultrafiltration membrane, filtration mode, and backwash water as parameters (Chang et al. 2011). Figure 11.3 illustrates the permeate backwash cleaning.

11.5.2 Chemical Cleaning

In the chemical cleaning method, oxidants, chelating agents, caustic acids, enzymes and surfactants are usually used for membrane cleaning (Gitis 2016). Each group of chemical cleaners are used for different types of foulants. For example, caustic cleaners such as NaOH are used to cure microbial and organic fouling. And, acids including nitric acid and citric acid are used to remove metal oxides and scales from fouling layers.

Both physical and chemical cleaning methods can remove the foulants to their extent, but care should be taken such that the membrane's primary function should not be affected by these techniques.

11.6 Conclusions

Nanotechnology is emerging as an efficient technology in various sectors, including water purification. It is noteworthy that nanofiltration membranes are efficient enough to remove monovalent and multivalent ions. Therefore, they were widely used in several applications, including surface and groundwater treatment, removal of organic contaminants and pathogens, etc. However, the fouling phenomenon limits the large-scale application of the NF membrane. Consequently, the present chapter discussed fouling, including organic, inorganic, and biofouling. The performance of the membrane is affected in two steps, namely concentration polarization and fouling. Accordingly, the present chapter discussed the mathematical models for the concentration boundary layer and Hermia's models of fouling. As fouling is unavoidable, the membrane should be regenerated by proper cleaning methods for long term use. Depending on the nature of foulants and operating conditions, physical, chemical or biological cleaning methods should be employed.

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Chapter 12
Nanofiltration Technology Applied for Peat and Wetland Saline Water

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Abstract Membrane technology in overcoming the problem of poor water quality. It has also become an interesting topic in the environmental issues in this modern era. Membranes have been applied for wetland water treatment which has high number of NOM (natural organic matter). In particular, wetland aquifer bodies is also facing sea water intrusion during hot season and bring out the water become saline. Then, nanofiltration (NF) is one of membranes technology which compatible to treat NOM content in the water. NF membranes are also employed the energy from the driven force. Here, the performance of the membranes such as permeability and selectivity in treated water is calculated. This chapter was providing an overview of the nanofiltration development applied for treating of wetland water. Operation condition which is influencing of NF performance for wetland water treatment has been described. Moreover, separation mechanism of NF and fouling control also clarified in this summary. The performance of NF as well as the operational barriers of NF membranes are discussed for review and future prospects of NF technology are described and conclusions drawn.

Keywords Nanofiltration · Wastewater · Saline water · Purification · Fouling

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_12

12.1 Introduction

The quality of raw water is increasingly being polluted and the content of pollutants, has become a topic of concern throughout the world. The rise of demands for clean technology towards a world green and clean of pollutants has led to innovations in technology development to produce clean water products clean water for activity. one of the methods for wetland water treatment using membrane technology (Assyaifi et al. 2021a, b; Elma et al. 2018, 2020a, b, c; Elma and Hairullah 2018; Elma and Riskawati 2018; Elma and Setyawan 2018; Lestari et al. 2020; Elma and Marhamah 2017; Rahma et al. 2020). Membrane is a barrier between two phases, capable of passing certain components (ions) and holding other components of a fluid flow that is passed (Mulder and Mulder 1996). The active components of the membrane are charged or neutral compounds that form complex compounds with ions in a reversible manner and carry them through organic membranes. Membrane filtration functions as a separation, concentration and purification of a solution.

The membrane process involves a feed (liquid and gas) and a driving force due to differences in pressure (ΔP), concentration (ΔC) and energy (ΔE). The most commonly used pressure membrane processes are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). In osmosis-driven membrane processes, typically represented by forward osmosis (FO) and reverse pressure osmosis (PRO), naturally generated osmotic pressure acts as a filtering force. UF membrane is proven capable to treat riched natural organic mater water as named peat water (Elma et al. 2022b; Mahmud et al. 2020). In other hand, perpavoration (PV) using silica based membrane also have been demonstarted for removing natural organic mater from both of peat and wetland saline water (Elma et al. 2021, 2022a; Mustalifah et al. 2021; Rahma et al. 2022). Both of natural organic mater and NaCl moluecules highly reduces by pervaporation, notwithstanding it is not in line with water fluxes obtained. Pervaoration membrane is more affordable and effetively for purification than for water supply. Nanofiltration (NF) membrane is a membrane with the main driving force is pressure which has properties between Reverse Osmosis (RO) and Ultrafiltration (UF) membranes. Nanofiltration membranes offer several advantages in the application of the desalination process such as requiring low energy, simple equipment, and high permselectivity. Due to these advantages, applications of NF worldwide are increasing widely (Mi et al. 2020).

The history of NF application was in the 1970s when RO membranes with reasonable water fluxes operating at relatively low pressures were developed (Fig. 12.1). Therefore, the high pressure traditionally used in RO membranes results in considerable energy costs. So, a membrane with a lower rejection of dissolved components, but with higher water permeability, will be a big improvement in terms of separation technology. Such low-pressure RO membranes are known as NF membranes. In the following half year, i.e. 1980s, NF membranes have been successfully established, and the first applications of NF membranes have been reported (Hilal et al. 2004).

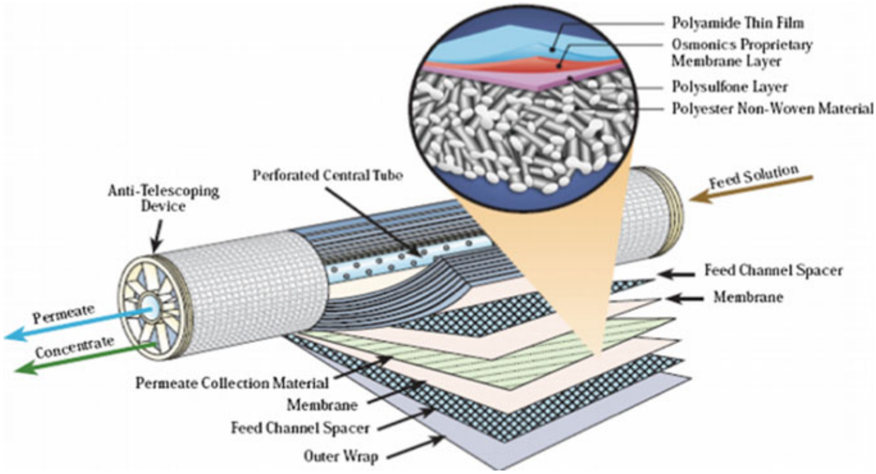


Fig. 12.1 Spirally wound nanofiltration membrane

In terms of characteristics, NF membranes have a pore size of usually 1 nm which corresponds to a cut-off molecular weight (MWCO) of 300–500 Da. As for the rejection, this membrane is usually negatively charged as a result of hydrolysis of the residual acyl chloride groups during the IP process. This means that the NF membrane has a high resistance to multivalent anions, however, it is less effective at repelling multivalent cations. The NF membrane in contact with aqueous solution is also slightly charged due to the dissociation of the surface functional groups or the adsorption of charged solutes. For example, polymeric NF membranes contain ionizable groups such as carboxylic groups and sulfonic acid groups that give rise to a charged surface. Similar to RO membranes, NF membranes have potential in terms of separation of inorganic salts and small organic molecules. The main distinguishing characteristics of NF membranes are low rejection of monovalent ions, high rejection of divalent ions, and higher flux compared to RO membranes. These properties allow NF membranes to be used in the applications in many fields especially for water and wastewater treatment, pharmaceutical and biotechnology, and food engineering.

Therefore, the advantages in water treatment using the NF membrane process are utilized to achieve clean technology that is environmentally friendly. Research reported by Pérez-González et al. (2015a, b) with the aim of reducing the adverse environmental impact of brine discharge, along with recovery of the valuable products contained in concentrated brine, specifically alkalis and acids. Brine pre-treatment was performed to remove salt and scaly impurities, followed by bipolar membrane electrodialysis (BMED) to recover hydrochloric acid (HCl) and sodium hydroxide (NaOH). As follows the NF Technology has proven to be technically feasible for the production of 1.0 M or higher acid and alkaline solutions. Based on the advantages of NF membrane, it is clearly needed in the various fields. In this case, a sequential process based on the right combination of membrane technologies, especially NF membranes, is described in this chapter so as to provide an overview of the development of nanofiltration technology applied in the treatment of peat water and wetland saline water. The performance of NF as well as the operational resistance of NF membranes are discussed for review and future prospects of NF technology are also well described.

12.2 Nanofiltration Technology for Peat and Wetland Water Treatment

12.2.1 Influenced Parameters

Parameters that affect nanofiltration membranes are temperature, feed flow rate used, pressure used, pH, variation of evaporation time and membrane pore size.

a. **Temperature**

Temperature The instrument applied to measure temperature an object, indicates the degree of heat objects. Simply put, the higher the temperature of an object, the hotter the object. Microscopically, temperature shows the energy possessed by an object. The higher the energy of the atoms making up an object, the higher the temperature of the object. Temperature can be detected in various objects that generate heat or are bound to heat in it, one of which is in the case of nanofiltration membranes. In the nanofiltration membrane there is a permeate flux in the Gd-DTPA solution. From the results of the study (Rahayu et al. 2016) the effect of temperature on the permeate flux of GdDTPA and Sm-DTPA solutions on the membrane is directly proportional. The higher the temperature employed, the higher the permeate flux produced. This is because the higher the temperature used, the larger the pore size of the membrane. The optimum rejection at 20 °C resulted in 99.73% Gd-DTPA rejection and 99.58% Sm-DTPA rejection. At 20 °C it is considered more effective to separate gadolinium and samarium because it has a slightly further difference than the separation at 25–40 °C (Rahayu et al. 2016). Based reported on NF process, the permeate flux is proportional to the transmembrane pressure at constant temperature. The relationship between temperature is related to three effects, with increasing temperature (1) the viscosity of the solvent decreases causing the membrane resistance to decrease, while the permeate flux increases, (2) the pore size increases due to the amount of water absorbed in the membrane and the pore surface decreases and (3) the increase in thermal energy helps to overcome the energy barrier caused by the friction of the walls in the pores (Tsuru et al. 2000; Yasukawa et al. 2020).

b. **Pressure**

Pressure is a force acting on a region of a surface. Pressure can affect objects. The effect of pressure on the membrane leads to rejection, namely the effect of pressure on flux permeat and rejection of Gd-DTPA and Sm-DTPA. The higher the pressure, the greater the flux of the solution. This is due to the influence of the driving force, the more molecules in the solution will pass through the membrane. Pressure affects the rejection, because the greater the pressure, the more rejection of Gd-DTPA and Sm-DTPA. This is because increasing pressure will increase the flow rate on the membrane so that the feed containing Gd-DTPA and Sm-DTPA will accumulate a lot on the surface or concentration polarization can occur. This indicates that water molecules pass through the membrane, due to the high pressure, the higher the permeate flux, so that the rejection is high. The results of the study (Rahayu et al. 2016) known that at a pressure of 6 bar the largest rejection occurs where Sm-DTPA rejection is 99.38% and Gd-DTPA rejection is 99.43%, but this is considered less effective in separating samarium and gadolinium because it has a rejection that is not much different (Rahayu et al. 2016).

c. **Power of Hidrogen (pH)**

One of the problems of the separation system using a nanofiltration membrane is the occurrence of membrane fouling due to the content of the main ingredients in the water used, especially in peat water. The fouling can be in the form of biological contaminants and macromolecular compounds. Fouling is organic matter that accumulates on the membrane surface because it does not take part in mass transfer. Due to fouling, the flux and membrane effectiveness decrease. research conducted by Nani et al. (2015) indicated relationship between variations in the pH value of water, especially in peat water, to the ability of the nanofiltration membrane to reject water organic substances and to determine the relationship of fouling that occurs in the nanofiltration membrane to changes in flux values. The pH of the peat water sample used in the experiment conducted by (Nani et al. 2015) as the determination of the best peat water pH was set from 3 to 7 with three trials.

The percentage of BOA removal continues to increase along with the decrease in the pH value. Research conducted states that decreasing the pH value can reduce the size of the BOA molecule and increase the adsorption on the membrane, thus causing a lot of fouling that occurs. This is in accordance with research conducted it has been done that at pH 3 and 4 the fouling that occurs is quite high. The amount and effect of membrane fouling is also determined by measuring the water flux through the membrane. The increase in the E_4/E_6 ratio in the permeate determined that the pore size of the membrane decreased with the result of BOA adsorption and pore limitation. UV–VIS spectroscope was used to determine changes in concentration and mean molecular size of dissolved BOA (Tian et al. 2018). The small pH value makes the percentage of BOA removal bigger because of the large amount of BOA that is retained on the membrane. At a lower pH, the E_4/E_6 ratio decreases which indicates that at a low pH there are still many molecules with large sizes seen from the value of the E_4/E_6 ratio. The small pH value makes the percentage of BOA removal bigger because of the large amount of BOA that is retained on the membrane (Nani et al. 2015).

d. **Feed Flow Rate**

The feed flow rate variable (v) has no statistically significant effect on the increase in the permeate flux value. Research from Uju et al. (2007) the rejection value of carrageenan reached 100% in all treatments. The 100% rejection value indicated that the carrageenan in the bait was successfully rejected by the membrane and entered the pathway. retentate, this indicates that the membrane pores with a diameter of 0.1 are sufficient to be used in the carrageenan separation process. Rejection values of phycoerythrin and phycocyanin pigments ranged from 36.36–59.44% and 27.61–59.05%, respectively. Based on these results, it can be seen that the phycocyanin pigments are relatively easier to pass through the membrane compared to phycoerythrins, this is due to the relatively lower molecular weight of phycocyanin (100–220 kDa) compared to phycoerythine pigments (240 kDa).The results of the analysis of variance showed that the feed flow rate variable had no significant effect on changes in the pigment rejection value (Uju et al. 2007).

e. Membrane Pores in Term of Rejection

When considering zeolites for water separation, the pore size determines the ion selectivity and the density of the framework determines the water permeability. Judging from the centrifuge process, a duration of 10 min showed optimal results in the working process of the membrane in filtering nitrate ions. The effect of fouling and polarization on mesh 40 with a duration of 10 min showed a rapid increase in the screening process. So the membrane permeability is low. PEG's role as anti-fouling does not work optimally (Nugroho 2014).

f. Variation of Evaporation Time

Variations in evaporation time can affect the characteristics in the manufacture of membranes. The solvent evaporation time clearly indicates that the longer the evaporation time will thicken the membrane surface and decrease the water flux but increase the selectivity of the membrane. The manufacture of membranes with varying times can affect the flux and membrane rejection values. For example, the manufacture of cellulose acetate membrane with an evaporation time of 3 min with a composition of 22% cellulose acetate, 15% acetone, 60% dimethyl sulfoxide (DMSO), and 3% dimethyl phthalate (DMP) produce an ultrafiltration membrane with a flux value of 2.2438 L/hour m^2 and rejection of 100–200 kDa dextran was 91.15%. Where in this example they conducted research by focusing on the manufacture of cellulose acetate membranes with acetone and DMSO as solvents and the addition of PEG as much as 5% of the total polymer solution. Variations in evaporation time used 0, 1, 3, and 5 min were then studied for their effect on porosity, flux, coefficient of permeability and rejection of 500 kDa dextran.

12.2.1.1 Characteristic of Feed Water

Wetlands include areas of brackish (saline), bog, peat whether natural or artificial, permanent or temporary, with running or standing water, fresh, brackish, or salt; including areas with sea water whose depth at low tide (low tide) does not exceed six meters (Soendjoto 2016). In Southeast Asia, the total peatland area is around 12% of mainland Asia (27.1 million hectares) (Hooijer et al. 2006). Most of the peat consists of humic substances which are natural and organic substrates (Jin et al. 2017). Indonesia's wetlands are land with an area of about 33.4 million ha of swamp consisting of 20.1 million ha of tidal swamp land and 13.3 million ha of lebak swamp, and of 13.3 million ha of lebak swamp consisting of lebak swamp shallow 4.2 million ha, middle lebak swamp 6.07 million ha, and deep lebak swamp 3.0 million ha, which are spread over Sumatra, Kalimantan, Sulawesi and Papua (Annisa 2021).

The quality of wetland water and peat water water generally have characteristics such as cloudy color, blackish brown caused by the accumulation of parent material such as clay, wood manure, twigs that sink and settle at the bottom of the swamp for years (Kamun et al. 2010).

Indonesia has 33.4 million ha of wetland, have great potential in various fields, such as the abundance of available water that can be utilized by the community (Fig. 12.2). The following is the distribution of wetlands in Indonesia, which are classified into 2 types of swamps based on the type of inundation, including tydal swamps and non-tidal swamps. Peatland or known as peat swamp can be found in conditions between the two swamps above. Tables 12.1 and 12.2 are the characteristics of wetland water in Indonesia.

Based on the table above, it is known that the wetland water in South Kalimantan contains a high organic matter content and it is necessary to process the water

Fig. 12.2 Wetland distribution in Indonesia (Sulaiman et al. 2019)

Table 12.1 The characteristics of wetland saline water in Indonesia, especially in South Kalimantan

No	Parameter	Unit	Wetland Saline Water	Reference
1	pH	–	6.67	Elma et al. (2020)
2	TDS	Mg/L	5400	
3	Conductivity	µS/cm	9350	

Table 12.2 The characteristics of peat water in Indonesia, especially in South Kalimantan

No	Parameter	Unit	Peat Water	Reference
1	pH	–	4.12	Mahmud (2016)
2	colour	PtCo	361.98	
3	Conductivity	μS/cm	68	
4	Organic compound	Mg/L $KmnO_4$	316.24	

into clean water. membrane technology was chosen as a tool capable of processing wetland water into suitable water for households. the development of membrane technology in treating water in wetlands, especially peatland and wetland saline water with the Nanofiltration process is an effort towards clean technology.

12.2.1.2 Operation Condition

Nanofiltration is a pressure driven membrane separation process with intermediate separation effectiveness between RO and ultrafiltration (UF). NF membranes are typically polymeric, asymmetric and consist of a low resistance support layer with a functionally active porous top layer. NF membranes have properties that combine size and electrical effects. The pores are typically near 1 nm in diameter and have fixed charges. Due to these characteristics, NF membranes retain multivalent complex ions and permeate small uncharged solutes and low charged ions. This, along with the small energy consumption of the process and the high fluxes attained, makes NF membranes extremely useful in fractionation and selective removal of solutes from complex process streams. However, the description of membrane NF separations is extremely complex and is dependent on the micro-hydrodynamics and interfacial events occurring at the membrane surface and within the membrane nanopores. There is significant debate as to the exact nature of these complex phenomena, and the rejection is typically attributed to a combination of steric and electrical effects. Modeling of transport through membranes is an essential engineering aspect; although many models for nanofiltration have been proposed by several researchers, a realistic model that describes rejection of charged molecules has never been well established. Thus, this work investigates experimentally and theoretically the NF separation of sulfate and chloride co-ions from highly concentrated solutions providing the tools needed for the design and optimization of the recovery of brackish and seawater RO desalination brines (Pérez-González et al. 2015a, b).

12.2.1.3 Properties of Nanofiltration Membranes

The membrane process is a separation process at the molecular level or very small particles. The separation process with membranes is possible because the membrane has the ability to move one component faster than the other components based on differences in the physical and chemical properties of the membrane and the components being separated. The singularity of these membranes is highlighted by their ability to selectively reject different dissolved salts; they have a high rejection rate of low molecular weight, dissolved components. Nanofiltration membranes with low transmembrane pressure, operating pressure of generally 5–30 bar, were developed to achieve high divalent ion rejection. It is expected that the rejected molecules can have a molecular weight of 200 g mol^{-1}; this corresponds to an equivalent of Stokes diameter of approximately 1 nm. Nanofiltration membranes are neither entirely dense nor entirely porous, so their retention mechanisms are determined by both size exclusion (porous membranes) and sorption and diffusion (dense membranes). Also, these kinds of membranes are principally used to partially soften potable water, allowing some minerals to pass into the product water, thus increasing the stability of the water and preventing it from being aggressive to distribution piping material. Additionally, NF membranes are discovering increasing use in purifying industrial effluents and minimizing waste discharge. The key to using NF membranes for particular applications is the selection of a membrane with the appropriate rejection characteristics and the design of a suitable process. In general, NF membranes are characterized by a high charge density and pore sizes in the range of nanometers; the surface charge is most often negative and has the greatest effect on the selective passage nature of these membranes. New studies have been developed, and new membranes having unique properties, including a varying range of hardness rejection and fouling resistance manufactured.

In general NF has two distinct properties:

a. The pore size of the membrane corresponds to a molecular weight cut off value of approximately 300–500 g/mole. Therefore, the separation of components with these molecular weights from higher molecular weight components can be accomplished.
b. NF membranes have a slightly charged surface. Because the dimensions of the pores are less than one order of magnitude larger than the size of ions, charge interaction plays a dominant role. This effect can be used to separate ions with different valences.

With these properties the most important application areas can be defined:

a. Removal of monovalent ions from: waste water, reaction mixtures in which NaCl is formed and whey.
b. Separation between ions with different valences.
c. Separation of low- and high-molecular weight components.

In nanofiltration, the distribution of a non-charged solute at the boundary layer/membrane interface is considered to be determined by a steric exclusion mechanism. Steric exclusion is not typical for nanofiltration but applies to ultrafiltration and microfiltration too. Due to its size a solute only has access to a fraction of the total surface area of a pore. This causes a geometrical exclusion of the solute from the membrane. A separation between solutes will only be accomplished when the solutes have a difference in size.

For charged solutes two additional distribution mechanisms can be recognised:

1. Donnan exclusion, which compared to other pressure driven membrane processes has a pronounced effect on the separation in NF. Due to the slightly charged nature of the membrane, solutes with an opposite charge compared to the membrane (counter-ions) are attracted, while solutes with a similar charge (co-ions) are repelled. At the membrane surface a distribution of co- and counter-ions will occur, thereby causing an additional separation.
2. Dielectric exclusion, which generally does not play a role in ultrafiltration and microfiltration but which is of major importance in electrodialysis. Due to the charge of the membrane and the dipole momentum of water, water molecules will show a polarisation in the pore. This polarisation results in a decrease of the dielectric constant inside the pore, thereby making it less favourable for a charged solute to enter. However, even in a situation that the dielectric constant inside the pore is equal to the one of water, a change in electrostatic free energy of the ion occurs when the ion is transferred from the bulk into the pore. This also results in exclusion.

12.2.1.4 Separation Mechanism of NF

NF combines removal of uncharged components at nanoscale with charge effects between solution and the surface of the membrane. The removal of uncharged components results from size exclusion or may be a result from differences in diffusion rates in a non-porous structure, which depend also on molecular size. The charge effect, on the other hand, results in removal of (mainly multivalent) ions; the former effect results in the removal of uncharged organic species. Thus, the separation performance of NF membranes can be identified into the sieving (steric hindrance) effect and Donnan (electrostatic) effect. Organics were rejected differently depending on the sieving parameters,based solute and pore size (Kosutic and Kunst 2002). (In addition, the polarity and charge of organics may influence the rejection process, especially when the pore diameters of membranes are big, the researchers determined. According to Chellam and Taylor, molecular diffusion is another element that influences rejection. Charge interactions between the membrane surface and the ions caused the rejection of ionic components in NF (Donnan exclusion). The retention of Na_2SO_4 and $MgCl_2$ was found to be high, but that of NaCl was substantially lower.

In nanofiltration, It is literally proposed two mechanisms for ion transfer:

1. Convection: the bigger ions are more retained (physical parameters);
2. Solubilization-diffusion: a function of solvation energies and partition coefficient.

In addition to the ionizable surface groups, NF membranes have a weak ion exchange capacity and in some cases ions from the contacting solution may adsorb to the membrane surface causing a slight modification of the membrane charge. Electrostatic repulsion or attraction takes place according to the ion valence and the fixed charge of the membrane that may vary depending on the localized ionic environment as a result of the aforementioned phenomena. The phenomena of dielectric exclusion are much less understood and there are two main competing hypotheses as to the exact nature of the interaction. These are the so-called '*image forces*' phenomenon and the 'solvation energy barrier' mechanism (Childress 1996).

Both exclusion mechanisms are effectively charge-based exclusion events that develop as a result of the severe spatial confinement and nano-length scales prevalent in NF membrane separations. These interactions have been well examined. The solvent flowing through the restricted pore structure exerts drag forces on solutes moving in free solution. The local environment has a significant impact on solute transportation in this limited region, and solute transport is believed to be hampered. Hindered transport has a convective and diffusive component, both of which contribute to the overall transport effect (Mohammad et al. 2015). Because the dimensions of the NF active layer are near atomic length scales, combined with current measurement technology limitations, detailed knowledge of the physical structure and electrical properties of real NF membranes has been delayed, resulting in uncertainty and significant debate over the true nature of the separation mechanisms, with the role of dielectric exclusion being particularly contested.

12.2.1.5 Separation Mechanism of NF in Eliminating Microorganisms

NF is a complex phenomenon that is heavily influenced by fluid flow, its properties, and interfacial episodes that occur on the membrane's outer surface and within its porous structures. Donnan, transport, dielectric, and steric processes combine to produce separation through NF membranes. The Donnan effect is the equilibrium and interaction of a soluble charged molecule with the charge on a membrane (Donnan 1995). The charge on the membrane is thought to be caused by the dissociation of various ionic groups on the membrane as well as the porous shape of the membrane. Depending on the type of materials utilized for membrane manufacturing, the ions can be acidic, basic, or amphoteric. The pH of the purification solution has a big influence on the dissociation of surface-available ionizable groups.

It's worth noting that membranes with amphoteric behavior can show isoelectric points at specific pH levels (Childress 1996). Apart from the presence of surface ionizable groups, the mild ion exchange property of the NF membrane may, under certain conditions, lead to adsorption of ions present in the solution to be treated, affecting the membrane properties. There may be attraction or repulsion according to the prevailing conditions, which are accounted for by charges on solute molecules and NF membranes. The mechanism of dielectric extrusion as a putative NF mechanism is poorly understood, and the "image forces" and "salvation energy barrier" hypotheses have been offered to explain the mechanical specifics of interaction.

Both behaviors are attributed to the NF membrane's dense spatial confinement, nanoscale dimension, and charge. Drag forces exerted by solvent passing through holes of various sizes affect solute mobilization in the solution phase. As a result, the properties of the solvent have a significant impact on the transport of solute molecules via distinct restricted holes, and the free movement of solute is hampered. The process of convection and diffusion thus determines the overall transport of a solute. Nonetheless, the true mechanical aspects of the NF membrane separation process remain a mystery, and the role of dielectric exclusion in membrane separation, in particular, need more research. Because of their size discrepancies, uncharged solute molecules are generally rejected (size exclusion).

12.3 Fouling and Controlling Process of Nanofiltration Membranes

Membrane fouling is caused by dissolved inorganics ($BaSO_4$, $CaCO_3$) or organic components (humic acids), colloids (suspended particles), bacteria or suspended solids (Hilal et al. 2004). The NF membrane retains substances with a molar mass higher than ~300 g mol and multivalent ions. The efficiency of the nanofiltration process is influenced by fouling on the membrane and other factors such as tangential velocity, pressure, temperature, turbulence, feed particle size, changes in concentration polarization on membrane properties, and membrane characteristics. The retention characteristics are highly dependent on how much free volume is present in the membrane, which can for some membranes be related to flux. Since the nanofiltration membrane has the characteristics of both an ultrafiltration membrane and a reverse osmosis membrane, its fouling characteristics are also somewhat unique.

The fouling is initiated by the membrane-solution material interaction; however, Van der Waals forces, chemical bonds, and Lewis acid–base interactions are the main phenomena involved in the resulting interactions between surfaces and solutes at the molecular level. As a result, the physicochemical properties of the membrane surface change and this facilitates the deposition of other molecules and other aggregates. The membrane-solvent interaction can be expected to diversify with changes in solvent properties, such as molecular size, surface tension, viscosity, and dielectric constant. Fouling may occur in pores of membranes by partial pore size reduction caused by foulants adsorbing on the inner pore walls, pore blockage and surface fouling such as cake and gel layer formation. Fouling will lead to higher operation costs: higher energy demand, increase of cleaning and reduced life-time of the membrane elements (Hilal et al. 2004).

Membrane autopsies are characterized for using techniques that are able to identify the inorganic and organic material found at the membrane surface (Arnal et al. 2011):

- Scanning Electron Microscope (SEM) and Scanning Electron Microscope coupled with Energy Dispersed X-ray (SEM–EDX) to determinate inorganic foulant elemental composition.
- Fourier Transform Infrared Spectroscopy (FTIR) to identify organic compounds.
- Targeted Energy Dispersive X-Ray Analysis (T-EDXA) as an indication of inorganic compounds.

For identifying biofouling, several techniques can be achieved during autopsies, such as:

- Total Direct Count, which determinates in the membrane surface the number of bacteria dead or alive, growth in a medium and counted with microscope per cm^2.
- Heterotrophic Plate Count, which scrapes a sample of the biomass attached on the membrane surface to determinate colony forming units (CFU) growth in a special medium.
- Adenosine Triphosphate (ATP), which is considered an essential indicator of living bacteria and gives a measure of the amount of active biomass over the membrane surface.

The presence of particles can be clearly seen in the SEM image of the nanofiltration membrane that is broken from the edges and the middle (Fig. 12.3). It is clear that the cluster structure is formed by pollutants on the surface of the NF film. Large-scale flocculant pollutants are observed on the surface of the film, and the scanning electron microscope image is clear.

The main elements in the membrane scale are C, N, and O, which indicates that the main pollutants in the membrane scale are organic matter and their combined weight ratio is as high as 86.74% (a), 87.52% (b), 94.11% (c), and 84.75% (d). Small amounts of Na, Si, Cl, K, Ca, Fe, Zn, Al, S were also obtained and these inorganic

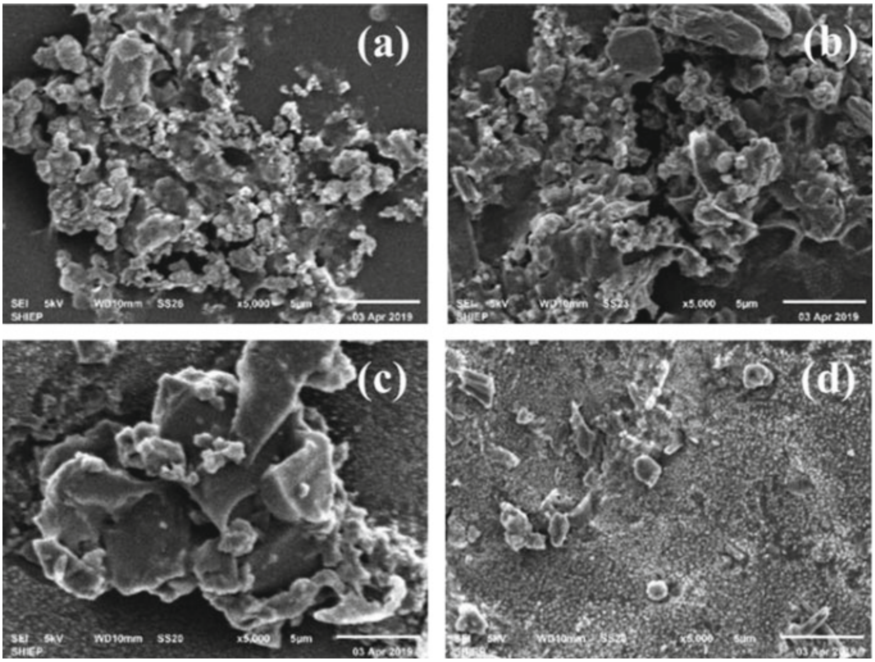


Fig. 12.3 SEM of the Nanofiltration (NF) membrane fouling. **a**, **b** Middle example magnified 1:5000, **c**, **d** edge scale enlarged 1:5000

elements might be the main reason for fouling of the membrane active layer and causing the membrane flux in the nanofiltration system to continuously decrease. Through complex processes involving crystal nucleation or transport mechanisms, membrane fouling arises. Inorganic ions may exist in the form of nanoparticles or colloidal particles and they are deposited on the surface of the film. Al and Si may appear as colloidal SiO_2 and colloidal $Al(OH)_3$ because Al and Si are difficult to form inorganic precipitates in leachate. Ca can form complex compounds with natural organic matter (NOM), thereby facilitating the subsequent formation of intermolecular bridges between organic fouling molecules and increasing membrane fouling. The interaction between foulant and foulant plays an important role in determining the incidence and level of organic foulants. The strong soil-foulant adhesion allows foulant to accumulate on the membrane surface faster, therefore the formation of NF membrane fouling can occur when these inorganic deposits are trapped on the membrane surface, and then colloidal SiO_2, $Al(OH)_3$ can be adsorbed on its surface under the influence of van der Waals force and electrostatic attraction. The pores gradually become smaller, and organic matter and microorganisms continue to be adsorbed and accumulated on the surface. Finally, a foulant layer of the nanofiltration membrane is formed. So, the foulant layer is the result of a combined reaction of organic matter, inorganic precipitation, colloids and microorganisms.

Fouling is an irreversible and time-dependent phenomenon; it is related to the characteristics of the membrane and solute–solute and solute-membrane interactions that cause an irreversible decline in the flow of permeate, which can only be recovered by the chemical cleaning of the membrane. In addition, some process parameters like equipment design, temperature, feed concentration, flow, and pressure can also contribute to membrane fouling. A number of factors contribute to fouling and are strongly interlinked. Organic, inorganic, particulate, and biological fouling are some of the main fouling categories. Also important are metal complexes, for example, Fe, Al, Si. Despite many research traditionally focusing on one category or fouling mechanism at a time, it is well accepted that in most cases, it is not one single category that can be identified. In most real-life applications, all four types of fouling go hand in hand.

To solve this problem, various strategies have been proposed which include pretreatment optimization, controlling operating conditions, and developing membrane with antifouling properties. One of the most important identified foulants found in surface water sources is organic substances. Organic fouling on the membrane surface can be controlled by endowing membrane surface with a more hydrophilic layer. The hydrophilic surface will reduce the fouling tendency of organic substances, which are typically hydrophobic, on the membrane. Modification of membrane can be done by blending of the original polymer with polymers having more suitable properties or by addition of polymer layers on the active surface of membrane.

To control the NF Membrane process, several strategies are needed to avoid blockages. The strategies obtained to control Foulan based on the contamination are shown in Table 12.3 as follows:.

Table 12.3 Foulant and its control strategy in the nanofiltration process

Foulant	Fouling control
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (scaling)	Operate below solubility limit, pre-treatment, reduce pH to 4–6 (acid addition), low recovery, additives (anti-scaling); some metals can be oxidized with oxygen
Organic	Pretreatment using biological processes, activated carbon, ion exchange, ozone, enhanced coagulation
Colloids (<0.5 μm)	Pre-treatment using coagulation and filtration, microfiltration, ultrafiltration
Biological solids	Pretreatment using disinfection (e.g., chlorination/dichlorination), filtration, coagulation, microfiltration, ultrafiltration

Therefore, the efficiency of a nanofiltration process depends on the size of the particles present in the solution and molecular loads.

Examples of this indicators and early warnings fouling (Arnal et al. 2011):

– Membrane Fouling Simulator (MFS): uses the same materials as spiral-wound RO and NF membranes. This tool is very useful to study and monitor fouling and biofouling over spiral wound membranes, monitoring pressure drop, in situ-real time observation of membrane surface and multiple analysis of coupons sampled form the membrane. The small size and low water and chemical use of the MFS facilitate to perform systematic parallel studies. With the MFS, fouling of membranes applied in water treatment can be characterized
– Visual Observation methods: recently, a new high-pressure optical membrane module has been developed to enable direct visual observation of bacterial deposition onto reverse osmosis membranes under practical seawater desalination operating conditions. The new optical membrane module withstands pressures up to 8.3 MPa while allowing high transmission of UV and visible light. Computational fluid dynamic analyses of the optical module suggest practically relevant cross-flow hydrodynamic conditions exist through the viewing area of the optical window
– In-line biofouling monitor: this recent development is based on accurate monitoring of normalized pressure drop, flow and temperature across first stage. It is very useful to monitories biofouling and scaling.
– Ultrasonic Time-Domain Reflectometry (UTDR): as an in situ, non-invasive real-time technique has been successfully used to quantify membrane fouling and cleaning. This ultrasonic technique is useful for quantitative study of the effect of magnetic fields on $CaCO_3$ scale deposition on the membrane surface during cross-flow nanofiltration (NF) and also in ultrafiltration (UF) membranes These results have been corroborated by comparing this technique with SEM and flux decline data also.
– Magnetic Resonance Imaging (MRI): this has been recently applied to biofouling studies of RO membranes, identifying both biofilm accumulation within the

module and the resultant effects on water flow. MRI thus offers an in situ and non-destructive method to quantify biofilm directly. It is also a tool for direct studies of chemical cleaning of bio fouled RO membranes, special for studying cleaning effectiveness.

Usually several types of fouling will be encountered in a membrane process. For instance, the existence of organic matter in feed solution will result in organic fouling and at the same time it will become the nutrient for microorganisms to grow and adhere to the membrane surface. But some observed that the presence of certain foulants might suppress the other fouling propensity. Operating conditions such as recovery rate and flow velocity will affect fouling propensity of a membrane process. Thus, fouling is a complex phenomenon where it involves the interaction between the feed solution, membrane properties and operating conditions. The factors affecting colloidal fouling propensity into three categories, which is membrane properties, feed water composition and hydrodynamic conditions. It has been reported that membrane fouling can either improve or deteriorate the quality and efficiency of membrane separation. Several studies about the type of NF membrane fouling and the mechanisms involved (Mohammad et al. 2015).

The first barrier to fouling is fouling indices through feed water analysis. Feed water analysis such as pH, ionic strength, turbidity, silt density index, TOC, COD, BOD, SUVA, salts' composition and concentration, MFI and biofilm formation rate can give some indication of likelihood of fouling and presence of contaminants. It affects the design of the processes to be used for the treatment purpose. Such analysis also provides a guide on what membrane to be used, mode of operation and operating conditions as well as the appropriate processes to be involved in the treatment system. Parameters like pH and salt will affect the filtration performance and NF membrane properties as well as fouling mechanisms. One of the most effective fouling control strategies is the feed pre-treatment before the NF membrane unit. Different types of pre-treatment have been used to reduce the foulants in the feed and thus decreasing the chance of severe membrane fouling in many operation processes. Successful pre-treatments prior to membrane units have been reported; such as coagulation, flocculation, ozonation, adsorption, H_2O_2/UV oxidation, UF/MF. However, it must be noted that those pre-treatment processes might not be able to eliminate all the foulants in the water, which means NF membrane process still requires some other fouling control strategies (Mohammad et al. 2015).

12.3.1 Pretreatment Requirement

Feed pretreatment is one of the major factors determining the success or failure of a desalination process. Different methods of pretreatment for desalination process were suggested by many researchers. Pretreatment such as coagulation, adsorption, and ozonation, before the membrane technology, had been used to remove NOM and to mitigate fouling also found that pretreatment coagulation can improve performance

Ultfiltration membrane, especially increasing removal of color and organic matter as well as reduction fouling (Abdi et al. 2013). The main problem in using conventional pretreatment is corrosion and corrosion products. For example, in the acid dosing system, corrosion of metallic surfaces and corrosion products will roughen the surface of the equipment, which provides active sites for precipitation of more scale deposits. In addition, this pretreatment is known to be complex (Hilal et al. 2004).

NF pretreatment of seawater in desalination plants:

1. prevented SWRO membrane fouling by the removal of turbidity and bacteria,
2. prevented scaling (both in SWRO and MSF) by removal of scale forming hardness ions and
3. lowered required pressure to operate SWRO plants by reducing seawater feed TDS by 30–60%, depending on the type of NF membrane and operating conditions.

The introduction of NF for water pre-treatment led to an increase in performance by maintaining an almost invariant energy requirement. NF is also used to treat brackish water which is quite efficient in reducing organic and inorganic content and provides high water resuscitation up to 95% (Hilal et al. 2004). There are several methods for modifying the membrane surface such as plasma treatment, in-situ polymerization, dip-coating, etc. In previous study [21], it has been demonstrated that the dip-coating method has successfully increased the hydrophobicity of a polypropylene (PP) membrane by creating a rougher surface. However, dip-coating method for increasing hydrophilicity of PP membrane in water treatment, especially for peat water filtration application is rarely reported. Composite PP membrane was prepared by coating PSf/DMAc solution. Preparation steps are shown in Fig. 12.4.

Results show that the simple dip-coating method was successfully employed to deposit PSf/PEG400/ZnO layer on PP membrane surface evidenced by the results of SEM analysis (Fig. 12.5). ZnO particles could increase membrane hydrophilicity shown by decreasing WCA from ~97.7 to 77.1 which resulted in higher PWP (from ~16 to ~46 L m^{-2} h^{-1} bar^{-1}). The higher hydrophilicity also reduced organic fouling tendency of the membrane during peat water treatment (FRR: from 63 to 66% and

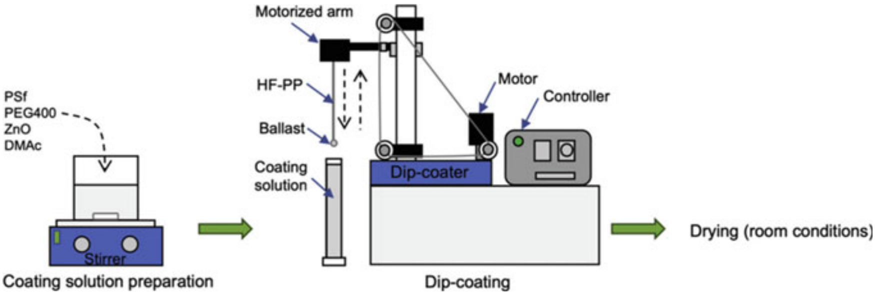


Fig. 12.4 Composite PP membrane preparation steps

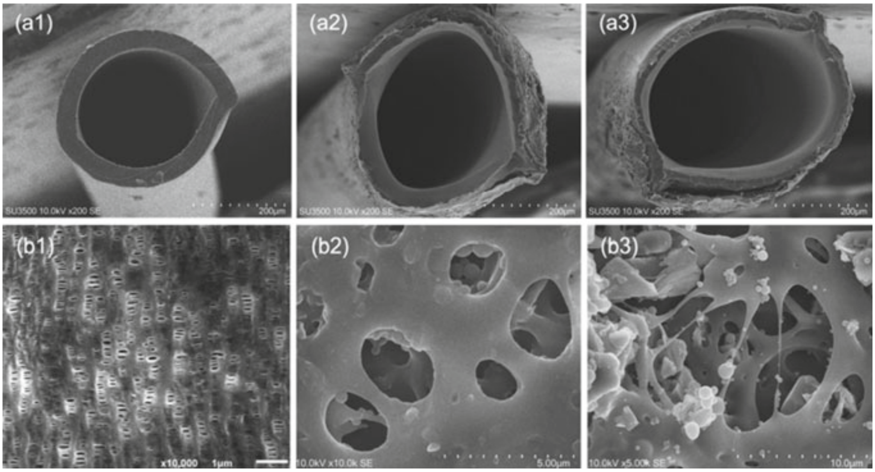


Fig. 12.5 SEM images of PP and composite PP membranes. **a** Cross-section, and **b** membrane surface. Membranes: (a1), (b1) = PP; (a2), (b2) = M-ZnO-0%; (a3), (b3) = M-ZnO-40%

RFR: from 53 to 44%). In addition, the composite PP membrane, MZnO-40%, was able to remove about ~70% humic substances from peat water.

12.3.1.1 Coagulation

Coagulation is a process by which destabilization of the added solution or suspension is carried out. The function of coagulation is to overcome the factors that increase the stability of a particular system. Primary coagulants refer to chemicals or substances added to certain suspensions or solutions to cause destabilization (Bratby 1980). In case of a metal coagulant (for example aluminum sulfate, ferric chloride etc.) is added to (say) a clay suspension, the metal coagulant is used as the primary coagulant. If a cationic polyelectrolyte is added instead of a metal coagulant, the polyelectrolyte is referred to as the primary coagulant. In both cases, a primary coagulant was added to destabilize the clay dispersion (Bratby 1980).

Metal Coagulant

It is commonly used metal coagulants fall into two general categories, namely those based on aluminum and those based on iron. Aluminum coagulants include aluminum chloride, sodium aluminate, poly Aluminum Chloride and aluminum sulphate. The iron coagulants include ferrous sulphate, ferric sulphate, ferric chloride and chlorinated copperas. Other chemicals used as coagulants include hydrated lime—$Ca(OH)_2$ and magnesium carbonate—$MgCO_3$. The popularity of aluminum and iron coagulants arises not only from their effectiveness as coagulants but also from their readily available availability and relatively low cost. The effectiveness of this coagulant arises from its ability to form multi-charge polynuclear complexes in solution with enhanced adsorption characteristics. The nature of the complex formed can be controlled by the pH system (Bratby 1980).

Polyelectrolytes

The term polyelectrolyte, as used herein, refers to a wide variety of natural or synthetic macromolecular compounds, soluble in water, which have the ability to disrupt or enhance the flocculation of constituents of water bodies. Strictly speaking, the term polymeric float is more appropriate as a general description, polyelectrolytes may be better used for those which carry ionized groups. However, due to its wide use, the term polyelectrolyte will be considered to include polymer flocculants which are essentially non-ionic (Bratby 1980). A polymer molecule can be described as a series of repeating chemical units held together by covalent bonds (polymer, from the Latin literal translation means many parts). If the repeating units have the same molecular structure, the compound is called a homopolymer. However, if a molecule is formed from more than one type of repeating chemical unit, it is called a copolymer. The individual repeating units are called monomers and the molecular weight of the polymer molecules is the sum of the molecular weights of the individual monomers. The number of monomer units is referred to as the degree of polymerization (Bratby 1980).

Adsorption

Adsorption technique is defined as a mass transfer process in which one or more substances (adsorbate) present in a gas or liquid stream are transferred selectively to the surface of a porous solid (adsorbent) (Sales et al. 2019). Usually the small particles of the adsorbent are retained in a fixed bed, and the fluid is passed continuously through the bed until the solid is nearly saturated and the desired separation can no longer be achieved. The stream is then diverted to a second bed until the saturated adsorbent can be replaced or regenerated (McCabe et al. 1993). The adsorption technique is widely used in water treatment, being a technologically and economically feasible technology, capable of removing organic pollutants with an efficiency of 99.9% (Ali et al. 2012).

Two types of adsorption are physical adsorption or fission-sorption (van der Waals adsorption) and chemisorption (active adsorption). Physical adsorption is a reversible phenomenon, which results from the intermolecular attractive forces between the solid and the adsorbed substance. Chemisorption is the result of chemical interactions, generally stronger than fission-sorption between the solid and the adsorbed substance. This process cannot be changed. It has importance in catalysis (Anantharaman and Begum 2017; Elma et al. 2020a; Mustalifah et al. 2021).

Photocatalytic

Photocatalytic is a reaction that takes place between photochemical and catalyst simultaneously. The photochemical reaction process involves the influence of a light (photo). Photocatalytic itself is a transformation reaction that takes place on the surface of a semiconductor catalyst material induced by light. A catalyst is a substance that affects the rate of a reaction without being chemically changed. The catalyst used can accelerate the photoreaction through its interaction with the substrate in either the ground state or the excited state, and also the photo product mainly depends on the mechanism of the photoreaction. Usually the catalyst used is a good semiconductor such as TiO_2, ZnO and CdS catalysts. Figures 12.6 and 12.7 show how the photocatalytic membrane works during the water treatment process (Assyaifi et al. 2021a, b; Cooker 2001; Wang et al. 2016, 2017).

(Cooker 2001), studied the effect of photocatalytic oxidation of natural organic matter (NOM) on low pressure membrane fouling. In this study, they evaluated the photocatalytic ability of natural organic TiO_2/UV materials to control film fouling by coating the film with a TiO_2 layer. The TiO_2 layer increased the reaction rate, but a decrease was observed as the total organic carbon content increased. At a concentration of 0.5 g/L TiO_2, micro and ultrafiltration membrane contamination was removed after 20 min of treatment. Analysis of UV Specific Absorption Rates and Natural Organic Molecular Weight Distributions revealed that their effectiveness in controlling membrane fouling is the result of changes in molecular properties due to preferential removal and conversion of naturally occurring hydrophobic large organics to. Other processes in which photocatalysts and antibacterial electrospinning nanofiber membranes are used include filtration, adsorption, and electrode catalysis.

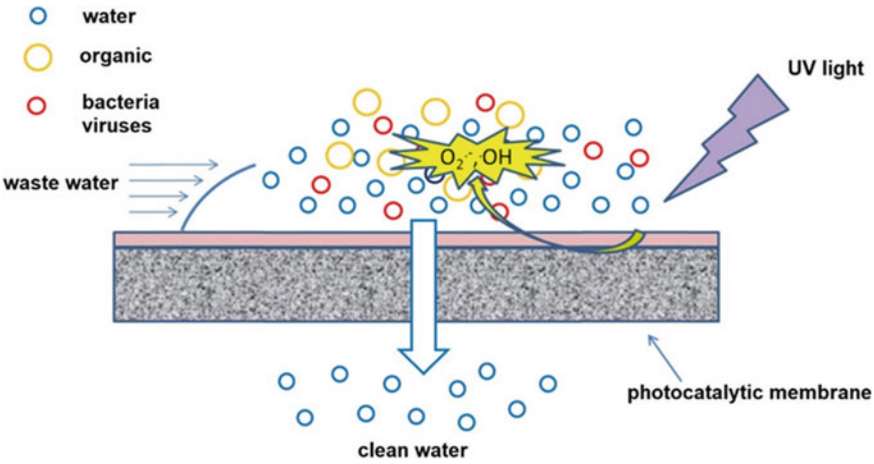


Fig. 12.6 Schematic of photocatalytic membrane operates with photocatalytic layer on top degrading pollutants and membrane filtering the remaining pollutants (Chabalala et al. 2021)

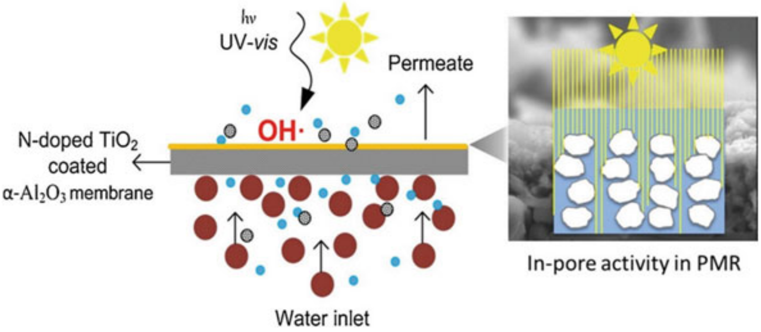


Fig. 12.7 Illustration of simultaneous filtration and photodegradation processes on a photocatalytic-filtration hybrid composite membrane (Chabalala et al. 2021)

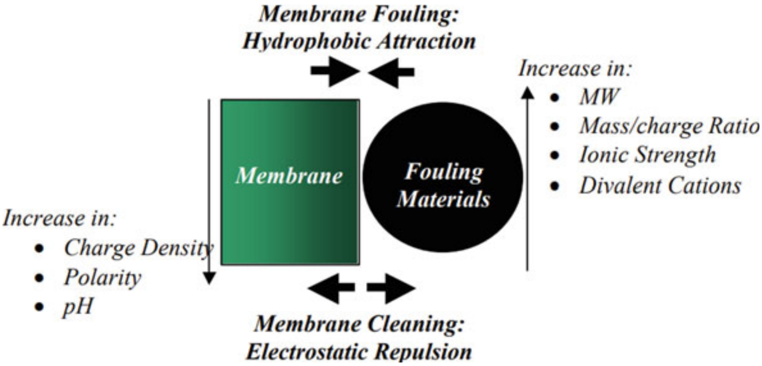


Fig. 12.8 Conceptual model of membrane fouling and cleaning (Liu et al. 2001)

12.3.2 NF Membrane Cleaning Process

Membrane cleaning methods can be divided into physical and chemical. In practice, physical cleaning methods followed by chemical cleaning methods are widely used in membrane applications. For membrane fouling dominated by the adsorption of natural organic matter, and dominated by microbial causes to a less extent, the fouling and cleaning can be illustrated by a simple conceptual model as in Fig. 12.8.

12.3.2.1 Physical Cleaning

Physical cleaning methods use mechanical forces to dislodge and remove foulants from the membrane surface. Physical methods include sponge ball cleaning, forward and reverse flushing, backwashing, air flushing (also called air sparging, air scouring or air bubbling) and CO_2 back permeation (Ebrahim 1994). Ultrasonic, electrical fields and magnetic fields are other physical cleaning methods that are described in detail in non-conventional cleaning methods point of this work.

a. Sponge Ball Cleaning

In this method, sponge balls made of polyurethane or other materials are inserted into the membrane modules for a few seconds for scrubbing the foulant from membrane surface (Ebrahim 1994). Sponge balls are normally used for cleaning large diameter tubular membranes when treating heavily polluted solution such as wastewater and industrial process water (Psoch and Schiewer 2006).

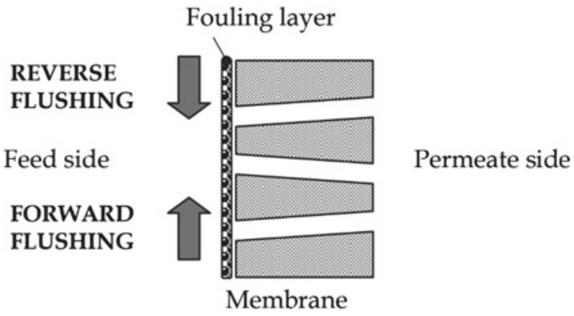
b. Forward and Reverse Flushing

Forward flushing consists in pumping permeate water at high cross-flow velocity through the feed side in order to remove foulants from the membrane surface (Ebrahim 1994). Because of the more rapid flow and the resulting turbulence, particles absorbed to the membrane are released and discharged. In the reverse flushing method the direction of the permeate flush is alternated for a few seconds in the forward (feed to brine) and for a few seconds in the reverse direction (brine to feed) (Fig. 12.9). Forward flush techniques are particularly useful in removing colloidal matter.

c. Backwashing

This is a reversed filtration process in which permeate is flushed through the membrane to the concentrate side. In porous membranes, when backward flush is applied, the pores are flushed inside out. The pressure on the permeate side of the membrane is higher than the pressure within the membranes, causing the pores to be cleaned. Some significant factors affecting physical cleaning when combining forward and backward flushing are production interval between cleans, duration of backwash and pressure during forward flush (Chen et al. 2003). A main factor of the backwash cleaning is the driving force, which results from a combination of concentrations and applied pressures from both sides of RO membrane. From the point of view of operating conditions, backwash cleaning may be divided into two cases: (1) with zero feed velocity and applied pressure, and (2) with feed velocity and pressure. Some works have shown that methods without pressure seem to have

Fig. 12.9 Cleaning flow direction in forward and reverse flushing



some advantages on methods with pressure (Sagiv and Semiat 2010). From the point of view of salt concentration difference between both sides of membranes, there is recent research on the use of hypersaline solutions in the feed side.

d. Air Flushing

The air flushing or air sparging method generates a two phase flow to remove external fouling and thus reduces the cake layer deposited on the membrane surface (Ngene et al. 2010). Air sparging can be applied either during the course of filtration to reduce fouling deposition or periodically to remove already formed deposits. Air sparging is typically applied in MF and UF membranes, and it seems to work best for tubular and flat sheet membranes and to a lesser extent in hollow fiber and spiral wound modules (Cui and Taha 2003). Anyway, it is clear that the use of air leads to an enhancement of flux in MF and UF. This positive effect is due to the presence of air bubbles which increase turbulence in the feed side of the membrane, thus increasing permeate flux as well as solute separation efficiency.

There have been little attempts to apply air sparging in NF membranes. In some studies, air sparging was applied to prevent fouling during NF, and it was prooved that poor benefits can be expected from air sparging in case of solutions containing only salt in water (Ducom and Cabassud 2003). (Cornelissen et al. 2007) used air/water cleaning for biofouling control showing that the best results in spiral wound NF modules were obtained when combining daily copper sulphate dosing with sporadic air/water cleaning. More recently, (Qaisrani and Samhaber 2011) have evaluated the potential of air sparging and backflushing for MF membrane regeneration. They have found that the combination of backflushing and air bubbling is the best method for improving membrane performance both in terms of fouling control and membrane cleaning time.

e. CO_2 back permeation

This is a method traditionally used for hollow fiber configuration in which CO_2 gas is forced from the permeate side through the internal fiber and out through them (Ebrahim 1994). More recently, (Fritsch and Moraru 2008) applied a CO_2 backpulsing system for cleaning a tubular MF membrane used in a dairy industry. They state that this is a very promising technique for maintaining a greater and more stable permeate fluxes.

12.3.2.2 Chemical Cleaning

Membrane fouling can be classified as physically reversible fouling which can be totally eliminated by physical cleaning or certain pretreatment, and physically irreversible fouling which cannot completely removed by physical cleaning or pretreatment (Gao et al. 2011). Irreversible fouling can only be overcome by chemical cleaning (Kimura et al. 2004). Chemical cleaning is the most common membrane cleaning method, especially in reverse osmosis membranes. In this type of cleaning, the choice of the cleaning agent is critical. Commercial cleaning products are often,

Table 12.4 Cleaning solutions according the type of foulant (Fritzmann et al. 2007)

Type of fouling	Chemical agent
Colloida	NaOH solutions, chelating agents and surfactants
Organic	NaOH solutions, chelating agents and surfactants
Metal oxides	Citri acid with low pH or $Na_2S_2O_4$
Silica	NaOH solutions with high pH
Carbonate scales ($CaCO_3$)	Citric acid or HCl with low pH
Sulphate scales ($CaSO_4$, $BaSO_4$)	HCl solutions or sequestration agents (EDTA)
Biofilms	NaOH solutions, chelating or sequestration agents, surfactants and disinfectants

Most chemical cleaning agents are commercially available, they are often mixtures of compounds, and many of them are recommended by membrane manufacturers according to the type of foulant, although in most cases the actual composition is not clearly specified (Ang et al. 2006). Anyway, in general acid (nitric, phosphoric, hydrochloric, sulphuric and citric) are often used to remove precipitated salts or scalants, while alkaline cleaning is suitable for organic fouling removal. Other categories of chemical cleaning agents are: metal chelating agents, surfactants and enzymes (Mohammadi et al. 2003). In addition, disinfectants (O_3), oxidants (H_2O_2, $KMnO_4$) or sequestration agents (EDTA) are often used for chemical cleaning of membranes (Lin et al. 2010). The most suitable and usual cleaning agents according to the type of fouling can be seen at Table 12.4.

Other important aspects concerning chemical cleaning are temperature, chemical concentration, pH, pressure and flow, and Some studies suggest that there is an optimal temperature for chemical cleaning (Bartlett et al. 1995). Usually, increasing temperature (always below membrane maximum temperature) increases cleaning efficiency, cross-flow velocity seems to have no effect on cleaning results, whereas increasing trans-membrane pressure may even decrease cleaning efficiency. Zero transmembrane pressure is recommended for maximum efficiency in deposit removal (Bartlett et al. 1995). With regard to the time required for cleaning it varies according to the foulant and the cleaning process.

12.4 Future Trends

The membrane industry has grown since the 1950s, but is still at a small production capacity. Sartorius Werke GmbH, a manufacturing company in Germany, manufactures small batches of ultrafiltration membranes and some cellophane membranes for laboratory-scale dialysis applications. The membrane permeability is still very small due to the thick and symmetrical structure of the membrane (like a sponge) so it is not competitive for large-scale applications. The monumental breakthrough in the development of new membrane technology occurred in the early 1960s after

Loeb & Sourirajan discovered the technique of making asymmetric membranes. This discovery is the starting point for the development of reverse osmosis (RO) which is currently widely used for seawater desalination processes and large-scale applications in various industrial sectors.

At present, there are only four cases in the literature that use laboratory results and modeling approaches to develop NF processes in production. Two of them are to separate the dye/salt/ai system and the salt cream from the dye solution by nanofiltration. The methodology should be tested for the development of other industrial NF process. From a theoretical point of view, it is necessary to analyze the distribution phenomena, including the dielectric effect, in order to determine whether the NaCl characteristic of NF membranes is sufficient to describe the distribution of other salts. A short study showed that impulse would cause heavy NaCl permeation. However, the difference in timing is only a matter of magnitude, and the development of buffer systems can make NF a viable alternative to wastewater treatment. Most of the literature written in NF considers the response. However, NF shows great potential in dehydration. In the chemical industry, solutions are often used as reagents, to dissolve reagents or to dissolve products before proceeding with products. Restoration is therefore a very important area. Distillation is the most important way to do this, but with the operation and integration of the membrane, NF should be considered as the first step to reduce energy consumption in the food industry, similar to water extraction.

12.5 Conclusion

Membrane technology has been proven to be capable of treating various water desalination processes. In the specific areas such as peatlands, the abundance of low-quality water, which riches of NOM (natural organic matter) has led to improvements in the technology for treating peat water and wetland saline water. The characteristics of specific peat water and wetland saline water should be taken into account first for selecting the treatment process. NF is one of membrane technology which is compatible to be treated NOM and salt in water. The advantages of using NF membranes in water treatment, especially wetland water, are technological development innovations in the production of clean water with environmentally friendly methods. Influence parameters in NF, separation mechanism and characteristics of the water to be treated must be investigated to determine the raw water pretreatment method. NF membrane is between UF and RO about separation process that acquire partially to reduce the salt in water due to its size exclusion and charge exclusion, majorly for sulfate and hardness ions. Wetland water consisting of peat water and saline wetlands with high NOM has an impact on membrane fouling. Understanding the membrane fouling mechanism is the basic of membrane fouling control and preventing. However, most of studies reported the treatment and desalination of NOM or saline water with NF only focuses the treatment efficiency, whereas the analysis of fouling mechanism is not sufficient. Future trends in the prospect of developing NF membranes are presented to enhance the development of modern technology treating wetland water using NF membranes. The alication of NF technology integrated with other water treatment technologies is exected to further enhance the peat water and wetland saline water treatment performance.

Acknowledgements The authors thank to Materials and Membranes Research Group (M^2ReG), Lambung Mangkurat University for the facilities. Muthia thanks the Applied Research of Universities Grant 2021–2023, Directorate General of Higher Education, Ministry of Education, Culture, Research, and Technology, Republic of Indonesia and National battery Research Institute (NBRI, Queen Mary University of London for Dissemination Awards and Research Prize through Climate Change Workshop funded by British Council 2021–2022.

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Chapter 13
Removal of Pollutants from Wastewater Through Nanofiltration: A Review

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Abstract The treatment and supply of drinking water are fundamental challenges globally. Different water purification techniques have some setbacks such as the addition of chemicals, energy cost and incapacitated treatment of large volumes of wastewater. Nanofiltration membrane has offered a wide scope for the removal of pollutants from industrial wastewater. This paper provides a review of the nanofiltration mechanism, some factors affecting the nanofiltration membrane, and a summary of the polymer membrane, metal-oxide-based and carbon-based membrane. These

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A. Ahmad and M. B. Alshammari (eds.), *Nanofiltration Membrane for Water Purification*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-5315-6_13

material types of the membranes have been demonstrated for the excellent purification and treatment technologies, following these advantages namely; simple scale-up, energy operational condition, environmentally friendliness, compact design, low energy consumption and high separation efficiency. But one of the issues associated with a membrane is fouling. The modification membrane also destroys the surface structure, leading to its instability after long-term filtration and the formation of nanoparticles agglomeration in the membrane matrix. Therefore, physical modification of membrane surfaces, blending with hydrophilic materials will help to control fouling. More research on modification to enhance its performance (decrease in the roughness of the membrane surface and improvement of membrane hydrophilicity) to control fouling should be considered for a holistic membrane performance for wastewater treatment.

Keywords Wastewater · Nanofiltration · Modification · Fouling · Hydrophilicity

13.1 Introduction

Water quality is an issue that limits human survival with the increase of industrialization like chemical industries. The conversion of precursors into useful products and separation of desired products from byproducts accompanied wastewater. The discharge of wastewater from industries like mining, metal plating, pharmaceutical, paper milling and tannery industries contains toxic constituents (organic and inorganic) which have become a serious challenge to the environment. In the past coupled decades, the rise of pollution of water from industries has led to huge water scarcity. The presence of heavy metals are toxic and non-biodegradable substances and can bio-accumulate in the human body. These substances such as arsenic, lead, chromium and cadmium are of global concern as a result of high toxicity even at low concentrations which cause damage to the body system and eventually result in diseases (Abdullah et al. 2021). They also harm aquatic and terrestrial lives (Peydayesh et al. 2020). These challenges faced by the less-developed and developing countries, having access to safe water is a critical issue that must be addressed.

Coagulation-flocculation, precipitation, photocatalysis, ion exchange, flotation, and other procedures have all been used to remove contaminants from wastewater in recent decades. However, these technologies have drawbacks such as the production of significant amounts of sludge and secondary pollutants, high sensitivity to pH, infeasibility, and high cost, among others. Membrane filtration, on the other hand, has developed as a versatile approach in recent years due to its high separation efficiency, low cost, lack of additional chemicals, lack of phase change, high controllability, environmental friendliness, ease of production, operation, and scale-up (Moradi 2021). Membrane technology based on thin-film composite membranes, on the other hand, provides a one-step treatment technique for eliminating tiny ions and has thus emerged as a viable alternative. Membrane separation technology has piqued attention due to its low operating costs, high efficiency, and environmental friendliness, and it is now widely utilized in water purification, desalination, and cleanup. Membrane filtration technology, which has various advantages over other traditional procedures, is regarded as an effective method for removing common pollutants from wastewater. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis are examples of membrane filtration technologies (RO). Nanofiltration is one of the most practical and widely used technology for removing contaminants such as heavy metals and dyes from wastewater (Yu et al. 2021). The technologies' separation mechanisms are primarily based on molecular sieving, Donnan exclusion, and solution diffusion (Peydayesh et al. 2020). Modifications of current membrane materials with high film-forming properties and mechanical strength are among the most important strategies for achieving superior membrane performance. Combining nanoparticles with membrane-forming polymers could be a viable approach to modification (Poolachira and Velmurugan 2019).

The composite membranes have received a lot of interest because they have greater thermal stability, performance, fouling, chemical, and physical stability. Composite membranes have been widely utilized for water purification, fuel cells, wastewater treatment, the dehydration process, and gas separation because they combine the benefits of both organic and inorganic materials. Membrane-based pollution removal is becoming more effective than traditional chemical/physical approaches due to its high separation efficiency, ease of construction and operation, ability to scale up quickly, and relatively cheap maintenance costs (Mehrjo et al. 2021). For example, in the presence of 2-chloro-1-methyl pyridinium iodide as an activating agent, a unique positively charged nanofiltration membrane was prepared by reacting carboxylic acids on the surface of a polyamide thin film composite with poly(amidoamine) dendrimer (Li et al. 2017). It was discovered that membranes with high grafting effectiveness had a high isoelectric point of pH 9.9, as well as excellent rejections of numerous hazardous substances. The 1,2,3,4-cyclobutane tetracarboxylic acid chloride (BTC) monomer containing a stereoscopic structure undergoes classic interfacial polymerization (IP) with polyethyleneimine (PEI) on the Polyether sulphone (PES) support membrane to produce a novel positively charged aliphatic polyamide NF membrane (PEI-BTC). According to (Li et al. 2022a, b), the PEI-BTC membrane had a higher mean effective pore size (0.285 nm), a thinner separation layer (40 nm), and a stronger positively charged membrane surface (7.25) than the typical PEI-TMC membrane. They found that the PEI-BTC NF membrane demonstrated outstanding hazardous heavy metal removal efficiency and that the nanofiltration membrane offers a unique industrial production potential for water softening and heavy metal removal. The antifouling nanofiltration membranes were made by introducing a tetrathioterephthalate (TTTP) filler into a Polyethersulfone (PES) matrix by phase inversion for effective heavy metal ion rejection from water (Moradi et al. 2020a, b). The fabricated T-PES membranes had higher hydrophilicity, porosity, pore radius, pure water permeation flux, and antifouling properties, while the addition of 0.1 wt.% TTTP to the PES membrane improved the hydrophilic quiddity of the TTTP fillers due to its functionalities such as C=S and C–S bonds. The produced membranes have a high rejection rate for heavy metal ions.

Different nanoparticles, such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), silver, carbon nanotubes (CNTs), and zeolites, were employed to change the polyamide (PA) layer of the NF membrane, resulting in the production of a novel membrane. One of the most significant advances in increasing membrane performance for wastewater purification is embedding nanoparticles within the PA layer. Surface defects in selective layers are caused by nanoparticle aggregation and poor bonding/compatibility between nanoparticles and polymer when nanoparticles are used to modify PA layers (Moradi et al. 2020a, b). However, nanocomposite membranes as an advanced class of materials had offered higher performance. Of course, rational development of these types of functional materials necessitates a thorough knowledge of their fundamental properties and the underlying science. The purpose of this paper is to discuss the present state of nanofiltration and to provide an updated overview of polymer, metal oxide, and carbon-based membrane technologies used in wastewater treatment.

13.2 Nanofiltration Membranes

Membrane technologies have been widely used in a variety of fields, including water treatment (disinfection, distillation, or media filtration), pharmaceutical and biotechnology industries, food processing, renewable energy storage and transformation processes in artificial photosynthetic systems, and redox flow battery membranes. The development of better materials and performance in membranes drives the combination of features such as permeability, selectivity, fouling resistance, chemical and thermal stability, low cost, and ease of manufacture to be improved. The surface and pore wall of a polymer membrane are connected to form a membrane adsorbent. When polluted water flows across the membrane, the functional active binding sites mix with the pollutants to remove pollutants from water at a high adsorption rate and capacity, as shown in Fig. 13.1. This could be due to the submicron-scale contact distance between the pollutants and the membrane adsorbents' adsorbed active binding site (Matsuura and et al. 2018).

Nanofiltration is a low-energy membrane separation technology that can effectively reject multivalent ions and organic molecules, and it has a lot of potential in water treatment. Nanopores in the range of 0.5–5 nm, with a molecular weight cutoff of 200–1000 Da, are present in nanofiltration membranes. When compared to reverse osmosis, nanofiltration has several advantages, including high elimination/rejection of environmental pollutants, reduced operation pressure, cost-effective operation due to lower energy consumption, and relatively higher flux (Kamari and Shahbazi 2019). The separation mechanism is largely driven by size- and charge-based exclusion, which is highly dependent on membrane structure as well as the interaction between the membrane and the solute. Operating conditions, membrane characteristics, and feed characteristics are all important factors that influence membrane performance, particularly nanofiltration.

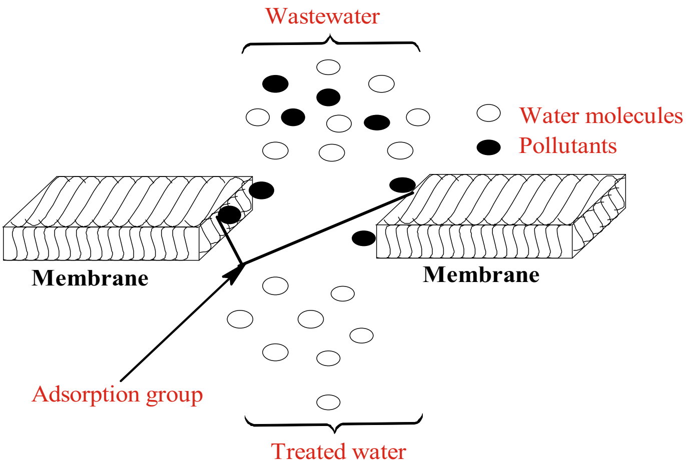

Fig. 13.1 Principle of membrane technology

13.2.1 Temperature

Water flux across nanofiltration membranes increases as the temperature rises, whereas uncharged solute rejection decreases as the temperature rises, and charged solute rejection varies depending on the ion and the membrane utilized. Although there is much experimental support for these findings, understanding of how the membrane changes and corresponding modelling work is still lacking (Roy et al. 2017). Membrane characteristics, or mobilities, are principally responsible for observable changes in permeate quality as temperature rises; values for each property are either calculated or fitted from experimental data. Model validation demonstrates significant trends in temperature-dependent property variation: pore size, net path length across membrane selective layer, and negative membrane charge all increase as temperature rises. The increase or decrease in permeate concentration due to each contributing element is explained using an analytical technique, exposing the opposing impacts of the two mobility factors. The findings of the modelling reveal that neither membrane parameter changes nor carrier mobility alone can explain temperature-related selectivity variations (Roy and Lienhard 2019). As the temperature rises, the solvent transport and net solute transport both increase. As a result, as the temperature rises, the rejection ratio drops. Furthermore, temperature increases the absolute value of the convective, diffusive, and electromigration contributions to solute flux. At each amount of membrane charge, these effects occur as a result of temperature-induced changes in membrane structural characteristics, solvent viscosity, and solute diffusivity. The increase in solute diffusivity owing to temperature increases over-compensates, resulting in pores that are larger in magnitude at higher temperatures. At higher temperatures, the potential gradient across the membrane is less in magnitude, similar to the concentration gradient. However, at higher temperatures, the flux increases primarily as a result of increasing solute diffusivity (Roy et al. 2017).

A study on the treatment and reuse of oily wastewater generated from the process of fuel oil treatment in a gas turbine power plant was studied (Al-Alawy and Al-Ameri 2017). The possibility of employing hollow fibre ultrafiltration (UF) and nanofiltration (NF) membrane type polyamide thin-film composites was explored, and the results suggest that pressure has the greatest impact on UF flux, while temperature and pressure have a similar impact on NF flux. Total dissolved solids (TDS) rejection appears to be most affected by temperature.

The average pore radius of the membrane grew from 0.39 to 0.44 nm when the feed temperature climbed from 20 to 40 °C, according to Dang et al. (2014). The thermal expansion of the polyamide skin layer has been suggested as a possible cause of membrane pore enlargement. This can be further explained by the fact that the pore architecture of NF membranes, such as pore diameter, thickness, and porosity, may change when the temperature rises due to thermal expansion. The membrane permeability increased as the feed solution temperature increased, which might be attributable to the decrease in water viscosity. At high feed solution temperatures, an increase in membrane pore size is a primary component of increased permeability. The permeate flux increases as the temperature rise because viscosity and concentration polarization decrease as the temperature rises. Temperature changes affect the diffusion coefficient and component absorption, which in turn affects flow.

13.2.2 Operating Pressure

Increased pressure causes a higher convective rate for solute transport to the membrane surface, raising its concentration at the interface, causing a rise in solute diffusivity in the opposite direction of the process pressure, and therefore lowering the permeate flow rate. It is also crucial to understand that for nanofiltration membrane, there is a linear relationship between flow rate and the inverse of the solvent viscosity, indicating that convection is the primary mass transport mechanism (Silva 2018). The pure water flux of the PES and the tetrathioterephthalate coated-aniline (T-AO) functionalized PES membranes as a function of operating pressure was investigated by Moradi et al. (2020a, b). The T-AO functionalized PES membrane had a pure water flux of 80.44 $\mathrm{kgm^{-2}\,h^{-1}}$ compared to 13.40 $\mathrm{kgm^{-2}\,h^{-1}}$ for the pristine one at a transmembrane pressure of 4 bar. Pure water penetration flow is influenced by surface hydrophilicity, porosity, and pore radius. The increase in surface hydrophilicity from aniline grafting and tetrathioterephthalate coating of the PES membrane overcame the loss of pore radius and porosity. The pure water flux of the T-AO functionalized PES membrane was improved as a result of this. Increased pressure is directly proportional to increased flow, but due to fouling and concentration polarization, this is not the case. The effect of operating pressure on flow and rejection of quaternized polyelectrolyte complex membranes (QPECMs), quaternized chitosan membrane (QCSM), PECM, and QPECM-4 at 25 °C was investigated by Ye et al. (2018).

Membrane water flux improves linearly as working pressure is increased from 2 to 8 bars, with a minor increase in salt rejection.

13.2.3 Flow Rate

Enhanced flow rate results in increased permeate flux and mass transport, as well as a decreased chance of concentration polarization. At a pressure of 4 bar, the ability of the manufactured membranes to remove heavy metals was assessed by measuring pure water permeance and rejection of $CuSO_4$, $CuCl_2$, and $PbCl_2$ salt solutions (Trang et al. 2020). In this study, the pristine thin film composite (TFC) membrane has low water permeance, as a result of the dense and smooth structure of the PEI membrane while it gave the best rejection for $CuSO_4$ with a rejection of over 99%, followed by $CuCl_2$ (98%) and $PbCl_2$ (92%). This was due to the size exclusion effect that the hydrated radius of metal ions followed this trend Cu^{2+} (0.419 nm) > Pb^{2+} (0.401 nm) while the SO_4^{2-} ions have a higher hydrated radius than Cl^-. When compared to the permeance of thin film nanocomposites (TFN) loaded with cellulose nanocrystal (CNC), the water permeance of 5.98 $Lm^{-2}\ h^{-1}\ bar^{-1}$ was recorded. This implies that the content of CNCs on the surface hydrophilicity of the PA layer enhances the water transport rate, thus increasing the surface area which could be responsible for the increased water permeance.

The magnetic graphene-based composite (MMGO) embedded polyethersulfone (PES) membranes showed higher dye rejection and permeate flux compared to the bare PES membrane (Abdi et al. 2018). The inclusion of MMGO hydrophilic hybrid increased both membrane surface hydrophilicity (reduced water contact angle) and pure water flux, according to the researchers. This is because the addition of nanoparticles to the membrane improves the water transport across the membrane. The inclusion of the MMGO hybrid boosted the membrane permeability by enhancing the membrane hydrophilicity (polyethersulphone). When compared to bare PES, the agglomeration of the graphene-based composite produced membrane pore obstruction, resulting in increased water permeability and the elimination of pollutants.

In comparison to the pristine graphene oxide (GO) membrane, the filtration ability of a developed membrane was assessed (Liu et al. 2019). The pure GO membrane in this study had a limited water flux, but by altering the interlayer distance (d-spacing) of GO laminar sheets, an effective channel for water transportation was constructed while other species were blocked. It's worth noting that the nature of GO allows for broad use in gas separation and nanofiltration for selective ionic and molecular sieving. As a result, additives with good compatibility with GO operate as intercalated voids between GO laminates, improving separation efficiency, wettability and flux rate during filtration.

13.2.4 Membrane Characteristic

Water is transported more smoothly through NF membranes when a solution of membrane polymer is mixed with high hydrophilicity nanofillers. This helps to overcome membrane fouling. These nanofillers have a large surface area, good chemical and physical stability, a large reactive surface, structural stability, surface modifiability, and a regular channel-like structure, all of which help to improve water transferring and flow. Polyethersulfone (PES) polymer materials, for example, are one of the most extensively utilized polymers for the fabrication of NF membranes because of their thermal stability, hardness, and resistance to mineral acids (Abdi et al. 2018). The development and modification of membrane surface chemistry and structure is a constructive method for improving NF performance for specific feed conditions by optimizing the chemistry on the surface of membranes. Antifouling against microorganisms, heavy metal ion removal, and antibacterial characteristics were all demonstrated by this functionalization and modification of the membrane. Due to the simplicity of design and modification of MOFs, as well as the compatibility of MOFs with the polymer matrix. Kuzminova et al. (2022) indicated mixed matrix membranes, in which metal–organic frameworks (MOFs) operate as fillers, hold a huge amount of potential. The porous structure of MOFs has a considerable impact on the hydrophilic–hydrophobic balance of the surface, sorption properties, and free volume of the polymer film when they are added to a polymer membrane.

The results of pure water flux for fabricated membranes in the nanofiltration system are 14.7, 24.4, 33.7, and 21.8 $Lm^{-2}\ h^{-1}$ were obtained for bare-PES, PES mesoporous organosilica p-phenylenediamine (PESPMO-PPD) 0.1 wt%, PES-PMO-PPD 0.25 wt%, and PES-PMO-PPD 0.5 wt%, respectively (Mehrjo et al. 2021). Due to improvements in membrane hydrophilicity, porosity, and mean pore radius, blended membranes with nanofillers have a stronger ability for water to penetrate than membranes without nanofillers. The permeability flux of the produced membranes is considerably altered in the presence of an additional PMO-PPD nanofiller (greatest pure water flux). It can be inferred that the nanofiller reduces the membrane's porosity and mean pore radius (resulting in decreased water flow), but the addition of PES-PMO-PPD increased the membrane's hydrophilicity and pure water flux.

A positively charged P84 NF membrane prepared by chemical cross-linking of asymmetric plain P84 membrane using hyperbranched polyethyleneimine (PEI) was investigated by Li et al. (2022a, b). The modified membrane exhibited higher surface hydrophilicity, surface roughness, and a positively charged surface, resulting in an excellent water flux of 43.2 $Lm^{-2}\ h^{-1}$ at 4 bar, according to the researchers. Furthermore, the cross-linked P84 NF membrane demonstrated high rejections of divalent heavy metals $PbCl_2$, $Ni(NO_3)_2$, $ZnCl_2$, and $Cu(NO_3)_2$, with rejections of 99.0%, 96.7%, 96.2%, and 99.8%, respectively, for the divalent heavy metals $PbCl_2$, $Ni(NO_3)_2$, $ZnCl_2$, and $Cu(NO_3)_2$. The membrane modification process revealed the importance of positively charged NF membranes in the removal of heavy metals from industrial effluents.

13.2.5 Feed Characteristic

Feed characteristic, like membrane characteristic, has a substantial impact on membrane performance and is connected to the chemical structure, pH, charge, and hydrophilicity of the solute. Cao et al. (2020) developed a negatively charged monomer piperazine (M-PIP) membrane and a positively charged monomer polyetherimide (M-PEI) membrane for RB-5 and intermediate acid (H-acid) sequestration from wastewater. The feed solution was used for filtration experiments at varied concentrations of single solutes, and the permeability for both membranes reduced dramatically from about 6.0 to approximately 1.6 $\mathrm{Lm^{-2}\ h^{-1}\ bar^{-1}}$ as the concentration of RB-5 increased, although the rejection decreased (99.0%). The enhanced filtration resistance can be due to concentration polarization and the deposition of solutes on the membrane surface, within the membrane pores, resulting in decreased permeability. Cao et al. (2020) also found that the permeability reduced greatly with the concentration of H-acid, also known as 4-Amino-5-hydroxynaphthalene-2, 7-disulphonic acid increased due to concentration polarization. The electronegative M-PIP membrane has a higher rejection for electronegative H-acid, but due to its smaller pores, M-PEI has a higher rejection for H-acid. Both membranes' surface electrical behaviour changes in response to pH changes. With an increase in pH, the permeability falls as the repulsive force of both membranes for the electronegative RB-5 and H-acid expands, lowering their enrichment on the membrane surface and allowing for more permeability (Cao et al. 2020).

The modification of the PES nanofiltration membrane showed a positive effect on salt rejection with the order of $Na_2SO_4 > MgSO_4 > NaCl$ (Mehrjo et al. 2021). The NF membrane improves the rejection of divalent ions and reduces the rejection of monovalent ions in salts. The large concentration of negative ions on the surface of modified membranes with PMO-PPD nanofiller was attributable to the influence of the Donnan exclusion theory, according to Mehrjo and Colleagues (2021). As a result, the negatively charged PMO-PPD repels negatively charged ions from the membrane while maintaining the positive charge ions and maintaining the feed solution's electroneutrality. Salt rejection with the same valence ratio of negatively and positively charged ions showed a substantial steric hindrance impact. A better rejection of $MgSO_4$ than NaCl could be a result of the lower hydrated radius of Na^+ (0.36 nm) and Cl^- (0.33 nm) than Mg^{2+} (0.38 nm) and SO_4^{2-} (0.38 nm).

13.3 Polymeric Membrane

The morphology of a membrane determines its performance; material selection and fabrication procedures have a substantial impact on membrane morphology. Due to a combination of specific properties such as permeability, selectivity, fouling resistance, chemical and thermal stability, low cost, and easy manufacturing, the optimization of membrane performances controls the interactions between morphology,

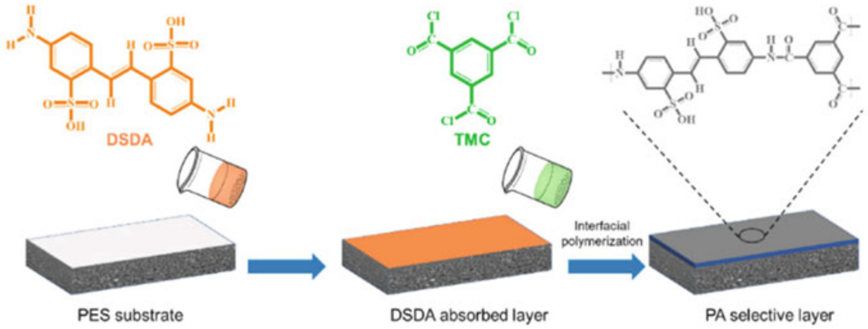

Fig. 13.2 The prepared NF membrane with an enhanced negative charge (Yu et al. 2021)

materials (porous polymeric), and fabrication technology for industrial applications. Polyethylene (PE), polysulfone (PSU), poly (vinylidene fluoride) (PVDF), polydimethylsiloxane (PDMS), polypropylene (PP), polyimide (PI), and polytetrafluoroethylene (PTFE) membranes are polymer membranes used in separation processes.

In the work of Yu et al. (2021) a novel amino monomer 4, 4′-dia- minostilbene-2, 2′-disulphonic acid (DSDA) with strong acidity was introduced into interfacial polymerization with 1, 3, 5-benzenetricarbonyltrichloride (TMC) aiming to enhance the negatively charged property of NF membrane as depicted in Fig. 13.2. The prepared membrane preparation has pure water permeance (PWP) of 10.0 ± 0.5 Lm^{-2} h^{-1} bar^{-1} and a Na_2SO_4 rejection (97%). The membrane maintains a negatively charged and Donnan exclusion effect which improved separation performance in the pH range (2 to 12), especially in acidic conditions. Thus, the optimal NF membrane has an improved and stable separation performance under a wide pH range and makes it potential for the treatment of acidic wastewaters containing Cr(VI) and phosphate.

To remove Ni(II) and Cr(VI) ions from metal plating wastewater, (Basaran et al. (2015) employed the NF270 membrane, which is made up of a piperazine-based semi-aromatic polyamide thin-film composite, and the NF90 membrane, which is made up of an aromatic polyamide-based thin-film composite. At a feed pH of 3.5–10, the impacts of operating pressure (10–30 bar) revealed that as the pressure increased, both the nickel and chromium permeate fluxes for the two NF membranes increased. The penetration rates of the synthetic membranes are higher at higher pressures, but the pressure did not influence the rejection of heavy metals. As a result of the solute diffusion rate being predominantly regulated by the solute concentration, an increase in pressure has no major impact on the solute diffusion rate.

KIT-6 is a mesoporous silica material having a three-dimensional bicontinuous cubic structure, a high surface area per volume ratio, good hydrothermal stability, large and controllable cylindrical pores with high interconnectivity, and thick walls. Functionalized curcumin (C-KIT-6) was employed in the study of Moradi (2021) to manufacture modified PES NF membranes to produce negatively charged surfaces using the phase inversion approach, as shown in Fig. 13.3. Mo (no added filler) had a water contact angle of 66.7°, while PES with 0.1 and 0.3 wt.% C-KIT-6 of M1-C-KIT-6 and M2-C-KIT-6 had water contact angles of 59.5° and 51.2°, respectively. The strong affinity for water molecules is due to the presence of hydrophilic functional groups on the membrane surface. Their results showed that the incorporation of C-KIT-6 on the surface of the PES polymer structure enhanced the mechanical properties like tensile strength and elongation at the break of the membranes and heavy metal ions (Pb^{2+}, Ni^{2+}, and Zn^{2+}) with the rejection of 91.4%, 93.1% and 98.0%, respectively. We noticed that the sorption exhibited using the nanofilter membrane for metal hydrated radius ($Pb^{2+} = 0.401$ nm, $Ni^{2+} = 0.404$ nm and $Zn^{2+} = 0.430$ nm) disagreed with most literature that explained that the highest metal ion removal is attributed to the smallest hydrated radius.

During the film polymerization of PIP and TMC, 1 wt% P-8NH_3Cl was added to produce a thin-film nanocomposite (TFN) membrane with water permeability of 5.4 Lm^{-2} h^{-1} bar^{-1} and rejections of 93.9%, 96.5% and 97.4% against $SeO_3{}^{2-}$, $SeO_4{}^{2-}$ and 97.4% and $HAsO_4{}^{2-}$ ions, respectively (He et al. 2016). When a mixed ion solution is used as the feed, the TFN membranes showed slightly higher rejection performance, and the loaded polyhedral oligomeric silsesquioxane (POSS) as shown in Fig. 13.4 and feed pH play important roles in the removal of selenium and arsenic. Electrostatic interactions were strengthened in the basic solution, and the $SeO_3{}^{2-}$, $SeO_4{}^{2-}$, and $HAsO_4{}^{2-}$ were repelled by the negatively charged membrane. The decrease in adsorption is likely due to larger POSS molecules on the membrane surface, which prevent the ions from interacting with membranes, resulting in fewer ions adsorbed.

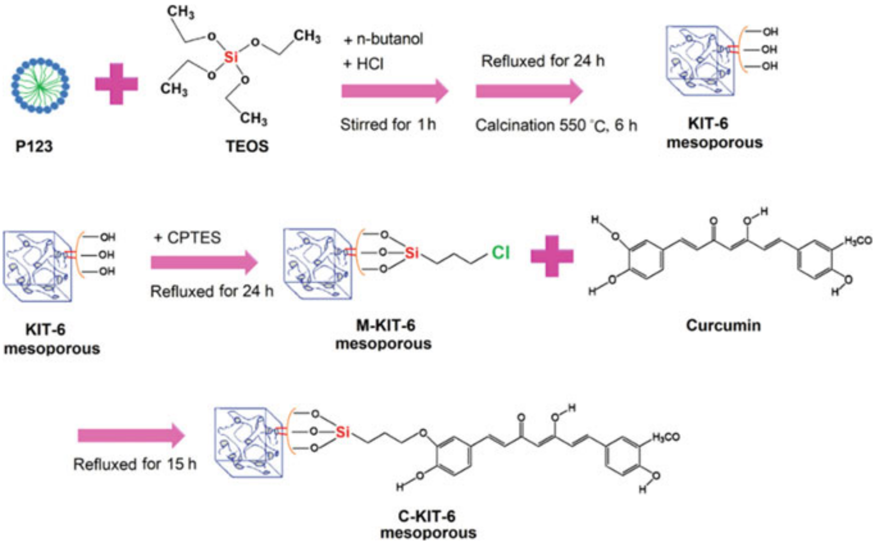

Fig. 13.3 Synthetic procedures of C-KIT-6 (Moradi 2021)

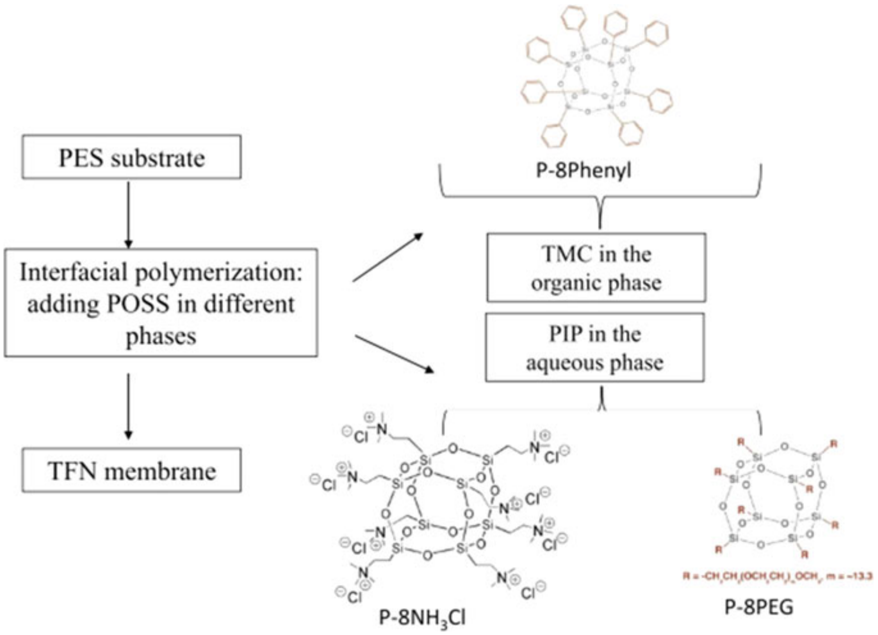

Fig. 13.4 Two routes to add POSS particles during the interfacial polymerization (He et al. 2016)

Zwitterionic polymers are non-specific fouling resistant materials that are used in medical coatings, blood-contacting devices, the marine sector, membrane-based water purification processes, and power generation to reduce protein and microbe adhesion (Asha et al. 2022). Zwitterionic polymers are more beneficial (stronger resistance to foulant adsorption) than poly(ethylene glycol) derivatives as hydrophilic materials for fouling resistant membranes because they are more stable in acid, basic, and oxidative environments. Phosphorylcholine, sulphobetaine, and carboxylbetaine are the three zwitterionic classes. The cheapest kind is sulphobetaine-containing zwitterionic material, which is simple to produce and scale-up. Electrostatic interaction allows one sulphobetaine unit with a positively charged quaternary ammonium ($N^+(CH_3)_2(alkyl)_2$) group and a negatively charged sulphonate (SO_3^-) group to strongly bond with roughly eight water molecules.

Figure 13.5 shows the impact of zwitterionic polymer content on polyamide surface properties, fouling resistance, and permeance (Duong et al. 2018). The zwitterion-modified membrane becomes more hydrophilic with reduced surface roughness, giving better fouling resistance, according to their findings. Furthermore, the zwitterion-modified membranes have a water permeability of 135 Lm^{-2} h^{-1} bar^{-1} and high selectivity in nanofiltration for organic dye rejection.

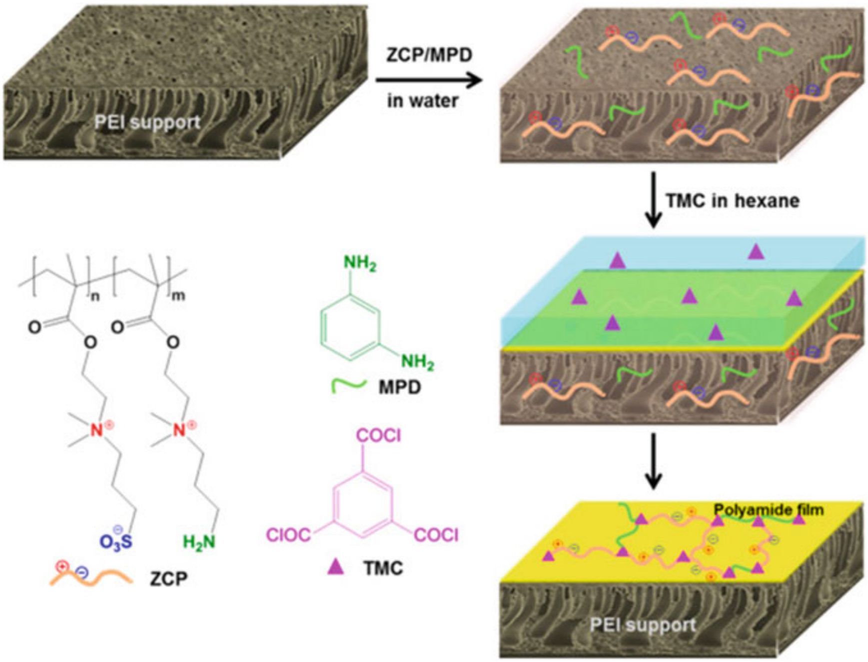

Fig. 13.5 The fabrication of polyamide membranes using poly(ether imide), zwitterionic copolymer (ZCP), m-phenylenediamine (MPD) and trimesoyl chloride (TMC) (Duong et al. 2018)

13.4 Metal Oxide-Based Membrane

Metal oxides and hybrid combinations of metal oxides and organic polymers can help improve membrane characteristics. For fouling mitigation and wetting challenges, metal oxide-based membranes exhibit superhydrophilic, superhydrophobic, and amphiphobic characteristics (Khan et al. 2021). To increase the physicochemical properties of the produced membrane, such as porosity, hydrophilicity, mechanical, and chemical strength, additives are frequently applied during the fabrication process.

The mechanism of membrane-type is similar to the adsorption process, in which molecules are transferred from the liquid phase to the solid phase's surface via physical or chemical interactions, as shown in Fig. 13.6.

Metal ions are smaller than the pore size of nanomaterials-modified membranes, but they nonetheless pass through easily. Adsorptive properties play an important role in eliminating metal ions throughout this operation. The following steps are involved in pollutant adsorption within membranes: (1) metal ion penetration and bulk diffusion into membrane pores and finger-like layer; (2) inner-sphere surface complexation on outer sites of nano-sized adsorbents present inside membrane structures; (3) metal ion transfer on the adsorbent interface; and (4) equilibrium stage. As a result, chemisorption on the exterior sites of adsorbents is the rate-controlling

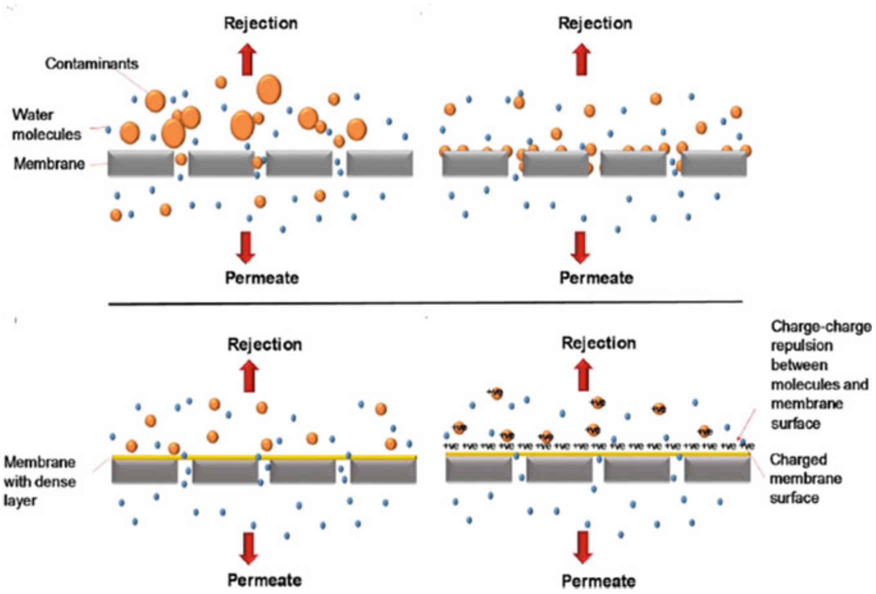

Fig. 13.6 Removal mechanism using metal oxide-based membrane

step for metal sorption, whereas metal ion transfer onto the adsorbent interface is the rate-limiting step (Abdullah et al. 2019).

The performance of the hydrophobic ultrafiltration polysulphone membrane by nitration via a chemical modification to membrane preparation was studied (Jyothi et al. 2016). The unmodified polysulphone membrane had a very high contact angle of 81.18°, which was reduced to 55.93° after alteration in the control hybrid membrane polysulphone/TiO_2. But a further increase in the contact angle occurs with a proportional increase in the dose of TiO_2. This means that the control mix membrane has higher hydrophilicity than the TiO_2 nanoparticles-added membrane and that the hydrophilicity declines as the TiO_2 nanoparticles are added. A cost-effective TiO_2 nanofiber membrane on porous fly ash ceramic as support (TNM-PFACS) was successfully constructed in another investigation by Zhang et al. (2021). When it came to removing divalent heavy metal ions (Cd^{2+} and Cu^{2+}), the modified membrane performed admirably. The huge surface area of TNM-PFACS and electrostatic force is responsible for the great removal efficiency.

Membrane Fenton-like process with cobalt–copper spinel catalyst is proposed to degrade nitrogenous organic hazardous in wastewater (Zhou et al. 2022). The problem of iron sludge and the pH operating range were addressed using a Co-based Fenton-like procedure. The ceramic membrane's surface hydroxyl stimulated. OH radical production at the interface, and the Cu^{2+} to Co^{2+} ion's lattice substation boosted oxygen vacancies and catalytic activity. $CuCo_2O_4^-$ based membrane Fenton-like processes, according to Zhou et al. (2022), provide a unique advantage for effective degradation of high-concentration nitrogenous industrial effluent. Application of this prepared nanocatalyst in Fenton-like oxidation will serve as an alternative method for an effective biodegradation method for high-concentration nitrogenous wastewater.

Functional Nanoscale zero-valent iron (nZVI) modified PVDF membranes were successfully prepared by a simple and easy-to-follow filter-press coating method and were applied in the ultrafiltration of 2-chlorophenol in wastewater (Li et al. 2021a, b). They found that nZVI was consistently distributed and loaded layer by layer on the PVDF membrane surface, indicating that it can reduce membrane fouling and improve water quality through enhanced treatment of sewage treatment plant effluent. Because of its incredibly small particle size, high specific surface area, and strong reducing activity, nanoscale zero-valent iron has gotten a lot of attention across the world. However, due to their tiny size effect and magnetic, nZVI particles tend to agglomerate, resulting in a decrease in reaction rate and efficiency. To overcome the aforementioned problems, immobilization of nZVI on a functional carrier material in powder or continuous media form is frequently utilized.

Mg, Ce, and Mn oxides were coated by co-precipitation onto a flat-sheet ceramic membrane as excellent ozonation catalysts in a work by Li et al. (2021a, b). When compared to a non-catalytic ozonation membrane, catalytic ozonation was more successful at degrading and removing organic pollutants. It was discovered that combining ozonation with membrane filtering (catalyst coating) resulted in an organic removal rate of 80% when compared to ceramic membranes that did not have the catalyst coating. Bi-metal oxides having unique structures, such as spinel or perovskite, have higher catalytic reactivity than single metal oxides. Bi-metal oxides, in particular, are more stable as catalysts than traditional metal oxides.

Figure 13.7 depicts the general heterogeneous nucleation and diffusion-controlled growth process of ultrafine metal oxide (ZnO)/graphene oxide (GO) nanocomposites. As presented in Fig. 13.6, the presence of oxygen groups from the mixture of ethylene glycol (EG) solution of GO and zinc acetate dihydrates ($Zn(CH_3COO)_2{\cdot}2H_2O$) contributes to the negatively charged surface of the positively charged $[Zn(EG)_2]^{2+}$ complexes through electrostatic interactions. The heterogeneous nucleation is due to the abundance of oxygen functional groups in the GO. Adsorbed $[Zn(EG)_2]^{2+}$ complexes hydrolyzed to adsorbed $Zn(OH)_2$, forming preferred sites under solvothermal conditions. The effective surface energy is lower on these types of sites, lowering the free energy barrier and allowing heterogeneous nucleation to occur. The nucleus form ultrafine nanoparticles on the surface of rGO by a diffusion-controlled growth process. The nanofiltration membranes as-prepared had a water permeability of 225 Lm^{-2} h^{-1} bar^{-1} and a methyl blue rejection of up to 98% (Zhang et al. 2022).

Heavy metal ions were removed using $Al–Ti_2O_6$ nanoparticles and polysulfone composite membranes that were produced (Sunil et al. 2018). They discovered that as the concentration of NPs rises, the water contact angle reduces from 740 to 510°. This means that adding NPs enhanced the membrane surface's hydrophilicity, and the hydrophilic nanoparticles naturally migrate towards the membrane surface, thus lowering the interface energy. The presence of nanoparticles lowers the water contact angle, which improves water absorption. It may be deduced that bi-metal oxide

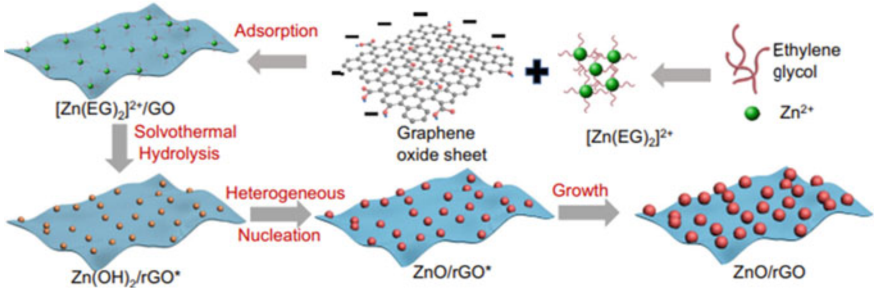

Fig. 13.7 Synthesis of ultrafine ZnO/rGO nanocomposites (Zhang et al. 2022)

nanoparticles have more electronegative atoms than single metal ion nanoparticles, which are capable of hydrogen bonding, thus showing more hydrophilicity.

13.5 Carbon-Based Membrane

Carbon nanotubes (CNTs) have been shown to exhibit outstanding mechanical, thermal, electrical, and partial antimicrobial capabilities. Multi-walled carbon nanotubes (MWCNTs) that can be employed in advanced nano-membranes have been prepared using the interfacial polymerization process. (Fatima et al. 2021) used a simple vacuum filtering process to describe electro-ceramic self-cleaning membranes constructed from nano-zeolite/CNTs with PVDF as a binder for better mechanical strength. Nano-Y reduces membrane electrical conductivity dramatically, which is thought to be owing to the non-conductive nature of ceramic particles. The homogeneous distribution of CNTs in the membranes acts as reinforcing agents, preventing the membrane from simply breaking.

Graphene is a new 2D substance that has high flexibility, surface area, electrical conductivity, and surface activity. It is, nonetheless, regarded as suitable membrane material, particularly for desalination. Water migration and very efficient molecular sieving are common features of graphene oxide (GO), which is made up of graphite-like and oxidized regions. Because GO is dispersible in water and many other polar solvents, it may be easily manufactured into laminated membrane materials for nanofiltration separations using solution processing procedures. Furthermore, the GO-based nanofiltration membrane possesses good antifouling properties as well as long-term stability, which is critical in nanofiltration. As a result, GO has emerged as a good candidate material for nanofiltration membrane fabrication (Chen et al. 2018). However, because GO nanosheets are very hydrophilic, they cause uncontrollable swelling and poor GO membrane stability in water. As a result, due to their thinner nanochannels, decreased swelling, and improved water stability, reduced graphene oxide (rGO) membranes with lower oxygen functional groups can give better performance. Unfortunately, due to the significant capillary force and the small nanochannel, water permeability through the stacked GO membranes is insufficient. However, the inherent elastoplastic nature of polymers and their uneven distribution on the GO surface, introducing polymer additives frequently results in only a minor increase in water permeability (Zhang et al. 2022).

GO/MIL-88A(Fe) (M88A) was prepared by a facile vacuum filtration method as presented in Fig. 13.8 for superior separation performance, self-cleaning performance and high photo-Fenton activity in water purification (Xie et al. 2020). Due to its short and weak nanochannels, the bare membrane (GO without Fe) had a low permeate flow of 3.8 Lm^{-2} h^{-1} bar^{-1} for MB solution. However, as the Fe content of GO/M88A membranes increased, the permeate fluxes for MB increased from 5.3 to 37.3 Lm^{-2} h^{-1} bar^{-1}, which can be attributed to enriched nanochannels and higher membrane hydrophilicity. The GO membrane had the lowest pure water flux of 9.4 Lm^{-2} h^{-1} bar^{-1}, but the GO/M88A membranes' pure water flux increased dramatically from 14.2 to 99.1 Lm^{-2} h^{-1} bar^{-1} as the Fe concentration increased. This means that Fe intercalation improved pure water flux, enriched nanochannels for easier water molecule transport, and increased membrane hydrophilicity, all of which resulted in increased flux.

A nano CuO/C_3N_4(g-CN) sheet as surface modifying fillers was successfully prepared for modification of the PPSU membrane as illustrated in Fig. 13.9 (Arumugham et al. 2019). The contact angle (53°), porosity, pure water and protein

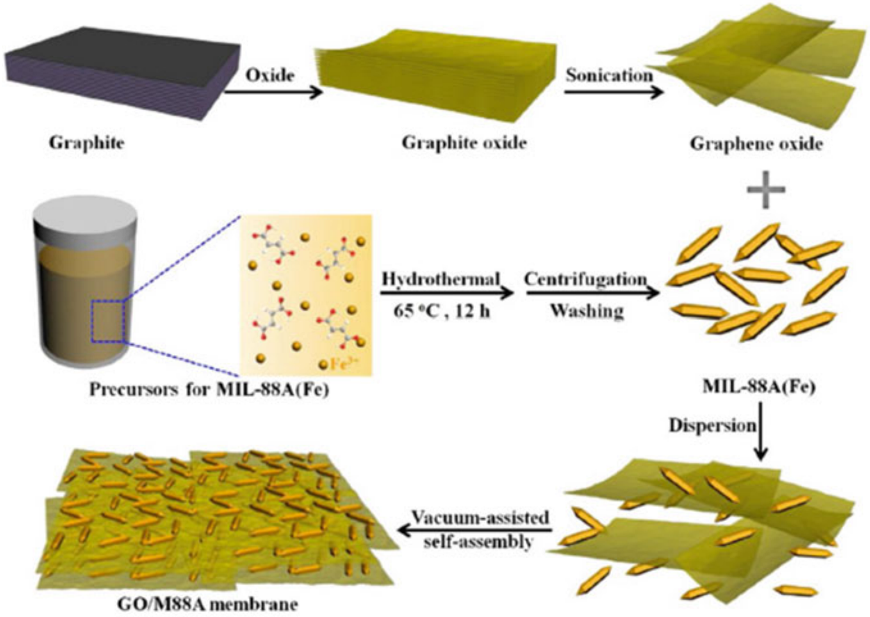

Fig. 13.8 The fabrication of GO/M88A membrane (Xie et al. 2020)

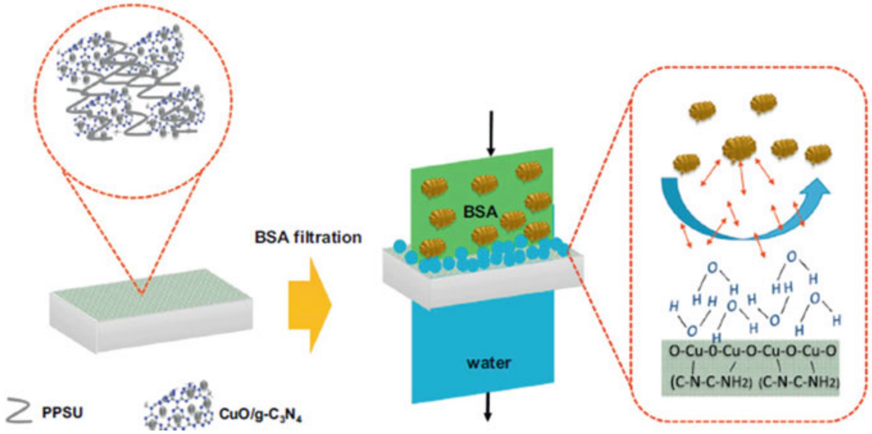

Fig. 13.9 The formation of CuO/C_3N_4(g-CN) hybrid membranes (Arumugham et al. 2019)

filtration tests, as well as antifouling and filtration resistance capabilities for nanohybrid membranes, were shown to be better than the bare membrane in this study. Graphitic carbon nitride (g-C_3N_4), on the other hand, is a promising material because its tris-s-triazine structure contains sp^2 hybridized carbon and nitrogen atoms that create-conjugated graphitic planes like graphene sheets or laminar structures. Because of the melamine re-arrangement reaction, the g-C_3N_4 sheets have NH/NH_2 groups in and around triangular nanopores. The formation of interfacial interactions with nanoparticles is attributed to these nanopores. The flux recovery ratio (FRR) of the membrane increased dramatically with an increase in CuO/g-CN sheets, according to (Arumugham et al. 2019). The combined effect of surface roughness and hydrophilicity of nanohybrid membranes is attributed to these findings, which suggest that CuO/C_3N_4(g-CN)/PPSU serve as good antifouling membranes.

A robust hydrophobic and superhydrophobic mixed matrix electrospun nanofibrous membranes (MM-ENMs) with either multi-walled carbon nanotubes or graphene oxide nanofillers was produced (Essalhi et al. 2021). The MWCNTs/GO single layer membrane (SL-MM-ENMs) demonstrated good surface hydrophobicity, high permeate flux, high salt rejection factor, and good direct contact membrane distillation desalination performance. The triple-layered membranes (TL-MM-ENMs) have much higher mechanical properties than the DL-MM-ENMs, with lower permeate.

Due to physical size sieving and electrostatic repulsion, a high performance GO nanofiltration membrane was produced, which demonstrated a high water flux of up to 11.13 Lm^{-2} h^{-1} bar^{-1}, high organic dyes rejection (>98%), and negatively charged dyes rejection (almost 100%) (Chen et al. 2018). The Donnan exclusion theory and the steric hindrance effect are both supported by the rejection performance of salt ions. Figure 13.10 shows a schematic depiction of water passing through a GO nanofiltration membrane and the rejection mechanism for charged organic dyes.

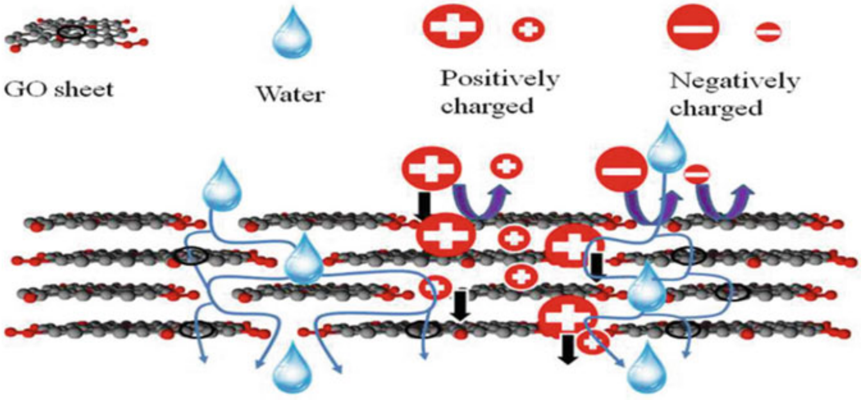

Fig. 13.10 The schematic view for water passing through GO and the rejection mechanism for charged organic dyes (Chen et al. 2018)

Negatively charged dyes are rejected by electrostatic repulsion, but positively charged dyes are attracted by electrostatic attraction and pass through.

13.6 Challenges of Nanofiltration and Future Prospective

Fouling is the most common and unavoidable problem in membrane applications because of their intrinsic hydrophobicity, especially NF, which not only decreases membrane performance but also reduces cost efficiency by diminishing flux over time. Fouling is defined as a soluble or suspended material, such as a colloid, an organic component, an inorganic component, or a biological component, blocking the surface and pores of a membrane. Chemical cleaning to control fouling causes long-term damage to membrane structure, lowering membrane performance and lowering membrane permeance either temporarily or permanently, increasing energy consumption, necessitating more effort for membrane cleaning, and limiting membrane lifetime. The major elements determining the early phases of fouling are membrane surface-foulant and foulant-foulant interactions. To reduce fouling in membrane filtration processes, it is indeed critical to keep track of these interactions. The most promising technique for this is surface modification.

NF is a wastewater treatment technology that is both innovative and cost-effective while also being environmentally benign. When NF is combined with other separation techniques, it can potentially give the best results in wastewater treatment, allowing the produced effluent to be reused. Given the wide range of selectivity of organic solute and salt, the future difficulties and opportunities of NF use are extremely promising, allowing for more research into diverse applications. NP-based membranes, despite their better performance, are still unsuitable for commercial applications. Therefore, more work is needed to increase the chemical compatibility and physical stability of NP-based membranes, so that advancements in membrane materials can lead to the development of long-term, cost-effective, and safe water production methods.

13.7 Conclusion

Membrane methods have shown promise in the treatment of wastewater containing heavy metals and other pollutants due to their high efficiency and ease of use. Nanofiltration (NF) is a novel pressure-driven membrane technology, yet fouling has proven to be one of the most difficult problems to overcome. NF membranes were successfully fabricated utilizing polymer, metal oxide, and carbon materials as additives to improve membrane performance and improve the membrane's antifouling property. The generation of reactive oxygen species, as well as high electrical conductivity, hydrophilicity, and negative charges, have all been linked to CNT membranes having better anti-fouling capabilities. The incorporation of these additives was also found to increase the hydrophilicity of membranes as evident from the water contact angle and improved water permeability. The nanocomposite modified membranes improved flux, solute rejection, mechanical properties, antifouling properties, and pollutants removal efficiency. The increase was attributable to hydrophilic groups in the membranes and increased surface roughness, which facilitated water molecule penetration through the membranes. It is hypothesized that combining polymer, metal oxide, and carbon in a membrane will provide better rejection of organic and inorganic micro- and nanopollutants in contaminated waters.

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