Chapter 4
Membrane-Based Remediation of Wastewater

Manoj Chandra Garg and Harshita Jain

Abstract Contamination of water resources has an overall impact and is a cause of worldwide concern because of which requirement for clean water is getting increasing. Membrane-based wastewater treatment technology may uphold effective techniques for the treatment, utilization, and reuse of water and the improvement of next-generation water supply frameworks. With progress in membrane filtration techniques, various sorts of membrane are arising for applications in water filtration and wastewater treatment technologies owing to their viability against both synthetic and natural toxins. This chapter discusses the utilization and applications of membrane filtration techniques that are being assessed or created as option for water treatment. Membrane filtration techniques are inherently preferable in terms of performance over different treatment techniques utilized in water purification on account of their high surface area, lower energy consumption, and high performance. Owing to these attributes, these might be utilized in future at large scale for water treatment.

Keywords Water treatment · Wastewater · Membrane technology · Biofilm · Nanomaterial

4.1 Introduction

Worldwide water assets are deficient in fulfilling the potable water needs of mankind. Rapid industrialization, changes in the environment, and other human exercises have additionally demolished the situation. In this regard, water reuse has turned into a broadly acknowledged way to deal with supporting the water supply (Elbasiouny et al. 2021). Wastewater treatment has for quite some time been executed to supply clean water and backing financial turn of events. Different types of

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customary innovations, for example, adsorption and coagulation are being customarily utilized to a huge extent. Desalination is the most common way of desalting water and is a rising innovation for resolving problems identified with water lack and contamination. The process of desalination is performed either thermally or through membrane-based treatments. At present, thermal-based membrane processes are generally utilized in numerous provinces which are under water stress, especially in Middle Eastern locales. A positive shift from these traditional innovations to the utilization of membrane advances has been observed due to its wider industrial and environmental applications. The expanding acknowledgment of membrane process in the desalination and treatment of water and wastewater is primarily a result of the capacity of membrane innovation for dealing with a wide scope of feed water having high functional dependability. Technologies based on membranes are additionally equipped for delivering water and freshwater that is of excellent quality concerning the expulsion of microorganisms, broken down particles, and suspended solids (Khulbe and Matsuura 2018).

Membrane technology also has other advantages, such as its compact footprint and versatility and could be effortlessly backfit in existing arrangement to provide a synergistic effect to ease the filtration process. Membrane performance can be improved with breakthroughs in the production of polymer and ceramic based membranes, allowing them to manage numerous developing contaminants that are too difficult for current treatment techniques (Rongwong et al. 2018). Membrane separation is essentially the process of separating unwanted contaminants and allowing pure water passage through selectively porous membrane. Desalination and wastewater can be divided into numerous membrane techniques on the basis of other factors including driving force and finite element analysis.

Membrane technology is divided into two types of processes: pressure-driven and osmotically-driven. Pressure is applied to the feed side of the membrane in the former process, which functions as a means of propulsion for separating contaminated incoming feed water into permeate having pure water and concentrate having impurities that is generally discarded/processed further (Shukla et al. 2021). Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration are the most prevalent pressure-driven membrane processes (MF). The natural osmotic gradient is the driving force in non-pressure driven membrane processes like forward osmosis (FO) and pressure-retarded osmosis (PRO). Filtration is propelled by osmotic pressure that is produced naturally. FO and PRO have grown in prominence as an alternative to traditional membrane techniques which employ excessive external pressure and waste a lot of energy while maintaining great water quality and production (Algieri et al. 2021). Fabrication of membrane and its structure design are two of the most significant tactics for ensuring membrane technology's efficiency and long-term viability. Efforts have been made to improve membrane performance using a variety of methods which includes the utilization of innovative and smart materials for fabrication, also the insertion of novel nanostructures and additives and the synthesis of a novel membranes which reveal aspects of traditional separation technology to accomplish pollutant removal synergy (Shukla et al. 2021). Such strategies are helping in the development of ideal membrane design and production techniques that outperform those now in use. Strong rejection capability; great chemical, physical, mechanical, and thermal stability; extreme resilience to harsh chemicals; strong integrity towards wide pH and temperature range are just a few of the benefits of these membranes.

This chapter gives an overview of membrane technology's unique and long-term development in wastewater treatment and desalination. The first section discusses membrane processes based on hydraulic and osmotic pressure. The evolution and progress of high-performance membrane design and fabrication are discussed. Membrane technologies are discussed in terms of desalination and treatment of wastewater treatment. Finally, the innovative and sustainable membrane techniques are addressed briefly and conclusions are reached.

4.2 Membrane-Based Techniques

4.2.1 Pressure-Assisted Membrane Techniques

The pressure-driven membrane processes utilize membranes as a barrier preventing undesired chemicals from passing through while enabling water to pass through. The propulsion that causes liquid to pass through the membrane holes is the pressure differential among the incoming and outgoing water. Unwanted chemicals are kept because of physical properties like charges, size, and shape (Homaeigohar and Elbahri 2017). Pressure-driven membrane processes can be classified into four categories based on retained particles size, i.e., RO, MF, NF, and UF. The largest pore size is of MF membranes (0.1–10 mm) with least applied pressure range among these techniques. MF membranes have a large pore size, which allows for great permeability at low pressure. In comparison to MF membranes, pore size of UF membrane is 2–100 nm with lower permeability and high applied pressure (Govardhan et al. 2020). The pressure range of UF is typically 1–10 bars. In both MF and UF, sieving is the primary method for successfully separating suspended particles, colloids, and microorganisms. MF and UF are often employed as a pretreatment in many membrane separation procedures to eliminate or decrease contaminants which causes difficulties in treatment techniques like NF and RO. With the pore range of 1 nm, NF possesses characteristics that fall between UF and RO (Koyuncu et al. 2015). Minute contaminants like dyes and organic biological particles can be removed by NF. Size exclusion and surface charge methods are used to separate NF. The ionization of carboxylic group and sulfonic group causes the membrane surface containing these functional groups to become mildly charged when exposed to aqueous solutions. They possess acidic or basic characteristics depending on the materials utilized. Since, NF membranes can be used to separate divalent ions, they are also known as loose RO membranes. As a result, NF has been used in water softening and desalination. For typical divalent ions like magnesium and calcium, NF can provide up to 95% rejection. With regard to filtration mechanisms, NF filtration is not only established on size exclusion but also Donnan and dielectric effects. In that the surface charges and charge particle diffusion play a role in rejecting ionic compounds (Ahsan and Imteaz 2019; Chuntanalerg et al. 2019).

NF and RO have a few things in common: they are both utilized to eliminate dissolved particles and need a lot of external hydraulic pressure to work. Membrane materials and configurations are also similar in NF and RO (Semiat 2010). In comparison to RO, nanofiltration has a better water productivity, whereas uses less specific energy. NF, on the other hand, only demonstrates rejection in the 50–80% range for monovalent ion separation. The separation of salts and microorganisms by membranes utilizing greater external pressure than natural osmotic pressure is what RO is all about. The desalination of seawater and brackish water is the most prevalent application of RO. Reverse osmosis has surpassed thermal desalination methods like multistage flash distillation (MFD) to turn out the most widely used desalination method. The salt rejection effectiveness of RO is up to 99.9% sodium chloride (NaCl) removal. Due to the subnanometer range of the RO membrane pores, RO can provide a nearly unbroken barrier for pathogen elimination (Ismail et al. 2019). As a result, RO is utilized in the treatment of wastewater for reusing water. The widespread utilization of RO process on a global scale is largely due to major advancements in process optimization and membrane fabrication, which has resulted in lower operational costs. The improvement in membrane flux has resulted in a significant reduction in energy usage as a result of these developments. Cleaning and membrane replacement expenses are also reduced as a result of the fabrication of more robust membranes.

4.2.2 Non-pressure Assisted Membrane Techniques

Non-pressure assisted membrane techniques like FO and PRO are becoming increasingly relevant in tackling global concerns such as potable water and a secure energy supply. For extracting pure water from the feed side, these techniques need a draw side (DS) that is of osmotic pressure higher than feed water. After that, using a suitable separation method, the product water is extracted from the draw solution. There are various advantages of FO over RO which makes it a viable option for desalination and treatment of wastewater (Jain et al. 2021). FO can solve the fouling problems that plague traditional pressure-based membrane techniques. Since, RO forces all particles from the feed stream onto membrane surface without discrimination, FO enables selective molecules to pass through the membrane by osmotic pressure, reducing fouling and compaction issues. Most importantly, during separation, FO uses almost no external power. To allow fluid circulation in the system, negligible pressure is needed. Poor performance of membranes and inappropriate draw solution that enables for inexpensive and easy recovery are the two biggest obstacles to FO's practical application. Ideal FO membranes shall show high salt rejection, high water flux, and low concentration polarization in general (Su et al.

2012). Moreover, the optimal draw solution should have characteristics like high osmotic potential and cheap cost, as well as the ability to be recovered using simple and cost-effective methods. Ammonium bicarbonate molecular weight is low and has high solubility that is why it was extensively utilized as the draw solution early on in its development. Warming up the chemicals to produce ammonia and carbon dioxide is a simple way to recover it.

Research attempts shifted to using magnetic draw solution generation which allows for easy recovery. Unlike FO methods, which is used for desalting and wastewater remediation, PRO is a new technique that might be utilized for collecting energy by mixing fresh water with saltwater. In theory, PRO is the opposite to RO, except instead of hydraulic pressure, PRO desalinates water while produces energy by using the osmotic pressure of seawater. PRO system utilize the feed solution which is a low concentration side that flows through a membrane into a pressured solution of higher concentration. Power can be generated by depressurizing the permeate with a hydro turbine (Gebreyohannes and Giorno 2016; Klaysom and Vankelecom 2016). The first PRO prototype was commissioned by Statkraft, a Norwegian business, for generating power on the basis of salinity gradient concept using PRO. However, due to the plant's tiny capacity and low osmotic power for practical usage, the unit was shut down a few years later. The most important factor in achieving a commercially appealing power density is a high-performance membrane. In the hybrid RO-PRO system, PRO has also been investigated as a supplementary technique for recycling and reusing RO brine. Instead of being released into the sea, the RO brine concentration can be recycled as a draw solution. Traditional RO membranes were used in PRO procedures throughout the early stages of development. The goal of PRO technology advancement is to create membranes for high-performance.

4.3 Membrane Development

4.3.1 Membrane Fabrication

The primary aspect of membrane manufacture is material selection. Polymers and ceramics are the two main materials to consider. The most prevalent type of material utilized to make membranes is polymers (Wen et al. 2019). Polymeric membranes can be made inexpensively thanks to the wide variety of polymeric materials available. The efficiency of many polymer-based membranes is widely examined, and the membrane market has attained maturity. polyetherimide (PEI), Polysulfone (PSf), polyvinylidene fluoride (PVDF), and polyethersulfone (PES) are some of the commercially available polymeric membranes (Jain and Garg 2021). These polymers have a number of desired properties for membrane construction, including simple synthesis, robustness and market availability. Figure 4.1 depicts some fabrication processes for membrane-based treatment of water and wastewater treatment,

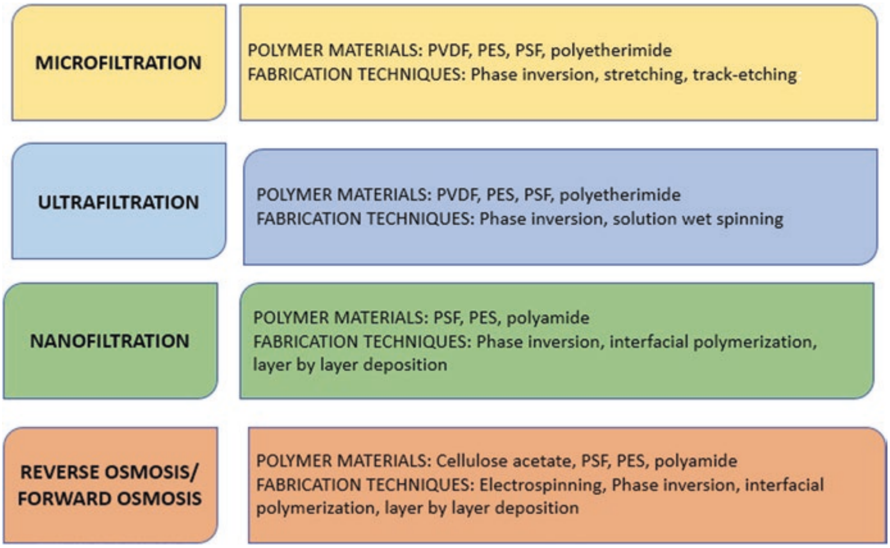

Fig. 4.1 Membrane processes, materials, and construction techniques for polymeric membranes

as well as the materials and construction techniques that are typically utilized. Ceramic-based membranes have a number of advantages over polymer-based membranes, including good stability as well as mechanical strength. Ceramic membranes can be used in a variety of difficult operating conditions, including a wide range of pH, the use of strong chemicals, and high temperatures (Li et al. 2021). However, when contrasted to their polymeric counterparts, the expense of materials and difficulty in production at larger scale are stumbling blocks that prevent ceramic membranes from being widely used on an industrial scale.

Alumina, zirconia, zeolites, and alumina are some of the commonly used materials for ceramic membranes. Ceramic membranes are predicted to be more feasible in more commercial applications as a result of studies which targets utilizing low-cost substances. Membranes can be constructed in a variety of formats depending on the structural and other operation needs such as throughput and footprint, the two most prevalent of hollow fibre and flat sheet membranes. Because it is simple to perform and because a large range of polymers and solvents are available, phase inversion is a popular method for fabricating membranes. In a nutshell, phase inversion is the separation of polymeric casting solution in a polymeric solid phase (membrane) and a liquid phase by phase shifts (Li et al. 2021; Dong et al. 2021). Surface of membrane is formed by the solid phase, while the liquid phase develops porous structure of the membrane. Surface morphology of the membranes are tailored using nanomaterials to match its application by modifying and optimizing the process' phase transitions. The most difficult aspect of phase inversion is finding a solvent that will thoroughly mix with the polymer and form homogenous blend. Solvents like *N*-Methyl-2-pyrrolidone (NMP), DMAc, and dimethyl sulfoxide (DMS) are routinely utilized to blend polymers including PVDF, PEI, and PSf.

Membrane fabrication via electrospinning is also becoming more prevalent. High voltage is used among a metallic collector and negatively charged polymer solution in this technique (Shiohara et al. 2021). The nozzle release the polymer fibres and these are gathered as a fibrous film with a random orientation. Electrospun fibres have a larger permeability and open porous structure that is interconnected better than a phase inversion membrane. These characteristics are appealing for improving membrane permeability. Commercial uses of electrospinning, on the other hand, are less due to the high cost and difficulty of large-scale production. The membranes utilized in MF, UF, and NF have an asymmetrical structure with a permeable sub-layer and an active top selective layer. The bottom layer generally functions as the support layer to offer mechanical strength, while the top layer determines the selective filtration capacity of the membrane (Tibi et al. 2020).

A thin film composite membrane is one that was commonly employed in RO, FO, and PRO processes (TFC). The TFCs are made up of two layers. To generate a polymeric substrate in the UF range, the bottom substrate layer is generally fabricated via phase inversion. Following that, two monomers undergo interfacial polymerization (IP) by dipping the substrate in organic and aqueous solvent to form an active layer, which is usually polyamide. The types and concentrations of monomers, the monomer contact time, the ageing period, and the temperature are all factors to consider during interfacial polymerization (Jain and Garg 2021). These variables can have a significant impact on the density of polymerization, surface shape, and selectivity of the polyamide layer generated. To reduce permeate flow resistance, the thickness of this selective layer is kept to a minimum. Another approach is to cast the polymeric substrate over a layer of polyester fabric to give the TFC membrane more mechanical strength. Layer-by-layer assembly is another appealing way for introducing a selective layer over the substrate. This method is extensively employed in the manufacture of thin films. It works by forming a thick selective layer out of multilayers of oppositely charged polyelectrolytes. Electrostatic attraction between layers is the sole basis for assembly. The layer-by-layer approach has superiority over IP in terms of simplicity and cost. The amount of layers could be adjusted to maximize the selective layer's width, water flux, and selectivity. TFC offers more material design flexibility than asymmetric polymer membranes, as the substrate and active layer can be composed of various materials depending on the solicit qualities for their utilization. Modifications of the membranes can also be carried out individually on the substrate and active layer (Jain et al. 2021).

4.3.2 Membrane Modifications

Membrane changes change the membrane's physicochemical properties, which improve separation performance in terms of flux and rejection. Another goal of membrane modification is to give changed membranes antifouling capabilities (Sadr and Saroj 2015). Fouling is a condition that occurs when chemicals accumulate on the surface or within the membrane structure. Fouling is an unavoidable occurrence which results in a significant drop in its efficiency, notably in terms of membrane flux and productivity (Liu et al. 2019) Fouling also adds to operating costs since it necessitates periodic cleaning of membrane and eventually its replacement. Alterations of membranes can be accomplished in a variety of ways. Polymer mixing can change the surface characteristics of membranes without affecting their bulk shape and properties (Jain et al. 2022). By combining polymers with desirable characteristics and enhancing the flow and selectivity of the resulting membranes, blending different polymers can drastically alter the hydrophilic-hydrophobic balance of the membrane. Physical and chemical approaches of membrane surface modification can be broadly classified. The altering substances are glazed on the surface of membrane in the first technique, which does not require the creation of covalent bonds (Seo et al. 2018).

As a result, the membranes' chemical characteristics are largely preserved after alteration. Dip-coating hydrophilic components like chitosan and polyethylene glycol onto the membrane surface can improve the membrane's hydrophilicity. Direct pressure sieving of hydrophilic substances over the membrane surface can be used to coat the surface. Physical interactions, such as electrostatic attraction, keep the coated or adsorbed compounds on the membrane surface. As a result, the coated components' poor adherence to the membrane surface is a shortcoming of this modification process. After a specific length of operation, the glazed substances separate from the surface smoothly. To address this issue, several attempts are made for functional groups introduction which acts like bridging agents and anchor sites, allowing chemical bonding among the glazed substances and surface of membrane to be established (Homaeigohar and Elbahri 2017). Covalent bonds are produced in chemical modification by interlinkage among agents and surface. Before reactions with foreign chemicals, the surface is frequently activated by irradiation chemically. Chemical alteration, as opposed to physical techniques, can provide more stability so the transformed surface would be intact for extended periods of time The use of plasma to produce active groups on the membrane surface is a straightforward modification procedure. The production of oxidative groups on the surface can be aided by inert gases like helium (He) and argon (Ar). The increased flux can thus be attributed to hydroperoxides and peroxides. The key issue with this technology is maintaining membrane integrity, as plasma treatment includes a complicated reaction that might destroy the membrane structure, resulting in a loss of mechanical strength. A diverse strategy to changing polymeric membranes is grafting, which involves activation of the surface utilizing processes such as polymerization, UV photoirradiation, and plasma.

Owing to its simpleness, power economy, and cost-effectiveness, UV photon irradiation is the most extensively used of these activation approaches (Oulad et al. 2021). It can be done on flat sheet and hollow fibre membranes both with UV irradiation generating surface radicals that serve as monomer anchor sites. Advances in nano science has paved the way for more novel membrane designs. The manufacturing of high-performance membranes has been made possible because to the intriguing features of diverse kinds of nanomaterials. The hydrophilic metal-oxide nanomaterials, the hollow structured nanocomposites, and the antimicrobial metal nanomaterials are used to increase the flux, rejection, and antifouling properties of membranes. Nanoparticles and membrane materials have been combined to generate nanocomposite or mixed matrix membranes, which aim to translate the unique features of nanomaterials to membranes (Giwa et al. 2016).

When metal oxides like TiO_2 and Fe_2O_3 are added to nanocomposite membranes, their hydrophilicity improves dramatically, increasing membrane flow and consequently separation productivity (Guan et al. 2019). Carbon nanotubes (CNTs) and titania nanotubes (TNTs) are employed successfully in these applications. The tubular structure of CNT helps in rapid and low-resistance passage of water molecules across the hollows. Hence, the water flux of the membrane can be increased by several orders of magnitude. Enhanced hydrophilicity of membrane also helps with antifouling qualities. The ability of nonpolar substances like proteins and organics to get attached can be lessened with increased hydrophilicity. Nanoparticles with antimicrobial properties such as silver-based nanomaterials and single-walled carbon nanotubes (SWCNTs) play a significant role in prevention of biofouling. Membrane adherence by algae, fungi, and bacteria exerts a substantial negative influence on the membranes. Biofouling, unlike the previously described inorganic and organic fouling can be a concern since the microbes have ability to replicate over time and cannot be properly dealt with standard cleaning (Adamczak et al. 2019). Silver nanoparticles' antibacterial capabilities help regulate and decrease fouling by preventing growth of biofilm on the surface. Several methods for introducing nanoparticles into the polymer matrix have been developed. One of the most often described methods is the direct incorporation of nanoparticles into the polymer casting solution prior to membrane casting or spinning. Grafting and coating nanoparticles onto the produced membranes is another widely used method. The nanoparticles are deposited onto the membrane surface as a result of the physical and chemical interaction, which provides the maximal nanoparticles exposure (Gann and Yan 2008).

Such strategies are especially appealing for nanomaterials with antibacterial characteristics. The direct interlinkage of silver-based nanomaterials grafted or coated on the surface of the membrane via wastewater having bacteria or fungus like Staphylococcus aureus and E. coli can optimize silver-based nanoparticles' growth inhibitory effects. Mechanical strength is a critical consideration, especially for extended high-pressure operations like RO and nanofiltration. The membrane's great mechanical strength allows it to keep its integrity, also, withstand collapse and structure change produced by high-pressure compaction. As reinforcing materials, carbon-based nanomaterials like multi-walled carbon nanotubes and oxide of graphene have been used. The incorporation of these nanoparticles into the polymer matrix improves mechanical strength by allowing load transfer between the two entities (Jiang et al. 2020). Despite the intriguing capabilities given by these nanoparticles in enhancing the characteristics of the nanoparticle loaded membrane, the dispersion condition of the nanomaterials within the polymers is the most important factor in successful membrane modification utilising nanomaterials. Because of their large surface area, nanomaterials tend to clump together (Kim et al. 2018). The creation of gaps at the polymer and nanomaterial interface occurs as a result of aggregation inside the matrix, reducing the nanomaterials' distinctive characteristics. Because of the creation of unwanted voids, the agglomeration of nanoparticles placed inside the active layer of thin-film nanocomposite (TFNC) membrane resulting in significant decline rejection efficiency. Various types of nanomaterial alteration have been researched to address this issue. Some frequent nanomaterial changes include silanization, molecular wrapping, mild acid oxidation, and surfactant dispersion (Ihsanullah 2019). Commonly, these changes can add surface functions to nanoparticles in order to improve the compatibility of modified nanomaterials with the polymer matrix and achieve greater dispersion. Another appealing concept for membrane alteration is the creation of a biomimetic membrane, which incorporates biological features such as aquaporin to mimic biological processes (Li et al. 2017). A membrane like this is stimulated by natural efficiency and selectivity transport which developed over billions of years in live creatures. The UF and RO-FO membranes are related by the exterior surface membrane layer having pore range of 2–8 nm and lipid nanoporous bilayer. The protein-facilitated lipid bilayer is employed like a channel to increase flow of the biomimetic membranes by facilitating water transport. The biological antifouling surface, which can be employed to treat biofoulants (tiny proteins or complete organisms) is an intriguing property that can be used to give biomimetic membranes antibiofouling properties. Surface physiochemical interactions that resist foulants, release compounds that hinder biofilm adhesion, and other mechanisms are all involved in antifouling and build a topology which can minimize interaction among the surface of membrane and the biological surface (Shen et al. 2014).

4.3.3 Innovative Membranes

Adding capabilities and extra roles to membranes is another excellent technique to improve the performance of membrane technology. Photocatalytic and adsorptive membranes are two relatively novel kinds of membranes obtained from traditional MF-UF techniques (Nascimbén Santos et al. 2020). Because of the unique properties of the materials, adsorption and photocatalysis are utilized for the treatment of wastewater. When exposed to UV or visible light, photocatalysts degrade undesirable organic contaminants through a photodegradation reaction. Adsorbents eliminate pollutants from the environment either by physical or chemical reactions between adsorbent and pollutants surfaces. In spite of efficiency of these procedures, the handling strain of photocatalysts and adsorbents after water treatment limits their practical utility. For separating particles from the aqueous media, further treatment is always required. Photocatalytic and adsorptive membrane innovations have helped to solve these problems. Adsorbents and photocatalysts are inserted inside matrix of membrane that acts as a host for such components in these membranes. Before being inserted into the polymeric membrane matrix, the photocatalyst and adsorbent materials are typically produced or adjusted for optimal performance efficiency. Synergistic effects can be accomplished by innovative membrane design so that membrane can undergo adsorption and photocatalysis and separating undesirable molecules (Zhang et al. 2021). Because the photocatalyst and adsorbent materials are incorporated into the membrane matrix, it can be re-utilized and the secondary particle separation process could get eliminated.

4.4 Membrane-Based Remediation of Wastewater

4.4.1 Removal of Heavy Metal Ions

The heavy metal ions like chromium (Cr), arsenic (As), and lead (Pb) have wreaked havoc on the environment and harmed people's health. Due to the surface charge and sieving effects of such ions, reverse osmosis and nanofiltration may efficiently eliminate heavy metal ions from water and wastewater (Qasem et al. 2021). However, due to the low productivity and higher consumption of power, attempts are made to increase the selectivity of traditional UF and MF membranes toward heavy metal ions. Utilizing cellulose acetate (CA) based UF membranes infused with titanium dioxide (TiO_2) nanomaterial, Gebru and Das (2018) were able to remove chromium (VI) ions. The titanium particles were treated with amine ($–NH_2$) functional groups to produce chemical interactions among metal ion and the amine groups, which improved the affinity of heavy metal ions toward the membrane and improved reduction efficiency. Because of the porous nature and high surface area of TiO_2 nanoparticles, aminations were easily carried out within the pores. Figure 4.2 shows different adsorptive membranes (AMs) in the removal of heavy metal (Vo et al. 2020).

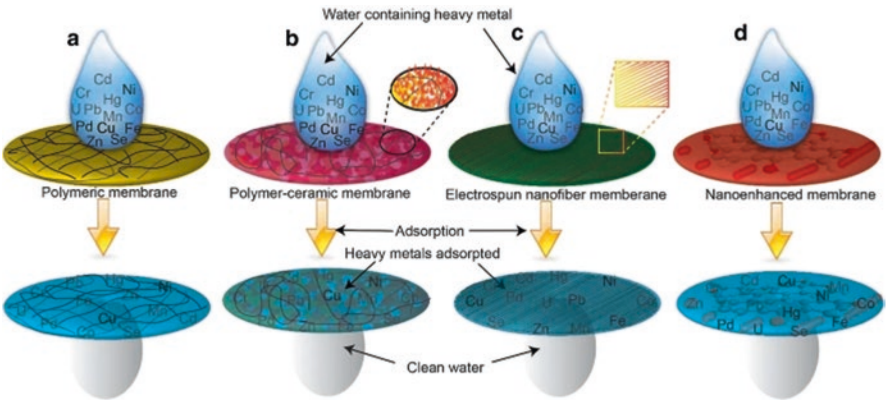

Fig. 4.2 Different adsorptive membranes (AMs) in the removal of heavy metal. (**a**) Polymeric membranes (PMs) are created from polymer (Vo et al. 2020). Source materials, (**b**) polymer-ceramic membranes (PCMs) are created from a combination between polymeric and ceramic (natural clay materials: bentonite, kaolinite, and montmorillonite) materials, (**c**) electrospinning nanofiber membranes (ENMs) are created from electrospinning method for forming fibers with nanometer to micron diameters, and (**d**) nano-enhanced membranes (NEMs) are created from incorporating nanomaterials (carbonaceous materilas, nanometal or nanometal oxides, and other organics)

At pH 3.5, the inclusion of TiO_2 nanomaterials enhanced reduction efficacy, resulting in 99.7% Cr (VI) removal. The protonated $–NH_2$ bonds in TiO_2 nanomaterials developed electrostatic contact with Cr (VI) anions like chromate (VI) ions at this pH. Addition of TiO_2 nanomaterials increased membranes' antifouling capabilities, making them easier to clean and regenerate. After regeneration and washing cycles, the reduction efficacy was only slightly reduced to 96.5%. Modified ultrafiltration membranes for the elimination of heavy metal ions was also reported by Fang et al. (2017). Adsorptive UV membranes were generated in their research by self-polymerizing polydopamine nanoparticles into the membrane's interior holes. Through circulatory filtration, a three-dimensional network of polydopamine was generated within the porous structure of the PES membrane from bottom to top. The inclusion of these nanomaterials increased the number of active sites and increased the contact time for heavy metal ion adsorption on the membranes. As a consequence, Pb^2, Cu^2, and Cd^2 adsorption capacities on PES-PDA-R membranes were 20.23, 10.42, and 17.01 mg/g, respectively.

However, regeneration investigations revealed that the increased polydopamine was not washable. As a result, only roughly 84.6% of the performance was recovered. The FO process is considered promising low-energy based method for the removal of heavy metal ions. To produce a polymer network, Liu et al. used a layer-by-layer technique to create a FO membrane. By using a polydopamine functionalized PVDF substrate, polyethylenimine (PEI), and sodium alginate were alternately constructed. Various heavy metal ions, including (Liu et al. 2017) Cu^2, Ni^2, Pb^2, Zn^2, and Cd^2, were removed from the aqueous solution using the resulting FO membranes. The bilayers amount in the membrane, the feed and draw solutions concentration, wastewater pH, time, and temperature were all investigated and compared. When three bilayers on the PVDF substrate with 1 molar magnesium chloride (MgCl) was employed on the draw side, an optimum 99% heavy metal reduction for all heavy metal was attained. The FO membrane's great rejection was due to optimal bilayers quantity that had produced an appropriate compactness and thickness to prevent heavy metal ions from passing through without impairing flow. The maximum rejection of 99.3% resulted in a flow of 14 L/m^2 h.

4.4.2 Removal of Colour

Large-scale discharges of colour through pigments and dyes in the water bodies are major source of worry since they possess immediate health and environmental risks. In this regard, ultrafiltration hollow fibre photocatalytic membranes with varied TNT weight fractions were produced by Subramaniam et al. (2018). TNT, which is a tubular shaped TiO_2 nanostructure which has been widely employed to enhance the hydrophilicity of the nanocomposite membranes. TNT has a large surface area functionalized with surface hydroxyl groups due to its tubular structure which provides more number of surface active sites for the attachment of functional groups. The PVDF-TNT membranes were utilized in that investigation to treat effluent of palm oil mill (AT-POME), that showed a brownish colour appearance. The fabricated PVDF membranes that had 0.5 weight fraction TNT amount gave the best filtering with 59.4% colour removal and a flux of 35.7 L/m^2 h. The increased flux was attributed by increased membrane hydrophilicity produced due to abundant hydroxyl groups observed at the TNT surface, as compared to the plain PVDF membrane. These hydroxyl groups made it easier for water to pass through the membranes. All the nanocomposite titania membranes had low fouling and maintained recovery flux of 80% after five cycles of operation, according to the membrane fouling and reusability analyses. The performance of that membrane photocatalytic membrane reactor under UV light irradiation was reported by the same group of researchers. TNT's photocatalytic property was activated by UV light, allowing for simultaneous filtering and photodegradation. When the photocatalytic property was activated, the colour removal effectiveness increased dramatically from 34 to 67% when compared to filtration alone. TNT served as a photocatalyst for lignin and tannin pigments to degrade in the AT-POME effluent in this environment, as well as an addition to increase the membranes' hydrophilicity. In addition, as the foulants photodegraded into smaller compounds, the photocatalytic activity showed positive effect by decreasing the fouling susceptibility. After five cycles of operation, the flux loss was only 5.7%.

PVDF NF membranes with halloysite nanotubes (HNT) were manufactured by Zeng et al. (2016). To combat HNT aggregation, the layered nanomaterials were treated by a coupling agent using a 3-aminopropyltriethoxy-silane silane to promote dispersion prior being added to the polymer dope. The ability of the resulting membrane to remove Direct Red 28 dye was tested. The inclusion of HNT enhanced the membranes' hydrophilicity, allowing for easier water transport while preventing dye molecules from passing through. Due to negative charges of HNT nanocomposite, an electrostatic connection between dye and membrane was generated, which enabled dye rejection. The developed membrane with 3 weight fraction silanated HNT achieved the greatest rejection of 95%. Chen et al. created a biomimetic dynamic membrane for dye wastewater treatment in another investigation (Chen et al. 2019).

Physical adsorption and filtration were used to introduce laccases and carbon nanotubes to the surface of a commercial UF membrane. CNTs worked as an absorbent in this nanocomposite system, preventing dye molecules from making contact with the surface of membrane. Laccase enzyme which was embedded inside absorptive layer boosted enzyme activity and aided pollutant breakdown in real time. Adsorption and fouling of membrane could thus be reduced at the same time. On dye removal, the effects of adsorbents and enzymes were investigated. A sustainable capacity was achieved at comparative high amount of laccase at 74.5 g/m^2 and the enzyme could successfully execute catalytic degradation to limit the propensity of absorption saturation. Furthermore, to obtain optimal dye removal efficiency, just 19 g/m^2 of CNT was required. The biomimetic dynamic membrane displayed greater antifouling performance and extended reusability due to the synergistic actions of the absorbent and enzyme. Moreover, after various cycles of operation, the flux remained over 120 L/m^2 h. The foulants might also be easily eliminated after the absorption process with a simple backwash cleaning.

4.4.3 Treatment of Oily Wastewater

Membranes in oily wastewater or generated water treatment tend to foul readily due to their nature (Barambu et al. 2021). As a result, it is preferable to build highly antifouling membranes for this application to ensure their long-term viability. Zwitterionic polymers are evolving as modifying agents which gives modified membranes antifouling capabilities. They possess equal number of anionic and cationic groups in their molecular chain, giving them hydrophilicity and resistance to nonspecific protein adsorption and bacterial adhesion. Zwitterionic substances surface grafting on UF and FO membranes has been widely used to treat oily wastewater. A double-skinned FO membrane was created by Ong et al., consisting of a PES substrate sandwiched between a selective polyamide top layer and a zwitterionic brush at the bottom layer. The hydrophilicity of PES was improved by grafting a poly(3-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl)ammonatopropanesulfonate) (PMAPS) brush to the bottom surface. The double-skinned membrane had a high water flux of 13.6 L/m^2 h and a reverse salt flux of 1.5 g/m^2 h when evaluated in a FO mode with 2 M NaCl as the draw solution, with a rejection of 99.8%. Lee et al. devised a more straightforward method of inserting the PMAP zwitterionic polymer onto the PES substrate of a FO TFC membrane. The hydrophilic nature of PMAPSs permitted the creation of finger-like structures on the PES substrate during phase inversion, that facilitated transport of water molecules. Moreover, 99.9% of oil rejection and flux of 15.7 L/m^2 h was observed when TFC was combined with 1 wt% PMAPs. When compared to the unaltered TFC, the flow was increased by over 30%. The membrane displayed good water recovery even after possessing very high oil emulsion concentration of 10,000 parts per million (ppm) due to its significant hydrophilicity. To recover the flow, only deionized water rinse was necessary. The hydration layer generated by hydroxyl bonding between the feed water and –SO_3 functional groups of PMAPS that prevented oil molecules from attaching to the membrane and increased its antifouling characteristics. Figure 4.3 shows the modified and unmodified membrane fouling mechanism.

Yan et al. (2008) used the intercepting outcome of a permeable CNT framework to create a hybrid membrane. Through covalent functionalization, polyacrylic (PAC) acid brushes that were hydrophilic in nature were introduced into the CNTs structure to generate a underwater superoleophobic structure. The membrane porosity was proportionate to its thickness and the functionalization was done using a simple filtration process. The superoleophobic surface of membrane facilitated quick water movement while obtaining a separation efficiency of 99% while filtration of the oily water under vacuum pressure of 0.09 MPa.

Ahmadi et al. (2017) created antifouling nanofibrous MF membranes incorporating GO. Electrospinning was used to create the membrane, which was made up of sulfonated PVDF, PVDF, and GO. Membrane hydrophilicity was enhanced at an optimal 0.5 wt% of GO due to existence of several hydrophilic groups on the GO planar structure. The membrane was able to completely remove the oil due to membrane smaller pore size, which successfully blocked oil particles transfer through the membranes. The antifouling properties were increased by repulsion among oil particles and sulfonic groups. Nanofibrous membrane showed less irreversible fouling (41%) with good recovery ratio (59%). For treating generated water, Ahmad et al. (2018) modified flat sheet polyvinyl chloride (PVC) UF membranes via incorporating bentonite particles to enhance morphology and antifouling characteristics. Bentonite particles having good cation exchange capacity played key role in modifying the viscosity of dope solution, as well as the morphology of the membranes. The introduction of bentonite nanoparticles increased viscosity of the gelation bath, which enhanced the exchange rate of water and solvent. The UF-PVC membrane with the largest loss tangent and dynamic viscosity had a polymer, solvent, and nanocomposite at a ratio of 12.0:87.23:0.77. As a result, the surface porosity, density, and roughness were significantly improved. On treating with oily water, the UF nanocomposite membrane had a 97% oil rejection and a flux of 186 L/m^2/h with the necessary morphological features. When operated with generated water with TDS of 35,000 ppm, the membrane achieved 93% oil rejection and 94 L/m^2 h water flux thanks to bentonite's strong hydrophilicity and antifouling capabilities.

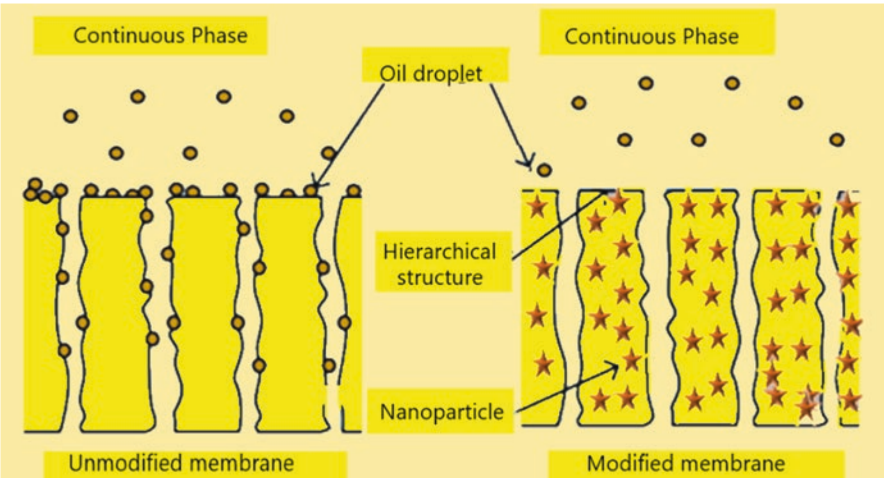

Fig. 4.3 Illustration of fouling mechanism of nanocomposite membranes

4.5 Innovative and Sustainable Membrane Techniques

Membrane-based processes plays a critical role in preserving water supplies from a variety of water sources, including wastewater and seawater. The long-term viability of membrane development is largely responsible for their growing acceptance and application in industries (Tufa 2015). Membrane technologies have a number of advantages over traditional techniques, which has spurred the move. Membrane process allows for localized reclamation and reusage, as well as the avoidance of long-distance product water transfers. It is also unnecessary to identify new protected catchments. Membrane techniques have also demonstrated promising factors in terms of technical factors including durability, easy handling, scalability, flexibility and adaptation. Different membrane techniques for desalination and the treatment of wastewater production have been evaluated with various economic, ecological, technological, and societal implications to assure the long-term development of membrane technology. The cost of desalination and the treatment of wastewater, as well as the environment impacts of these techniques are major drivers for membrane development's long-term viability (Goh et al. 2020). The biggest impedance in terms of economics is energy consumption, particularly in the case of RO saltwater desalination. To create 1 m^3 of freshwater, modern RO plants typically consume 3–4 kWh of electricity. The pressurization of seawater to 60–70 bars consumes a significant amount of energy. Another major concern with pressure-based membrane techniques is the release of greenhouse gases (GHGs) and other pollutants into the atmosphere, that may accelerate climate change. Alternative resources, such as renewables, are one long-term answer to this problem.

The ideology of employing renewable resources is appealing, and the number of studies is growing as a result of the enormous potential of renewable resource-driven RO desalination plants to meet water demand while lowering CO_2 emissions. Solar, geothermal, and wind energy have all been examined as potential sources of power for desalination plants. However, various technological restrictions linked to resource stability and building expense must be overcome before large-scale applications can be implemented (Eggensperger et al. 2020). To justify ethical difficulties linked with membrane implementation, it is vital to identify probable environmental dangers involved in membrane manufacture and during the procedures. Direct and indirect environmental effects are two types of potential environmental consequences. In the case of desalination, the direct effect is caused by the intake of saltwater, that results in a significant reduction of aquatic species when brought near desalination plant. If the discharge is not effectively handled, membrane processes can pose a harm to the environment, particularly to marine organisms. The brine discharge with high total dissolved solid (TDS) contents from RO plants, in particular, has considerable negative environmental consequences. The Ashkelon desalination plant, which has a monthly seawater input of roughly 315 million m^3 and releases brine with a TDS about double that of seawater, has been confirmed to be one of the world's largest facilities. Material selection, regulatory enforcement strategies, and process intensification can have a significant role on minimizing the global environmental concern. Membrane fabrication development and utilization is expanding. The incorporation of nanoparticles as additives in membrane production offers a significant performance boost (Fane and Fane 2005).

As previously noted, several developments in studies have seen the promise of reducing membrane process energy consumption by inventing revolutionary nanocomposite membranes that can efficiently boost the flow and supply of fresh water. In spite of their benefits, nanoparticles' environmental friendliness, stability, and applicability in improving membrane techniques are still contested. To synthesize nanomaterials, various hierarchical techniques have been well-entrenched. Some of these methods, however, necessitate elevated temperatures and the toxic chemicals usage. The green synthesis of nanoparticles, which can limit the creation of toxic by-products to the ecosystem, is an essential area for concentration in this subject to ensure sustainable development. Furthermore, the leaching of nanoparticles from nanocomposite membranes could be hazardous to the environment. Coating and grafting are two nanocomposite membrane production procedures that include the deposition or attachment of nanoparticles on the membrane surface. The durability and stability of the membrane might get impaired in the coarse of extended operations and high pressure conditions, resulting in nanomaterial leakage into water bodies. Hence, long-term performance review is essential to avoid secondary contamination. Nanomaterials' unique features, as well as the nanocomposite membranes that result, have allowed for extraordinary improvements in membrane performance (Buonomenna 2013).

Production of nanoparticles on larger scale to fulfil industrial necessities, on the other hand, is a huge obstacle that must be overcome. Many nanomaterial synthesis processes necessitate meticulously controlled reaction conditions in order to achieve a low yield of nanoparticles with desirable characteristics. To accelerate the use of this invention in industry, easy, reliable, and repeatable synthesis procedures are required. The long-term reliability of membrane techniques is critical for the technology's long-term development. Membrane fouling is a key source of worry, since it has resulted in a drop in performance. The impact of membrane fouling on flow and productivity has been thoroughly examined using the concept of critical water flux. Cleaning of membrane is done on a regular basis to eliminate fouling layers before membrane replacement. Various cleaning regimens have been thoroughly investigated; the most simple and successful cleaning processes uses the treatment with chemicals. Chlorine bleach, sodium hydroxide (NaOH), and hydrochloric acid (HCL) are some chemicals used in the chemical cleaning process to eliminate the foulant before the conventional backward or forward flushing. Though, the brine discharge did not pose substantial toxicity on the examined aquatic creatures, Park et al. (2011) found considerable toxicity in the additives, chemicals and solvents utilized for cleaning of membrane in a case study based on the desalination facility at Chuja Island, Korea. To reduce negative consequences of chemical discharge, ecofriendly chemicals must be chosen and low concentrations must be used.

4.6 Conclusion

Membrane technology for desalination and wastewater treatment has shown continuous and continual improvement. Membrane-based processes are becoming popular replacement to several commonly utilized procedures due to its benefits. The membranes structural design to improve filtration efficiency is one of the most significant areas of advancement in this industry. The choice of an appropriate membrane technique and the membrane parameters optimization for the specific application criteria are critical since they determine the effectiveness of salt and impurities removal capability as well as the cost of the technique. This chapter focuses on developing high-performance membranes for a variety of applications, including heavy metal ions and colour removal, treatment of oily wastewater and desalination. Various manufacturing processes for membrane modification have been devised and effectively used to increase membrane separation performance and long-term stability. The affinity of membrane materials with additives, the durability and stability of membrane fabrication materials for modifications that may imply extreme conditions, economic efficiency, separation purpose, operation types and feasibility for large-scale operations, all play a role in the selection of an appropriate method. High-performance membrane process is expected to evolve in different filtration technologies, feasibility on a large commercial scale, as improvements in membrane development and system optimization are made. Moreover, despite membrane technologies' potential in solving numerous challenges connected to desalination and treatment of water and wastewater, their adoption should be constantly studied in order to assess its extended time period impacts, especially from an ecological and environmental standpoint.

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