Materials Horizons: From Nature to Nanomaterials

Ashok Kumar Nadda
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Membranes for Water Treatment and Remediation

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Materials Horizons: From Nature to Nanomaterials

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Membranes for Water Treatment and Remediation

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Preface

Crisis of fresh water resources has been intensified due to climate change, rapid population growth, and global increase in urbanization. Reclamation of wastewater has been considered crucial for reducing fresh water usage and achieving water sustainability. Reclaimed wastewater has been considered as an alternative water resource for non-potable or (indirect) potable use, especially in the counties or regions facing water scarcity. Various membrane-based techniques have been widely investigated for treatment of wastewater and production of treated water of superior quality. Over the last two decades, wastewater reclamation has received considerable attention as it offers an option to meet the requirements of the communities that are unable to access centralized wastewater facility; facilitate commercial buildings for achieving water sustainability; reduce water supply costs and decrease the load on centralized wastewater treatment systems; and spend less energy. It also releases lower CO_2 in comparison to centralized wastewater reuse systems as it does not need a higher degree of treatment in terms of wastewater characteristics. Reclaimed wastewater may have more public acceptance in comparison to municipal wastewater reuse due to cultural resistance and barriers in some countries.

In recent years, application of membrane-based techniques in wastewater treatment has been considered as a promising technique and has gained increasing scientific attention. Compared to other wastewater treatment technologies, membrane-based systems offer several advantages. Membranes provide a permanent barrier to suspended particles (including bacteria and virus) and macromolecules greater than the pore size of the membrane material, which result in an improved quality of treated wastewater. Decreased membrane price and development of new membrane materials facilitate membrane systems to achieve more efficient wastewater treatment with economic feasibility. Membrane systems exert less environmental footprint due to their compact nature. Despite more technical progress and practical applications of membrane-based wastewater treatment, a major challenge is membrane fouling, which inevitably occurs during wastewater treatment and leads to a higher energy demand and increased maintenance cost. Membrane-based separations are commonly performed with polymeric membranes due to their higher flexibility, easy pore forming mechanism, good film forming property, mechanical strength, chemical stability, high perm selectivity, selective transfer of chemical species, inexpensive materials for its fabrications required pore sizes for various filtration processes, low cost and smaller space for installation as compared to other membranes. Owing to these properties these membranes are widely applied in pressure driven processes such as ultrafiltration, nanofiltration and reverse osmosis for wastewater treatment.

This book aims to present comprehensive information on membrane-based techniques in wastewater treatment including direct pressure-driven and osmotic-driven membrane processes, hybrid membrane processes (such as membrane bioreactors and integrating membrane separation with other processes), and resource recovery-oriented membrane-based processes.

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Chapter 1
Polymeric Membranes for Water Treatment

Swati Sharma, Shreya Gupta, Sukhminderjit Kaur, Deepak Kumar, Priya Banerjee, and Ashok Kumar Nadda

1 Introduction

The most critical challenge faced by mankind nowadays is the shortage of fresh water caused by urbanization, industrial development, population growth, energy plant, and climate change [14, 62]. As the growing population and industrialization are increasing rapidly demand for safe, clean, and drinkable water is also increasing. In oceans, around 97% of water is stored as salty water that is not suitable for agricultural use or human consumption, only (>3%) of water on earth is available for agriculture and drinking purpose, and a large amount of this present is locked in the form of underground water, glaciers, and ice caps [86]. Various organic and inorganic contaminants are introduced into the water systems by the effluents from industrial and agricultural activity making them unsuitable for consumption. The main problem that needs to be solved is water quality, water quantity, and the removal of contaminants needed to avoid the side effects on human health and the environment. To produce clean water, many economical and multifunctional processes are developed.

For the treatment of wastewater, many technologies have been developed, including methods such as ion exchange [12], adsorption [35], reverse osmosis [110], and gravity [16], among these methods, adsorption is a widely used method for

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the removal of water contaminants because of its low cost, easy to use and availability of different adsorbents. The use of activated carbon, polymer composites, magnetic nanoparticles, and nanotubes are included in the different adsorbents, they can remove various types of contaminants including heavy metals [48, 54, 84, 85]. Despite being able to remove most of the water pollutants/contaminants, adsorption also shows some limitations like less use of these adsorbents commercially and a lack of appropriate adsorbents with high adsorption capacity [26]. Therefore, there was still a requirement for more efficient techniques/methods such as membrane technology. For wastewater treatments and desalination, membrane technologies are proving to be leading methods as membrane filtration presents some advantages such as maintenance and monitoring, a lower footprint, simple operation, lower mass storage tubes, compact modular design, and fewer flow rates of chemical sludges during the production of high-quality water from different sources [25, 46, 73]. This technology is known to be an effective water separation process because of its high contamination rejection of high-quality treated water yield [25]. The removal of soluble components and suspended particulate matter from the wastewater semipermeable membranes is the general idea behind the membrane-based wastewater separation. The application of membrane technology especially in water treatment has been increasing rapidly over the past few decades, increasing the amount of efforts by membrane scientists/researchers [68]. The membrane is the functional component of a membrane filtration process. The separation of different materials through the membrane depends on molecular size and pore [122], therefore various membrane processes including nanofiltration (NF), microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and forward osmosis (FO) have been developed with different separation mechanisms (Fig. 1).

Both polymeric and inorganic materials can be used to prepare/form membranes, polymeric membranes are mainly organic in nature whereas inorganic membranes are mostly metals, oxides, and ceramics [70, 99, 114]. In comparison to membranes fabricated from inorganic materials, membranes prepared from the polymeric membrane are low-priced [70]. During fabrication, it is easy to handle polymeric membranes and can also be used for the high-water production capacity [51, 70, 99]. The aim of this chapter is to review the different polymeric membranes used for the treatment of wastewater and the fabrication of different polymers for the membrane technologies. The operating cost of water treatment along with permeate quality is determined by the type of polymer used for the filtration. To avoid the issues such as unwarranted energy consumption and frequent membrane replacement it is crucial to select the proper or most suitable type of polymer for a filtration process. The future work, applications, pros, and cons of polymeric membranes are also discussed briefly.

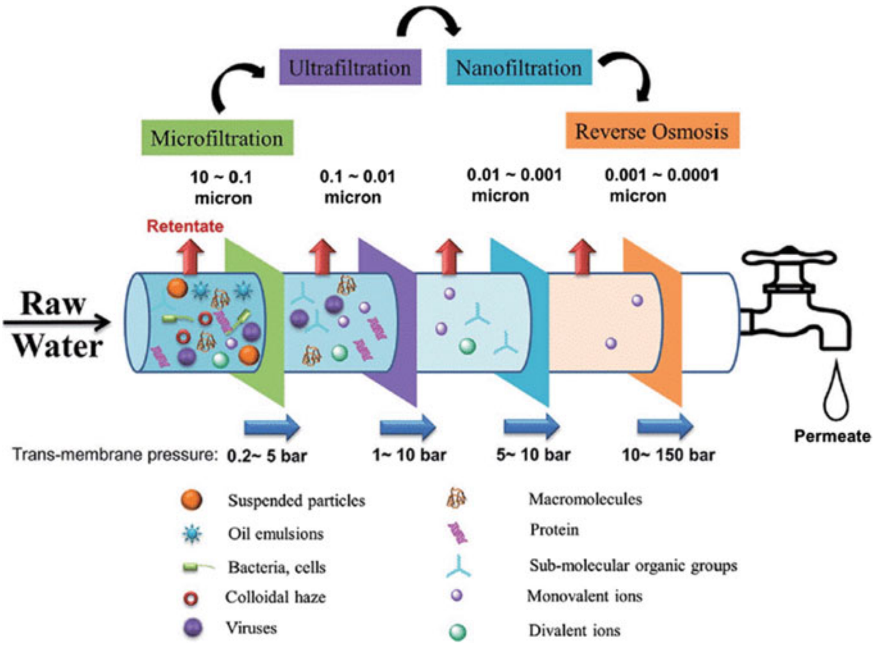

Fig. 1 Pressure-driven membrane processes for water treatment technologies, showing the particles effectively captured by each process along with the pore sizes of the membranes used for each process [53]

2 Polymers Used for Membrane Filtration (Water Treatment)

Polymers namely polyamide (PA), polysulfone (PSF), polyvinyl chloride (PVC), polyacrylonitrile (PAN), polyvinyl alcohol (PVA), poly (arylene ether ketone) (PAEK), poly (ether imide) (PEI), cellulose acetate (CA), polyvinylidene fluoride (PVDF), polyethersulfone (PES), polyaniline nanoparticles (PANI), polyimide (PI), polyethylene glycol (PEG), poly (methacrylic acid) (PMAA), and poly(arylene ether sulfone) (PAES) have been used in the fabrication of different membrane processes (NF, UF, MF, RO) [33].

3 Membrane Processes and Polymers Used

3.1 Nanofiltration

In recent decades, NF membranes have attracted attention as a potential for water treatment/filtration because of their advantageous properties like low energy consumption in comparison to RO and high retention of neutral molecules (low molecular weight) and divalent salts [28, 60, 124]. For some highly polluted waters, NF is pre-treated to make it more effective, also because of their moderate stability these membranes can only endure an aqueous solution having a pH range of 2–11. In a study, textile wastewater is treated with NF membrane and it was reported that the prepared membrane exhibited decent removal of common salts and dyes and heavy metal ions, displaying high removal efficiency toward cationic dyes and metal ions. Nowadays, most available NF membranes are consisting of different polymers such as PA, PAN, PI, and PVA in TFCs [4, 94, 98, 102–105, 115, 121]. Though, when in contact with a few amines PIs are not stable, and also in polar solvents they display very poor stability and performance, therefore, in aqueous solutions having strong acids/bases, strong amines, and chlorinated solvents these PIs are not favored, but through the crosslinking process they can be modified and better resistance against such chemicals can be obtained. In a study, PEEK is used as a material for NF membrane, and it was reported that PEEK membranes are highly resistant against different acids, bases, and solvents and have a low degree of sulfonation, but these membranes show low water permeability. These membranes demonstrated water permeance of 0.7–0.21 and 0.2–0.8 L/h m^2 bar when tested for their separation performance in dimethylformamide (DMF) and tetrahydrofuran (THF), respectively [18]. Yang and co-workers, reported the use of PMIA/GO composite NF membranes for the treatment of water. In comparison to the pure PMIA, the fabricated composite membranes exhibited a better/larger hydrophilic surface that as a result gave rise to pure water flux, and also high dye rejection, and increased fouling resistance to BSA (bovine serum albumin) were achieved [111, 112].

3.2 Microfiltration (MF) and Ultrafiltration (UF)

(A) **Microfiltration**

In microfiltration, separation mainly occurs through sieving because of its large pore size (approx. 0.1–1.0 m), and removes little or no organic matter, MF mainly removes the suspended solids or particles, bacteria [20]. However, when pre-treatment is applied then maybe there is an increase in organic matter removal. MF can be used as a pre-treatment to reduce fouling potential in RO and NF [96]. MFs main drawback is that they cannot remove contaminants such as dissolved solids (<1 mm in size), and it does not act as a barrier to viruses. Microfiltration membranes have been mainly utilized in wastewater treatment, membrane bioreactor, and membrane distillation [1, 9, 30–32, 102–105].

A membrane bioreactor (MBR) is an active sludge process in which MF and UF membranes are combined together for wastewater treatment in different industries. In the configuration of MBR, the membrane is submerged into the bioreactor, and treated water is permeated using a vacuum whereas solids are reserved in the bioreactor. In comparison to a traditional side stream configuration, the current MBR configuration lowers energy consumption and also reduces the membrane fouling amount [52]. Polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyethylene (PE), and polyethersulfonate (PES) are mostly used as polymeric membrane materials for applications of MBR. Among these PVDF accounts for about 45% of MBR polymeric membranes and because of PAN's lower affinity to extracellular polymeric material it is most likely the most fouling-resistant one [59].

Normally, MBR membranes have a pore size between 0.03 and 0.4 m, PES and PE membranes are mostly available with a pore size of 0.03 and 0.2–0.4 m respectively, while PVDF membranes are available in the whole range of pore sizes due to their versatile manufacturing [41]. Compared to UF membranes the integrity of MBR membranes is less [1].

The two-stage process of CAS (conventional activated sludge) including biotreatment and clarification is replaced by MBR a single integrated process. Some advantages such as reduced footprint, nearly complete separation of suspended solids from the effluents, product consistency, and reduced sludge production make MBR superior to conventional treatment [91]. Because MBR systems operate at a higher concentration of mixed liquor suspended solids (MLSS) they remove a large range of biodegradable and hydrophobic trace organics more efficiently than CAS processes, MBR systems also offer a definitive boundary layer proving a complete suspended solid retention [40]. Consequently, MBR effluent has the potential to be used as process water, irrigation water, also as feed to potable reuse applications [50].

(B) **Ultrafiltration**

In ultrafiltration, compounds can be separated between 0.005–10 μm, these membranes are highly water filters with less consumption of energy in the removal of suspended matters, macromolecules, and pathogenic microorganisms [47, 80]. UF has some drawbacks such as maintaining high-pressure water flow regular cleaning required and any dissolved inorganic substances in water can't be removed [120].

In UF membranes as polymeric materials mainly PS and PES are used due to their strong chemical stability, wide pH operation range, and good mechanical properties [22, 61, 76, 87, 90, 100, 108]. But the applications of these membranes in the treatment of water are limited because of their hydrophobicity that leads to decreased permeability of the membrane, also mostly polymeric materials of UF membrane show hydrophobic properties. Recently for the UF membranes fabrication, some other natural hydrophobic polymeric materials such as PMAA, PVC, and PVDF are also used [11, 38, 58, 102–105, 111, 112, 123].

During the operation there can be a decline in water flux because of membrane hydrophobicity as organic compounds get accumulated favoring the attachment and growth of microorganisms onto the surface of the membrane, leading to fouling and failure of the membrane [102–105]. It is important to modify these polymeric materials to improve their properties and increase their applications in the treatment of water. The main motive to modify these membranes is to increase the hydrophilicity of the membrane, enhancement in the membrane hydrophilicity also increases the antifouling properties of the membrane for liquid water-based filtration.

Some polymeric materials such as PSF, PVC, PMMA, and PES are incorporated with different types of particles or nanoparticles (TiO_2, MSP-1, ZnO, silica) to improve their properties mainly hydrophilicity [24, 33, 70, 81, 118].

3.3 Reverse Osmosis (RO)

RO technology (Fig. 2) is used for the removal of smaller particles and dissolved solids, this method is only permeable to molecules of water [72]. To make water overcome the osmotic pressure enough/high pressure should be applied to RO. In comparison to UF, the pore size of RO membranes is tighter, these membranes are able to convert hard water to soft water and require low maintenance [107]. They have extremely small pores and have the potential to remove all particles smaller than 0.1 nm including bacteria and organics [109]. The main disadvantages of RO membranes are the high-pressure use, prone to fouling, and being expensive in comparison to other membranes. Desalinating of water through RO is considered the most efficient and popular method as it is appropriate for potable and near-to-potable water production [45, 55].

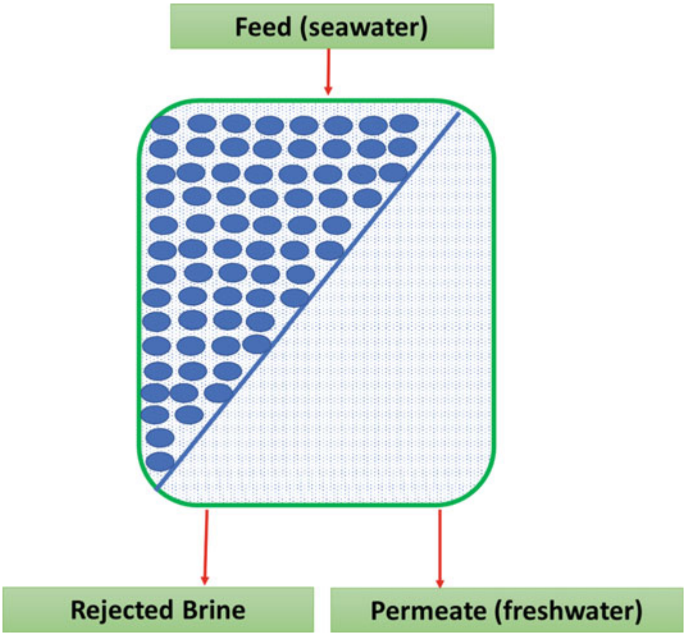

Fig. 2 Reverse osmosis process showing the separation of salt from water

Commercially available RO membranes consist of polymeric materials like PA and CA [15, 31, 32]. CA is a natural polymer mainly obtained through the esterification of wood, recycled paper, bagasse, and cotton, CA is eco-friendly, renewable, and biodegradable and also known for its high potential flux and hydrophilicity, biocompatibility [21, 29, 66, 79]. PA membranes have the ability to withstand higher temperatures and operate under a wider pH range making it more preferable over CA [113].

However, as PA membranes have continuous exposure to chlorine and some oxidizing substances, so their practical application is limited [119]. The amide group present in the membranes of PA is sensitive to attacks of chlorine during chemical cleaning [31, 32, 101]. So, to prevent the PA membranes degradation, the concentration of chlorine is reduced by an additional step of de-chlorination. Also, Poly (arylene ether) copolymers, especially poly (arylene ether sulfone) have been used to overcome this problem, as these polymers are highly resistant to chlorine attacks due to the absence of susceptible amide linkages [74, 75].

Nebipasagil and coworkers, prepared photo cross-linkable disulfonated PAES copolymers for the applications of RO, initially they synthesized PAES oligomers with controlled molecular weights and degrees of sulfonation by nucleophilic aromatic substitution. The molecular weight of the PAES was controlled by using Meta-aminophenol and thamtelechelic amine end groups were installed. The novel cross-linkable PAES oligomers with acrylamide groups presence on both ends were obtained by reacting meta-aminophenol end-capped oligomers with acryloyl chloride. In order to obtain, PAES copolymer thin films, UV radiation is used in the presence of a UV photoinitiator and a multifunctional acrylate to cross-link the acrylamide-terminated oligomers. It was observed that the smooth surfaces of cross-linked disulfonated PAES films had improved high water passage and also there was a reduction in water uptake [69].

PVC can also be used as polymeric material for RO membranes, due to its durability and flexibility, and also with better biological and chemical resistance. PVC/CA polymers are used as membrane binders to achieve enhanced separation properties and special selective characteristics in membranes. Hydrophilic characteristics of the membrane can be improved by increasing the concentration of CA in the PVC/CA polymers solution and rejection capabilities of the fabricated membrane can be improved by increasing the CA concentration by around 10% [3, 29, 77].

4 Types of Polymeric Membrane

The polymeric membranes are classified broadly into two categories; porous and non-porous. The two are each categorized into two subcategories.

4.1 Porous Membrane

The porous membranes are used for microfiltration and ultrafiltration purposes. Microfiltration entails membranes whose pore sizes are expressed in terms of micrometers. The pore sizes range from about 0.1 μm and above. These membranes are often used as the first step of filtration before the water progresses to the other stages. Among the materials removed by this type of membrane are suspended solids, micelles protein, bacteria, and fats. Ultrafiltration membrane also falls under the porous category. The average pore size is between 0.001 and 0.1 μm [8]. The membranes operate based on the principle of molecular exclusion. They remove macromolecules, protein, and enzymes, as well as starch from the solution. The membranes are in most cases made of polyethersulfone or polysulfone molecules [92].

4.2 Nonporous Membrane

Non-porous polymer membranes are another main category. The membrane is relatively dense compared to the porous membranes and water diffuses through the membrane only by the application of pressure, concentration, or electrical potential gradient [49]. Non-porous membrane falls under nanofiltration or the reverse osmosis technique [49]. The type of polymeric material used in both categories makes the difference in the permeability and selectivity of the membrane. In most cases, organic nanofiltration membranes are made by applying a thin film of a polymer to a polyethersulfone or polysulfone ultrafiltration substrate. Those in the nanofiltration category mainly remove amino acids, multivalent salts, and polysaccharides. The reverse osmosis membrane filters out salts and other minerals leaving only clean water for consumption. Separation occurs through the diffusion of dissolved species through the membrane and overcoming the osmotic pressure of the process fluid [99].

5 Polymer Membrane Filtration Process

As noted, [33], the use of polymer membranes to treat water is also referred to as reverse osmosis. In its simplest form, the process entails pressuring water through a semipermeable membrane to remove impurities and contaminants. The membrane is made of polymer materials that distill or remove the dissolved organic solids, including salts, from the water to make it clean for consumption. The process is as demonstrated below in Fig. 3.

The process has three main stages. The first stage is the Pre-filtering stage. Here, the water from the supply line enters the reverse osmosis pre-filter first. Herein,

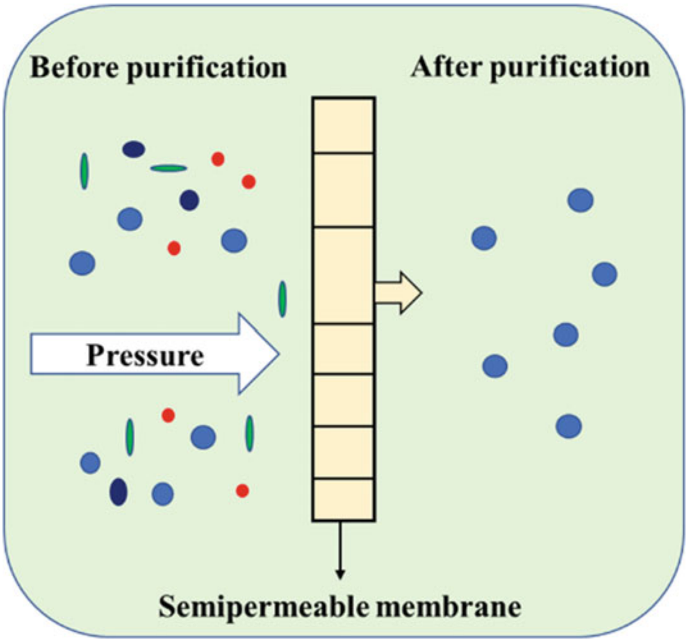

Fig. 3 Reverse osmosis: a water purification process

sediments and carbon filters remove the sand, silt, dirt, and other sediments that may potentially clog the system. Chlorine and phenol, which can cause major damage to the polymer membranes used in the reverse osmosis process, are also removed using carbon filters [97]. The second stage is the reverse osmosis membrane, which in this case is a semipermeable polymer membrane. The membrane removes dissolved salts, aesthetic contaminants, and health-related contaminants. Once the water is filtered through the membrane, it enters the pressurized storage tank for storage. There is a final post-filter stage that removes any remaining odors or tastes using the same polymer membrane. The water is then ready for distribution [57].

6 Membrane Fouling

The polymeric membrane is also used for the treatment of produced water. In industrial waste treatment, membrane-based separation plays an important role which comprises Produced water treatment. For industrial separation using membrane have many advantages including simple operation, no phase change, ease to scale up, cost-efficient, and less area occupied [43]. In layer filtration, the membrane has a particular barrier in the middle of two phases of perfuse matters. The particular transport is attained based on differences in physical or chemical properties of perfusing matter to the other side of the membrane. In porous membranes (microfiltration, ultrafiltration) separation rate of particles is based on sieving, size exclusion, and on the other hand in the case of the nonporous membrane (nanofiltration, reverse osmosis) separation is based on the solution–diffusion mechanism of solutes and solvent. The polymeric membrane show utility to form better filtration membranes is low cost, flexible, and has a border spectrum to be utilized in desirable separation techniques [63]. The high salinity of PW restricts its beneficial uses. Membrane mainly reverses osmosis and selective nanofiltration lessens the high salinity of produced water (PW). Some RO and NF membranes are used in PW treatment are NF1, polyethersulfone, NF90, and polyamide [6, 64].

Mainly the membranes which are used in PW treatment are NF and RO that are thin-film composite (TFC) membranes. TFC consists of three layers, the upper dense layer is made up of polyamide compound, and the middle layer is composed of polysulfone which is supported by the third layer of polyester microporous compound [65]. The membrane separation processes of NF and RO are determined by water-possessed pressure and depend on diffusive-based mass transfer. Membrane fouling increases the flux or increases the transmembrane pressure (TMP). Factors that cause fouling are depositions of inorganic components, because of this the pores of the membrane block [125] and result in reversible and irreversible membrane fouling [23]. When there is an attachment of particles on the surface of the membrane called reversible fouling and when the attachment of particles on the surface of the membrane which is cannot be removed by physical cleaning called irreversible fouling.

6.1 Fouling Control

It is controlled by ultrasonic cleaning, membrane cleaning using chemical agents, and membrane modification.

(A) **Ultrasonic treatment**

The process involves the removal of thick foulant originating from the surface of the membrane. The fouling of polymeric membranes by various pollutants between the active layer surface of the membrane and foulant molecules needs harsh thermal or chemical treatment to remove but this gives damage to the original membrane which is impossible to recover. To control the membrane fouling uses cleaning strategies such as a designed process, membrane cleaning by ultrasonic techniques, and hydraulic cleaning [17, 36].

(B) **Fouling control by chemical cleaning**

The ideal chemical cleaning agents have the following properties:

a. Solubilized foulant.
b. Hydrolyzed foulant.

c. The agent should not damage the membrane or system.
d. Avoid new fouling while in solution [82].

Chemicals that we used are to clean the foulant from the surface of the fouled membrane and the selection of chemicals is based on the components which cause fouling are:

- **Sodium dodecyl sulfate (SDS)**: It is a surfactant that contains hydrophilic as well as hydrophobic components and forms micelles with fats and oils which helps in ameliorate fouled cleaning [106].
- **Disodium ethylenediaminetetraacetate (EDTA)**: Known as a chelating agent used to remove metal ions and foulant from the fouling layer [7].
- **Sodium hydroxide (NaOH)**: In comparison with SDS and EDTA, sodium hydroxide is a more effective cleaning agent. In a study, SDS was found more efficient when applied for 5 min and it restores permeability completely. Both disodium ethylenediaminetetraacetate and sodium hydroxide have a similar range of cleaning efficiency and both are inferior to SDS [5].

(C) Fouling control by surface modifications

By transforming, the surface properties of membrane fouling can be managed. The degree of fouling is influenced by the roughness of the surface [71] charge of the surface hydrophilicity, and hydrophobicity. The membranes which are more susceptible to fouling are rough membranes although the smooth and neutral surface of the membrane is less prone [67]. Membrane surface hydrophilicity is the main criterion for the antifouling property of polymeric membranes [63]. To fouling, surface modification is very important for polymeric membranes. The surface modification includes grafting blending, and incorporation of nanomaterial such as carbon nanotubes [95], TiO_2-based polymeric membrane [13], ZnO-based polymeric membrane [89].

(D) Removal of membrane fouling using nanoparticles

In polymeric material, researchers concentrated on integrating inorganic nanoparticles resulting in the development of a Nanocomposite membrane, and because of this physiochemical and mechanical properties were enhanced. Nanomaterials are used as fillers for example carbon nanotubes (CNTs), nanosized $TiO_{2,}$ and nanosilver.

Carbon nanotubes (CNT): It is a single-wall carbon tube made up of carbon with a diameter in the range of nanometers. Carbon nanotubes have various properties like carbon nanotubes have high hydrophilicity and good chemical stability. Carbon nanotubes with properties of antibacterial, high centralized strength, and improved porosity it has been ideally utilized in membrane augmentation [19]. There are many methods utilized to manufacture inorganic polymer membranes based on Carbon nanotubes which involve blending, direct coating, in-situ polymerization CVD, and CVD template [56]. In a process of polymer membrane formation, CNT is used as a substrate to intercalate with polymerization [83].

Silver nanoparticles: Silver nanoparticles (SNP) have properties of bactericidal, increased oxidative stress, and high-affinity silver ions because of this it is drawn into the field of mixed matrix membrane [10, 93]. Silver is a non-allergic, non-toxic, and eco-friendly metal, so it has fewer hazards toward human cells [2]. Also, it is efficient when the bacterial solution is incorporated into the matrix of the membrane [117] because of this antibacterial ability and low toxicity apropos humans, silver ions take on in membrane fabrication. It was found that the Ag-containing membranes have unique antifouling properties [37].

7 Future Research

Recent decades of research and developments in this field have concentrated on appropriate techniques to procure clean water by filtering and reutilizing water to support human health and water scarcity. The process of removing impurities and pollutants from water to procure suitable water is called water purification. Due to its high efficiency and low cost, water purification technologies are dominated by membrane technology. In comparison with other types of membranes, membrane separation industries are led by polymeric membranes as they are economical and practically favorable. But the membrane use has less chemically and thermally divergent which reduces their utility. A major area that required more research to enhance flux, selectively, and reduce membrane fouling is a crucial barrier in the utilization of membranes for water purifications. Currently, research is focused on the addition of Nano-filters and polymers in the second phase of membrane preparations to enhance the selectivity and pursuance of the membrane.

8 Pros and Cons of Polymeric Membranes

The first major advantage of polymeric membranes over other membranes, such as the use of ceramics is the fact that the membranes are cheaper to use. The materials are not only affordable to use but have low associated costs, especially in terms of energy use. While noting that in some cases polymeric membranes cannot withstand high temperatures and some chemicals, cost-effective polymeric membranes are cost-effective and offered businesses a major cost advantage in large-scale water purification [34].

The other advantage of polymeric membranes pertains to effectiveness. Compared to other traditional mechanisms, polymeric membranes have proven to be reliable over long periods. This is coupled with the fact that the membranes can continuously be improved so that the quality of the filtration becomes even higher. Such improvements have seen the production of membranes that are even more chemically stable and thus removing high chemical reactions at the surface of the membrane. The chances of growth in this area mean that the effectiveness of the membranes even in the future is going to surpass other mechanisms that could be in use today. The other advantage that the membranes have is energy efficiency. One of the biggest challenges that have existed about water filtration has revolved around energy efficiency. This is especially the case of desalination of salty water covers the largest portion of the earth's population. The energy that has been required in the past to make the water suitable for drinking has resulted in major conflicts, especially balancing between non-renewable energy sources that cause pollution and the need for clean water. However, polymeric membranes have provided cheaper energy alternatives, especially for commercial use. The idea that there is room for improvement promises that the energy efficiency may improve even in the future making it possible to provide the world with enough water for drinking especially from salty water.

One of the biggest challenges facing the use of polymeric membranes is the problem of fouling [78] defines fouling as the process through which colloidal or particulate matter deposits itself in the pores of the membrane or on the surface, which adversely affects the effectiveness of the membrane in water filtration. The continuous movement of water that contains microbes, macromolecules, colloids, and particulates over the membrane leads to the accumulation of the materials on the surface of the membrane meaning that the water flux is reduced. In addition to that, the cake layer formed on the top of the membrane also affects the overall rejection performance of the membrane [39]. To deal with the fouling problem, the membrane needs to be constantly cleaned, which increases the cost In addition to that, the membrane must also be continually replaced, which raises the cost. More energy is also required to move the water across the membrane, thus increasing the cost as well.

The weakening of the membranes presents a major risk, especially in the case of water filtration. According to Praneeth et al. [78] sometimes the duration of use for the polymeric membranes may be shorter than expected. In that regard, their use may be extended to a time in which they have already become weak. During such a time, the selectivity of the membranes becomes unacceptably low. This means that some of the materials that need to be filtered out pass through the membranes. Among them could be health contaminants that pose a major risk to the health of the individuals who rely on the water from the system. Water is used for industrial processes; the presence of some materials can result in major losses as a result of poor product quality. This is especially the case when the water that passes still has some odor or dissolved salts. And polymeric membranes cannot resist high temperature because at that temperature membrane plasticizes which results in a loss of flux [44].

9 Applications

Polymeric membranes are engaged in applications such as desalination, removal of water hardening, municipal wastewater treatment, production of potable water, and industrial and household water treatment. It offers a simple technique to be used widely, cost-effective, environmentally friendly, stable, and divergent applicable in a range of temperature, pressure, and pH. Membrane fouling and membrane sensitivity to toxicity are the main extremities and problems of membrane technology. For this reason, Researchers have established several ways to overcome membrane technology. These ways consist of the amalgamation of nanomaterial such as graphene oxide and nanometer-sized metal oxides (zinc oxide), among others [88]. Overall, it can be concluded that membrane technology is a very advantageous technique for wastewater treatment. Many research approaches are focused on having efficient solutions and approaches to prolong its lifetime [42, 56, 116].

10 Discussion

The chapter identifies why water purification through polymeric membranes is critical in today's world. The process of water filtration using the polymeric membrane is also explained. The various types of polymeric membranes are identified and so are the advantages and disadvantages. And why do we need this treatment?

As identified, the world's freshwater sources are currently under pressure to meet the demand for freshwater by the growing global population. According to [27], less than 1% of the world's water sources are freshwater. 97% of the sources are salty and 2% of them are already contaminated by human activities. The competition for the available water is shared between three major areas. 70% of the freshwater is used for irrigation to feed the growing population in the age of major pollution effects. 20% of the water is used for industrial processes that are also critical for human existence [27]. Only 10% of the water is allocated to human consumption. Globally, more than 1.2 billion people do not have access to fresh water while another 2.6 billion have contaminated freshwater [27]. Poor access to clean fresh water, especially for developing countries is devastating. To bridge the gap between supply and demand for freshwater, it is evident that mechanisms need to be put in place that makes both the salty and contaminated water safe for consumption. Since the pressure on water demand will most likely increase in the future, there needs to be low-cost, highly efficient methods of water purification that can be relied on to meet the growing need. Polymeric membranes thus present a major opportunity for water filtration to meet the demand in a low-cost and energy-efficient way.

11 Conclusion

One of the most critical threats facing the world in this century is the supply of clean water with satisfactory quality from water resources. Polymeric membranes are a critical part of water purification today. The membranes offer a chance to bridge the gap between the supply and demand for fresh water at home and in industries. The biggest advantage of the membrane is the fact that they are energy-efficient and also low-cost compared to other mechanisms. That area continues to grow for even more efficiency in the future. Therefore, it concluded that prolonged studies are required for optimizing the characteristics properties, and performance of membranes. It includes such as antifouling, increased durability, impaired energy consumption, improved selective permeability, and enhanced thermal, mechanical, and chemical stability. The membrane which is used in water treatment has higher flux, is less selective and less prone to various types of fouling, and is more resistant to the chemical environment.

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Chapter 2
Sustainable Wastewater Treatment Using Membrane Technology

Sahita Karmakar and Shramana Roy Barman

1 Introduction

Water is one of the most important components of life on earth [61]. In many places of the world, water is commonly developed as an economic and social asset. Only around 2.5% of the world's total water content is pure water, which makes up roughly 71% of the overall water content [19]. Fresh water is required to sustain life and the environment afloat. Fresh water resources include rivers, lakes, ponds, ground water, and streams [56]. Around 1% is accessible for human and industrial needs, with the rest being unusable groundwater sources and glaciers [122]. However, due to population growth and industrialization, these resources are decreasing [47]. Climate change, inter-annual climate variability, and its use in energy generation are all factors that contribute to fresh water scarcity and depletion [89]. Fresh water scarcity has become a major environmental concern. It is necessary to recover water from existing wastewater or establish alternative water sources for human consumption to address water scarcity challenges [123]. Waste water treatment, in which water is recovered from industrial waste water, could be a viable solution [49]. Large volumes of wastewater generated by uncontrolled industrialization have been discharged into the environment in recent years without being properly treated. As a result, the water quality of adjacent water bodies has rapidly deteriorated. Chemical precipitation [24], microbial decomposition [125], and physical adsorption are all common methods for removing pollutants from water [69]. Both the environment (i.e. plants,

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animals, ecology, and climate) and humans are harmed by these pollutants. One of the biggest sources of pollution is industrial waste water [30, 122, 123]. Due to the huge quantities of effluent, composition of effluent, and number of industries, waste water treatment has been viewed as a critical priority for environmental protection. Among the toxins present in industrial waste water include heavy metals, dyes, pesticides, herbicides, medications, and other aromatic compounds [95, 100]. These compounds pose a major threat to the environment when they enter the environment. These contaminants are harmless at low concentrations, but their accumulation over time can have dangerous consequences. Toxic compounds are present in mine, petrochemical, textile, and dye effluents, posing a health risk to humans [78, 97].

Several attempts have been made over the years to incorporate various wastewater treatment technologies into this environment, including conventional filtration, coagulation-flocculation, and biological treatment systems, among others [53]. However, membrane technology is one of the wastewater treatment technologies that has witnessed a significant increase in popularity over the last several years [32]. Despite the fact that membrane technology is not a new concept, the varying nature and complexity of wastewater allows for future developments in terms of efficiency, space requirements, energy, permeate quality, and technological capabilities [118].

2 Causes of Water Pollution

Environmental Pollution poses a significant threat to global biodiversity and the human race. The quality of soil, air, and water are impacted by the discharge of industrial effluents into the environment. Domestic, municipal, industrial, and agricultural runoff, sewage from septic tanks, and rainwater are the most common wastes dumped into water channels, lakes, rivers, and streams, respectively [2]. The direct discharge of hazardous chemicals into water from the textile, petrochemical, pharmaceutical industries, refineries, and mining sectors causes water pollution and has major consequences for humans, plants, animals, and aquatic species. Large numbers of pathogenic bacteria and xenobiotic chemicals are disposed of directly in waste water, and even minor physiochemical properties of polluted water pose major health risks to aquatic organisms and people [8].

2.1 Domestic Wastewater

Generally, domestic wastewater can be divided into two basic categories. These are brown wastewater (kitchen, bath, laundry) and the black wastewater (urine, faeces and toilet paper) [7]. It contains low amount of solid usually being 99% of water. It contains millions of bacteria per ml which may cause cholera, dysentery and typhoid fever. It has number of synthetic detergents, resistant to biodegradation.

2.2 *Municipal Wastewater*

Municipal wastewater, composed mainly of urban wastewater intended to be removed from communities, is also regarded as a renewable resource from which water, materials, and energy can be recovered [80].

2.3 *Industrial Wastewater*

Industrial wastewater encompasses any sewage from any producing, manufacturing, processing, institutional, commercial, agricultural, or other operations when the sewage discharged includes considerable quantities of wastes of non-human origin, excluding domestic sewage and uncontaminated water [52]. Industrial sewage also includes polluted water from cooling or condensing systems and air-conditioning systems from any of the preceding operations, without limiting any of the foregoing [20].

2.4 *Agricultural Runoff*

Soil washed off fields is the most common source of agricultural water contamination [3]. Rainwater picks up soil particles (sediment) and deposits them in nearby lakes and streams. A buildup of silt in the water can veil it, lowering the amount of sunlight reaching aquatic plants. Pesticides and fertilizers used in agriculture, as well as organic livestock wastes, antibiotics, silage effluents, and processing wastes from plantation crops, can contaminate both groundwater and surface water [59, 113].

2.5 *Sewage from Septic Tank*

A septic tank is an underground container composed of concrete, fiberglass, or plastic into which sewage (domestic wastewater) flows for primary treatment, which includes settling and anaerobic solids and organics reduction [28].

2.6 *Rainwater*

Rainwater carries bacteria, parasites, viruses, and toxins that can make people sick, and it's been connected to disease epidemics. Especially when rain follows several days of dry weather, dirt and germs might be washed into the roof's collected rainwater [119].

3 Common Steps Involved in Wastewater Treatment

Before the water is released into the environment, wastewater treatment is a procedure in which impurities or pollutants are removed from the aqueous phase using a variety of physical and chemical techniques. Residential and nonresidential wastewater can be treated in a variety of ways; most wastewater is first sent to a municipal sewage treatment plant [43]. These treatment plants can remove a large amount of the contaminant if they are correctly constructed and operated [37].

Wastewater from homes, businesses, and storm runoff must transit through multiple steps before becoming potable, in order to provide all of the water required [1]. We will acquire a greater grasp of the effort that goes into generating safe drinking water for everyone if we understand the three stages of wastewater treatment systems. To generate treated wastewater, a variety of techniques are used, which can be divided into three categories: primary, secondary, and tertiary [88].

3.1 Pre-treatment

Although there are three basic processes, there is one crucial step that must take place before any of them can begin. This is known as the pre-treatment stage, and it entails removing contaminants from the wastewater that may otherwise harm or block the pipes. Sanitary items, nappies, plastic, leaves, and other big objects are often removed during this operation [35].

3.2 Primary Treatment

The first of the three processes is to separate the organic waste and sludge from the rest of the water [86]. Allowing wastewater to pass through massive settling tanks, where particles sink to the bottom and grease and oils rise to the top, accomplishes this. Heavier substances sink to the bottom, whereas lighter solids rise to the top due to gravity. To remove even more sediments, chemicals might be used as coagulants [91]. Oils and grease are skimmed off the top of the surface on a regular basis, and sludge is scraped into the centre of the floor with massive scrapers. The water is then pumped away while the rest is treated in a secondary treatment facility [61].

3.3 Secondary Treatment

The removal of soluble organic matter solids that escaped primary treatment is part of secondary treatment. It can also handle smaller suspended solids [91].

Secondary treatment methods include:

- Bioreactors
- Filter beds
- Aerated ponds
- Activated sludge
- Rotating biological contactors

The best way to remove organic impurities is to use a membrane bioreactor, which uses a biological process in which microorganisms devour the organic matter for energy. Solids are formed when bacteria replicate. After that, the solids are filtered by the membrane, which produces effluent [14, 92].

The key benefit of this method is that it does not require the use of a secondary solids clarifier or filter system. The biological process in the reactor is integrated with the physical separation of solids in one technique [117].

Filter beds, aerated ponds, biofilters, activated sludge, and rotating biological contactors are some of the other secondary treatment options. Membrane bioreactors, on the other hand, are the most efficient and modern technology [124].

Secondary-treated water can be discharged into the environment without causing harm to aquatic life or ecosystems.

3.4 Tertiary Treatment

Water is disinfected to the highest standards through tertiary treatment, also known as polishing. This step is required to generate water that has specific requirements, such as technical waters, as well as to treat wastewater for public water systems [46].

Tertiary treatment methods include:

- UV disinfection
- Chemical disinfection

UV disinfection does not necessitate the use of chemicals and can be used instead. This elimination has the need for an additional additive filtering stage. Although ultraviolet light has no effect on the pH, look, taste, or odor of water, it can destroy microbes [58]. Bacterial control is usually achieved using UV light wastewater treatment, which prevents organisms from replicating. It's also capable of removing chlorine, chloramines, ozone, and bromine, making it excellent for generating ultrapure technical waters [95].

The addition of a chemical to the water is required for chemical disinfection. Chlorine is the most frequent. Chlorination destroys bacteria and viruses, but it has the drawback of necessitating a stage of dichlorination before being released into the environment. Iodine is another chemical that is used to disinfect water. When it comes to killing viruses and bacteria, this is just as powerful as chlorine [93] (Fig. 1).

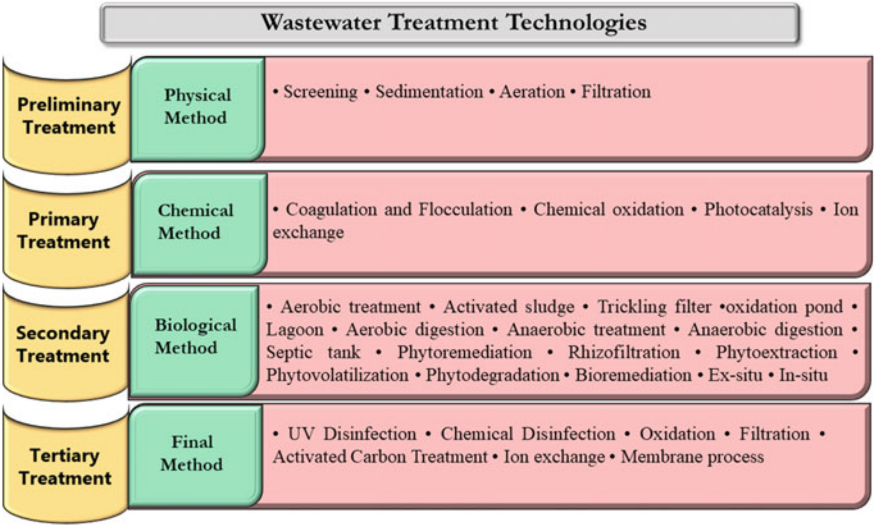

Fig. 1 Traditional wastewater treatment steps

4 Techniques Available for Wastewater Treatment

Various wastewater treatment methods have been used to remove toxic contaminants from the water.

4.1 Physical Methods

Physical events, rather than biological or chemical changes, are used in wastewater treatment systems to finish the removal process. Physical methods include screening, sedimentation, and filtration. To remove oil and grease particles, sand filters are sometimes employed in the oil water separation process [104].

4.1.1 Screening

Screening is the initial step in a physical wastewater treatment system. This technique comprises eliminating large non-biodegradable and floating particles from a wastewater treatment plant, such as rags, papers, plastics, tins, containers, and wood [103]. If these pollutants are removed efficiently, the downstream plant and equipment will be safeguarded from potential damage and pipe jams. The two most frequent methods of wastewater screening are coarse and fine screening.

4.1.2 Sedimentation

Gravity settling isolates particles from a fluid in this procedure. Due to the decrease in water velocity throughout the water treatment process, the particle in suspension remains stable in quiescent conditions, after which the particles settle by gravity force [43, 101]. In the sedimentation process, particle size is extremely important. The residual time for particle settling can be described as settling velocity. Sedimentation is used to reduce the concentration of solids before coagulation to reduce the amount of coagulants used in the coagulation process. In the treatment of dirty water, three main forms of sedimentation can be used.

Type 1—Particles settle at a constant velocity and sticking or flocculation does not occur.

Type 2—Due to change of particle size constantly it affects settling velocity and the particles Flocculate.

Type 3—High concentration of particles settle down. Two distinct zones such as sludge zone and clear zone were formed.

Some chemicals become adsorbed on the suspended material during organic chemical sedimentation. Pollutants with a higher density than water deviate from the fluid streamline flow and settle at the bottom. Solid particles undergo physical and hydrodynamic processes as a result of shear forces in the water stream, which affect the aggregation process and solid removal efficiency [87]. Gravity sedimentation, flocculation, and thickening all affect sedimentation efficiency.

4.1.3 Filtration

Filtration is the process of removing contaminants according to their size. Water can be reused for a variety of applications after pollutants are removed from wastewater. Depending on the impurities in the water, different types of filters are utilized in the method. Particle filtration and membrane filtration are the two main forms of wastewater filtration [5]. Particle filtering is the primary process in the wastewater treatment technique. It's made to get rid of solids that are bigger than one micron in size. The particle shape, size, texture, density, and quantity all influence the type of filter employed in the filtration process. The two primary types of filters used in the filtration of polluted water are bag and cartridge filters [81]. Solid wastes are confined inside bags in bag filters, and the filtration media includes activated carbon, nylon, and other materials [59]. The wastewater is poured into the bags, which trap the solid particles while allowing the liquid to flow. Bag filters are best for small-scale wastewater treatment since they produce less solid waste than cartridge filters. In comparison to other filter systems, bag filters collect less total waste. Cartridge filters catch solid particles outside of the filter media. Polluted water enters the filter vessel at the top, flows through the filter medium, which traps solids, and then exits through the lower section. There are three types of cartridge filters: disposable, back washable, and cleanable. The constraints of using cartridge filters are difficulties in air reversal and filter material selection [35]. Filtration can be used to remove suspended particles, particulate matter, microorganisms like bacteria and viruses, as well as other chemical pollutants.

A membrane process is a method of filtering or removing particles from water using a membrane barrier. At the cellular level, each action necessitates a different layer that acts as a filter or separates water from contaminants [53]. Depending on the pore size and cell size, different materials are employed to distinguish the membrane

Microfilteration (MF),
Ultrafilteration (UF),
Nanofilteration (NF),
Advanced/ Forward Osmosis (FO) and
Reverse osmosis (RO).

4.2 Chemical Methods

Chemical treatments are used in addition to physical or biological approaches to reduce the discharge of pollutants and wastewater into water bodies [99]. Different chemical procedures for the conversion into end products or the removal of pollutants are used for the safe disposal of contaminants. Some of the chemical methods are

- Coagulation and Flocculation
- Chemical oxidation
- Photocatalysis
- Ion exchange.

4.2.1 Coagulation and Flocculation

In industrial wastewater treatment, coagulation and flocculation are essential for solid–liquid separation. The addition of specific compounds known as coagulants to the coagulation process destabilizes colloidal suspensions by neutralizing their charges, resulting in the aggregation of smaller particles [68].

In some cases, flocculants are used to speed up particle aggregation and improve the efficiency of settlement. Various coagulants/ flocculants have different properties due to structural differences such as functional groups, charge, ionic strength, and molecular weight [64].

Coagulants neutralize the negative electrical charge on particles, which destabilizes the forces keeping colloids apart [29]. Coagulants for water treatment are made up of positively charged molecules that neutralize the charge in the water when combined. In order to remove suspended solids from water, inorganic coagulants, organic coagulants, or a combination of both are commonly utilized [112].

Flocculants gather the destabilized particles causing them to clump together and fall out of solution.

4.2.2 Chemical Oxidation

Chemical oxidation diminishes the wastewater's biological oxygen demand and may reduce the toxicity of some contaminants. Some contaminants are converted to carbon dioxide, water, and biosolids during secondary treatment. For disinfection, chemical oxidation is commonly utilized [11, 15].

4.2.3 Photocatalysis

The photocatalysis technique is an advanced oxidation method for removing persistent organic pollutants and bacteria from water. Solid, semiconductive catalysts generate active oxygen forms on their surfaces during photocatalysis when exposed to light of the appropriate wavelength [16, 17]. The oxidation and reduction of substances adsorbed on the catalyst surface are carried out by these oxygen forms. The main objective of photocatalysis using TiO_2 as a semiconductive catalyst is to carry out a sequence of redox reactions on the catalyst surface. It is only associated with the characteristics of electrons in the outer molecular orbital. When a photon energy ($h\nu$) larger than or equal to the valence to the band gap energy (TR) of TiO_2 is exposed onto the catalytic surface [23]. Semiconductive photocatalysis using UV or sun radiation has proven to be a viable approach for both mineralization and disinfection of organic molecules. The process's integration with other treatment procedures creates a viable alternative to conventional water and wastewater treatment technologies.

4.2.4 Ion Exchange

The ion exchange technique is used to replace ions or ions in wastewater treatment [57]. Contaminants and changed structures that have the same type of electrical charging can be either harmful or beneficial. Water that is too hard to clean with is difficult to use and frequently leaves a greyish residue. Water hardness is caused by ions such as calcium and magnesium. Positively charged sodium ions are added to the water in the form of dissolved sodium chloride salt to soften it [60]. The sodium ions take the place of hard calcium and magnesium ions, and the free sodium ions are simply discharged into the water. However, after softening a considerable amount of water, the softening solution may get clogged with calcium and magnesium ions, necessitating a sodium ion recharge [9].

4.3 Biological Methods

Biological operations are crucial in the wastewater treatment process. These biochemical activities can be classified based on three factors: the biological environment, the type of the biological environment, nature of biological transformation and reactor configuration [94]. This is the process by which dissolved and suspended organic chemical elements are eliminated through biodegradation, with the addition of microorganisms in an optimal proportion to mimic the natural self-purification process. Microorganisms can breakdown organic substances in wastewater using two different biological processes called biological oxidation and biosynthesis [40].

Although biological wastewater treatment appears to be a simple and easy process on the surface, it is a complex process involving biochemistry and biology. Natural mechanisms are employed to aid in the dissolution of organic elements. In order to break down the organic wastes, biological treatments uses common cellular processes that bank on small organisms, bacteria, and nematodes [85].

Biological methods include (i) aerobic treatment, (ii) anaerobic treatment, (iii) phytoremediation, (iv) bioremediation.

4.3.1 Aerobic Treatment

Aerobic wastewater treatment processes include simple septic or aerobic tanks, and oxidation ditches; surface and spray aeration; activated sludge; oxidation ditches, trickling filters; pond and lagoon-based treatments; and aerobic digestion. Biological treatment procedures include constructed wetlands and other types of filtration. While the wastewater is being treated, diffuse aeration systems can be used to enhance oxygen transport and reduce smells [75]. As beneficial bacteria and other organisms breakdown organic components in wastewater, aeration produces oxygen.

Aerobic microorganisms require oxygen to support their metabolic activity. Special aeration equipment provides oxygen to the effluent in the form of air during effluent treatment [108]. Bacteria transform organic compounds into carbon dioxide and biomass using dissolved oxygen. Furthermore, aerobic microorganisms convert ammonified organic nitrogen compounds to nitrate by oxidising ammonium and nitrite (nitrification). A sufficient amount of nutrients in relation to the amount of biomass, a specific temperature and pH regime, and the absence of toxic substances are all important factors in the success of an aerobic process [22].

4.3.2 Anaerobic Treatment

It is a slow process that can take up to three months to occur due to excessive decay [15, 45]. There could be an unpleasant odor that needs to be addressed in order to eliminate water waste. Bacteria are used in anaerobic treatment to assist organic material to decompose in an oxygen-free environment [27]. Anaerobic procedures are employed in lagoons and septic tanks, but the most well-known anaerobic treatment is anaerobic digestion, which is used to treat food and beverage effluent, as well as municipal wastewater, chemical effluent, and agricultural waste [31].

One of the most robust areas of resource recovery is energy recovery, which is driven by anaerobic digestion. Anaerobic digestion is utilised to produce biogas, which is mostly constituted of methane, in this type of energy recovery, also known as waste-to-energy. Operators can use it to create energy, which will help them reach their goal of being energy net zero, or even turn waste streams into revenue streams [126].

4.3.3 Phytoremediation

Phytoremediation is a cheaper and feasible sustainable method for removal of pollutants. At the same time, it is environmentally beneficial, and it has no negative impact on people who live and work in the surrounding area because it cleans the environment with plants [72]. Aquatic plants are important in biological wastewater treatment systems because they may be employed for phytoremediation using processes like rhizofiltration, phytoextraction, phytovolatilization, phytodegradation, and phytotransformation. The period of exposure, the concentration of pollutants, environmental factors (pH, temperature), and plant features (species, root system etc.) all play a role in pollutant eradication. However, it is worth noting, that other aquatic plant species have been successfully used in the wastewater phytoremediation process [25].

Various plant species have endogenous qualities that can help to clean up water contamination. The ability of plants to accumulate various metals (essential or non-essential) is the basic principle underpinning phytoextraction [54]. Phytoremediation of wastewater is a new low-cost method for removing harmful metal ions from industrial wastewater that is still in its early stages of development. Heavy metals such as cadmium and lead are not easily absorbed by microorganisms [1, 109]. These poisons would be the ideal treatment option if they were bioaccumulated by normal plant metabolism. Aquatic plants have an excellent deal of ability to reduce harmful metals, BOD, and total solids in wastewater. It is also a cost-effective, aesthetically beautiful technology that conserves the ecosystem in situ [26, 130].

4.3.4 Bioremediation

Bioremediation is a method of removing nutrients from wastewater by using naturally occurring microorganisms and other features of the natural environment [115]. Single-celled organisms grow until they reach a specific size, at which point they divide into two. This type of endeavour opens the door to environmentally and economically sound treatment options. Due to the extensive time and planning required for efficient treatment, wastewater treatment and bioremediation is a cost-effective method. Bioremediation is a technique for restoration of ecological damage by enhancing the ability of some living organisms (for example, plants, fungi, and bacteria, for instance) to remove, breakdown, or change hazardous organic molecules into harmless or less dangerous metabolic products [10]. Hydrogeologic conditions, the pollutant, microbial ecology, and other geographical and temporal considerations all have a role in a successful, cost-effective microbial bioremediation programme. The pollutants are used as nutrition or energy sources by the introduced microorganisms in any bioremediation procedure. Some common microorganisms used in the process of remediation are *Acromobacter, Alcaligenes, Arthrobacter, Bacillus, Cinetobacter, Corneybacterium, Flavobacterium, Micrococcus, Mycobacterium, Nocardia, Pseudomonas, Vibrio, Rhodococcus* and *Sphingomonas* species [33].

The two main types of bioremediation are in situ bioremediation and ex situ bioremediation. The term in situ bioremediation refers to cleaning up a contaminated site right where it happened. The removal of contaminated material from its original location to be treated elsewhere is known as ex situ. There are various technologies used, Bioaugmentation, Biostimulation, Bioreactors, Fungal Remediation, Phytoremediation, Electrobiorremediation, Leaching, Chelation, Methylation and Precipitation [41] (Table 1).

5 Polymeric Membrane for Pollution Remediation

Membrane (MBR) technology has become a crucial component in water reclamation schemes due to the possibility of providing water of high quality (e.g. as particle-free permeate from membrane bioreactors, removal of microbiological contaminants) [65]. Polymeric membranes are commonly used for water treatment, such as agro-food, textile, and petroleum industry waste streams, or for the removal of pollutants from drinking water, allowing the concentrate to be treated or discharged and, as a result, reducing contaminants discharged directly or indirectly into wastewater [96]. Obtaining a remediated effluent is also a cost-effective method. It is cost-effective and environmentally friendly for usage in remote areas [76]. A membrane is a selectively restrictive barrier that separates two phases by preventing component mobility [129] (Fig. 2).

Membranes can be classified as isotropic or anisotropic based on their properties. Isotropic membranes are composed of compatible materials and same physical structure. They can be microporous, which implies they have large permeation fluxes, or nonporous (dense), which means their applicability is severely limited due to low permeation fluxes [79]. On the other hand, anisotropic membranes are made up of multiple layers with varied structures and compositions that are non-uniform over the membrane region. A thin selective layer is supported by a thicker, highly permeable layer in these membranes.

Table 1 Different wastewater control techniques and their advantages and disadvantages

Sl. No.	Wastewater control techniques	Advantages	Disadvantages
1	*Physical methods*		
(i)	Screening	1. It removes objects like rags, paper, plastics, and metals 2. It prevents damage and clogging of downstream equipment, piping, and appurtenances [104]	1. Damage to other process equipment 2. Reduction in efficiency of the whole system [103]
(ii)	Sedimentation	1. No energy requirement 2. Excellent reproducibility [101]	1. Selective process 2. Lacks precision [87]
(iii)	Filtration	Autoclaving can be done in some cases [5]	Clogging of filters may occur [35]
2	*Chemical methods*		
(i)	Coagulation-flocculation	1. Used for fine particle removal 2. Removes metals, colour and turbidity [68]	1. Multiple process step 2. Toxic if improperly used 3. High sludge production [112]
(ii)	Chemical oxidation	1. Do not introduce new hazardous substances into water 2. All organic materials and can remove some heavy metals 3. No sludge production as with chemical or biological processes [11]	1. Relatively high capital and operating/maintenance costs 2. Complex chemistry tailored to specific contaminants [15]
(iii)	Photocatalysis	1. Environmental friendly 2. Complete degradation of pollutants 3. No secondary pollution [16]	1. High cost 2. Complex catalysis [23]
(iv)	Ion exchange	1. Possible to regenerate resin 2. Zero hardness can be achieved 3. Rapid separation process 4. Small area requirement [57]	1. Pre-treatment is required in most of the effluents 2. Ionic competition 3. Fouling of matrix [60]

(continued)

Table 1 (continued)

Sl. No.	Wastewater control techniques	Advantages	Disadvantages
3	*Biological methods*		
(i)	Aerobic treatment	1. Simplicity of activity 2. Limits creation of odor 3. Decreases pathogens and fats 4. A more prominent number of microbes types can be utilized for Processing [75]	1. Cost expensive 2. Maintenance problem [22]
(ii)	Anaerobic treatment	1. Produces renewable energy 2. Less environmental pollution [15]	1. High capital cost 2. Odor nuisance [27]
(iii)	Phytoremediation	1. Low capital requirement 2. Low energy requirement 3. Environmental friendliness [1]	1. Limited to shallow contaminant 2. Phyto-toxicity of contaminants 3. Slower than conventional methods [26]
(iv)	Bioremediation	1. Natural process 2. Onsite treatment 3. Cost-effective process 4. Complete destruction [41]	1. Slow process 2. Heavy metals are not expelled 3. Bioremediation site must have soil with high penetrability 4. Considerable gaps exist in the comprehension of microbial Environment [41]

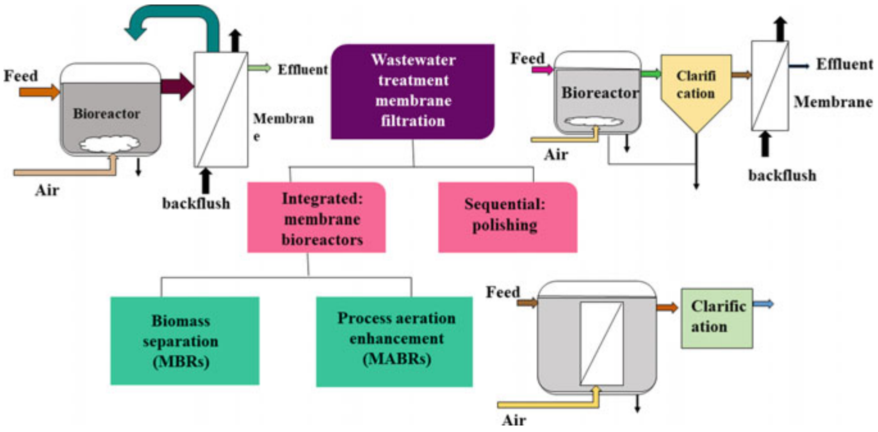

Fig. 2 Membrane filtration in wastewater treatment

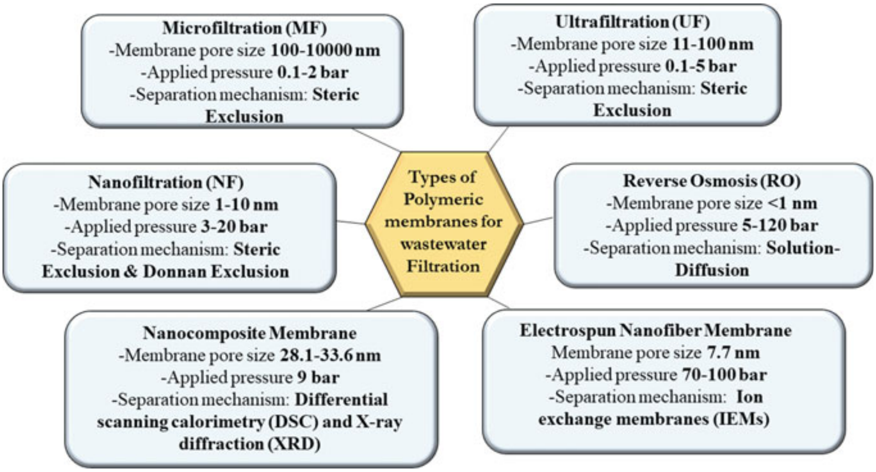

Fig. 3 Types of polymeric membranes for wastewater treatment

Membranes are classed as organic or inorganic based on their material composition. Synthetic organic polymers are used to create organic membranes. Synthetic organic polymers are almost solely used to make membranes for pressure-driven separation processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) [74]. Polyethylene (PE), polytetrafluorethylene (PTFE), polypropylene, and cellulose acetate are examples of these materials. Ceramics, metals, zeolites, and silica are used to create inorganic membranes. Aside from that, adsorption is the most widely used method for removing pollutants from water due to its low cost, wide range of adsorbents, and convenience of application. Adsorbents such as magnetic nanoparticles, activated carbon, nanotubes, and polymer nanocomposites have been used to remove a variety of contaminants, including heavy metals, which are exceedingly dangerous even at low concentrations [38]. The adsorption mechanism in the membrane separation process is based on the hydrophobic interactions between the membrane and the solute (analyte). Increased rejection occurs as the membrane's pore size diminishes as a result of these interactions. How well materials travel through the membrane is determined by the size of the pore and the molecules. As a result, a variety of membrane processes with various separation methods have been created. Organic membranes are among them [84] (Fig. 3).

5.1 Membrane Processes

5.1.1 Microfiltration

Microfiltration (MF) is a physical filtration technique that separates microorganisms and suspended particles from process liquids by passing a polluted fluid through a particular pore-sized membrane [102]. MF is a pressure-driven separation method that can be used to concentrate, purify, or separate macromolecules, colloids, and suspended particles from a solution [4]. Microfiltration is accomplished using membranes with pore sizes ranging from 0.1 to 10 μm. All microorganisms are removed via microfiltration membranes [18]. Even though viruses are smaller than the holes of a microfiltration membrane, the method only collects a percentage of the viral contamination. This is due to the fact that viruses can bind to bacterial biofilms. Microfiltration can be utilised in a variety of water treatment processes when particles larger than 0.1 mm in diameter need to be removed from a liquid [21].

5.1.2 Ultrafiltration

The method of water purification known as ultrafiltration (UF) involves pushing water through a semi-permeable membrane [98] Water and low-molecular-weight solutes pass through to the permeate side of the membrane, while suspended particles and high-molecular-weight solutes remain on the retentate side [13].

UF can eliminate most organic compounds and viruses, as well as a range of salts. It has gained popularity since it produces consistent water quality regardless of the source water, has a small physical footprint, removes 90–100 percent of pathogens, and requires no chemicals except for cleaning membranes [66].

The structure of Ultrafiltration membrane can be symmetric or asymmetric. A symmetric membrane's thickness (porous or nonporous) might range from 10 to 200 μm. The entire membrane thickness determines the resistance to mass transfer. When the thickness of the membrane is reduced, the rate of penetration increases [128]. Ultrafiltration membranes have an asymmetric structure that consists of a dense top-layer or skin with a thickness of 0.1–0.5 μm, which is supported by a porous sub-layer with a thickness of 50 to 150 μm. Ultrafiltration membranes have pore sizes ranging from 0.1 to 0.01 μm, although "molecular weight cut-off" (MWCO) is now one of the finest terms to characterize them [50]. These membranes combine a dense membrane's high selectivity with a thin membrane's high penetration rate. Ultrafiltration membranes must be cleaned on a regular basis to avoid fouling from solids, scaling, and microbiological agents including bacteria and algae. Contaminants that have been separated and condensed in the UF retentate must be discarded [67] (Fig. 4).

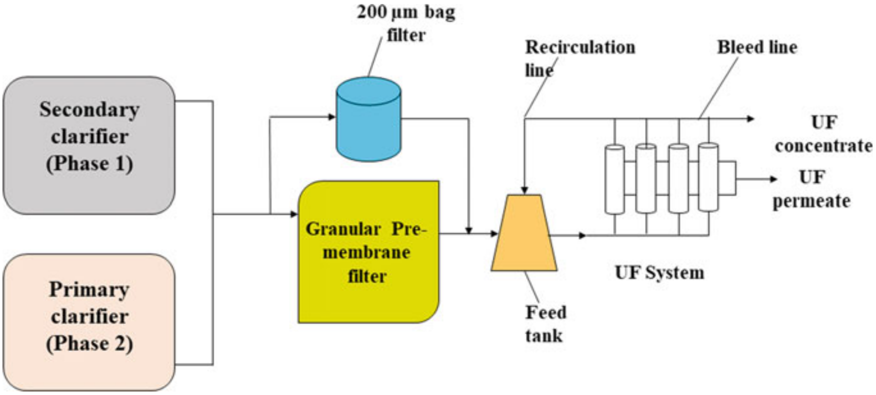

Fig. 4 Wastewater treatment by ultrafiltration technique

Application

- Wastewater and industrial process water treatment and recycling
- Removal of particulates and macromolecules
- In existing water treatment plants, augmenting or replacing secondary and tertiary filtering stages.
- Capable of exceeding regulatory standards of water quality, achieving 90–100% pathogen removal.

5.1.3 Nanofiltration

In terms of its ability to reject molecular or ionic species, nanofiltration is a pressure-driven membrane technique that falls in between ultrafiltration and reverse osmosis [121]. The nanofiltration (NF) membrane technique is a popular method for removing organic matter, colour, odor, taste, residual disinfectant levels, and trace herbicides from vast bodies of water. The properties of NF, which include a 1–5 nm pore size and a 7–30 operating pressure, are utilized to separate low molecular weight solutes such as lactose, glucose, and salt, as well as hardness, dye, and heavy metals [110]. Colloids, organic composites with reduced molecular mass, and divalent salts are all filtered out by an NF membrane. In comparison to RO, higher flux can be achieved with NF, which operates at low pressures of 8–30 bar, resulting in lower process operating costs. The two operating processes that control transport through the NF membrane are the sieving mechanism and the Donnan effect. NF can replace reverse osmosis (RO) in a variety of applications due to its low operating pressure and increased permeate flux (Fig. 5).

Application: In industry, pharmaceuticals, water purification, wastewater treatment, biotechnology, and brackish water desalination, nanofiltration is becoming more widespread. In industry, the NF process is used to separate colours in the textile sector, recover metal, and treat effluent from olive mills [116]. In comparison

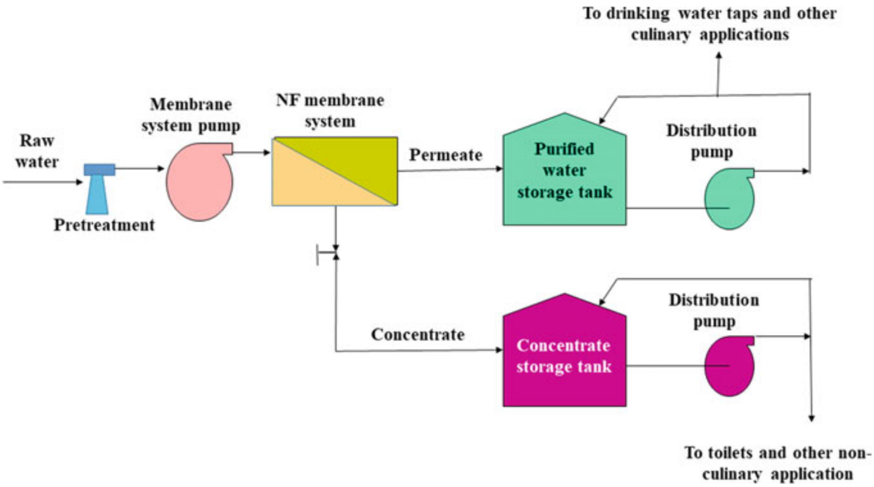

Fig. 5 Wastewater treatment by nanofiltration technique

to a conventional physicochemical approach, NF and RO integration effectively eliminated soluble monovalent and divalent ions from OME (olive mill effluent). NF was also employed in the treatment of coke wastewater, pulp and paper, oily wastewater treatment in the oil and petroleum industries, and the elimination of acid sulphate from mine water [83]. There were also many applications on domestic sector, e.g. treatment of municipal wastewater, Leachate, car wash wastewater, and restaurant effluent. When compared to aerobic and anaerobic procedures, chemical coagulation and electrocoagulation, and electroflotation, NF-90 effectively reduces BOD 5 and increases conductivity by over 80%.

5.1.4 Reverse Osmosis

For wastewater reclamation plants, reverse osmosis (RO) membranes provide a cost-effective water purifying alternative. Total dissolved solids, heavy metals, organic pollutants, viruses, bacteria, and other dissolved contaminants have all been demonstrated to be greatly reduced by RO membranes [114]. It's a pressure-driven method for removing dissolved solids and tiny particles, only water molecules can pass through by RO [70]. The pressure delivered to the RO must be high enough for the water to overcome the osmotic pressure. The pore structure of RO membranes is significantly tighter than UF i.e., smaller than 0.1 nm and they convert hard water to soft water, and they are practically capable of eliminating all particles, bacteria and organics, it requires less maintenance [111].

Application:

- Treatment and recycle of wastewater generated from metal finishing and plating operations.
- Printed circuit board and semiconductor manufacturing (treatment and recycle of rinse waters used in electroplating processes).
- Automotive manufacturing (treatment and recycle of water used for cleaning and painting).
- Food and beverage (concentration of wastewater for reuse and reduction of BOD prior to discharge).
- Groundwater and landfill leachate (removal of salts and heavy metals prior to discharge).

5.1.5 Nanocomposite Membranes

Nanocomposite membranes for water treatment are a promising modified version of traditional polymeric membranes with three primary characteristics: enhanced permeation, improved rejection, and reduced fouling [62]. Nanoparticle materials (the filler) are introduced into a macroscopic sample material (the matrix) to create nanocomposite membranes. Before membrane casting, nanoparticles can be deposited on the membrane surface or disseminated in the polymer solution [71]. Polymer-nanocomposite membranes, also known as mixed matrix membranes (MMMs), are created by incorporating secondary components known as fillers into the main polymeric matrix. Polymer-based nanocomposite membranes have gotten a lot of interest recently among diverse nanocomposites [105]. Phase inversion (PI), interfacial polymerization (IP), physical coating, electrospinning and cross-linking, self-assembly, layer-by-layer assembly, and chemical grafting are some of the processes used to disperse nanoparticles (NPs), nanotubes, nanofibers, or nanosheets into the polymer matrix. The incorporation of engineered nanoparticles including metal oxides (Al_2O_3, TiO_2, SiO_2, ZnO, MgO, Fe_2O_3, and zeolite), metals (Cu, Ag), carbon-based materials (graphene, carbon nanotube (CNT), carbon nanofibers (CNFs)), and nanofiber polymers (polyurethane, polylactic acid, polyethylene oxide) in polymer matrices imparts tunable physicochemical properties and unique functionalities to the membranes [63]. Nanocomposite membranes have developed as viable water purification technology, giving improved hydrophilicity, thermal and mechanical stability, permeability, targeted degradation, solute rejection, and magnetic, antibacterial, and anti-fouling capabilities over traditional polymeric membranes. Polymeric membranes are still a popular choice because of their low relative cost, wide range of pore sizes, design flexibility, and scalability [44].

Different types of Nanocomposites and their applications

- **Metal Nanocomposite**: Polymer-supported nanosilver exhibits antibacterial capabilities of polyurethane, and cellulose acetate impregnated nanosilver-fiber composites have good Gram-positive and negative bacteria inhibitory activity.

Polyurethane foam dispersion nanoparticles have proven to be efficient antibacterial filters [34]. Nanosilver was also employed to create cost-effective microfilters for managing drinking water, which is very important in unreachable regions.

- **Metal oxide Nanocomposite**: Metal oxide nanocomposite (MONC) are frequently employed as adsorbents, photocatalysts, and devices to combat pollution issues. For the elimination of various organic and inorganic contaminants, MONC is combined with graphene, silica, other oxides, carbon nanotube (CNT), and polymers [127].
- **Carbon Nanocomposite**: The cationic dyes were removed from aqueous solutions using a magnetic multi-wall carbon nanotube (MMWCNT) nanocomposite as an adsorbent. The MMWCNT nanocomposite was made up of multi-wall CNTs that were still alive and iron oxide nanoparticles (IONPs) [6]. The use of MMWCNT nanocomposite adsorbent to remove Methylene Blue (MB), neutral red, and brilliant cresyl blue was purposeful.
- **Polymer Nanocomposite**: PNCs (polymer nanocomposites) are a superior type of tool in which nanoparticles are dispersed in a polymer matrix, resulting in novel materials with distinct physical and chemical properties. Polymers are unique nanomaterial supports because they often have tunable porosity topologies, high mechanical qualities, and chemically attached functional groups [48]. PNCs are looking for materials that work well in water and wastewater treatment. Contaminant adsorption by PNC is one of several treatment strategies that is considered an advanced instrument in water treatment technology. PNCs can be made by fusing nanoparticles to polymer structures or by attaching polymers to nanoparticles [82].

5.1.6 Electrospun Nanofiber Membrane

An electrospun nanofibrous membrane (ENM) is a membrane made by electrospinning that possesses appealing properties [42]. Electrospun nanofibrous membranes (ENMs) are a cutting-edge membrane technology that outperforms traditional membranes in terms of flux and rejection rate. Electrospinning is a new and unique fabrication approach that produces nanofibrous nonwovens using a simple nanofiber production technology [39]. Electrospinning has opened up new and exciting possibilities in a variety of fields, including the environment, catalysts, energy, and health. Electrospun nanofibers' unique properties make them a good fit for a variety of additional applications, such as functionalized composite constructions, electrode materials for batteries and energy devices like solar cells, protective apparel, food and agriculture, and tissue engineering [51]. After considering this, it's worth noting that the applications for electrospun nanofibers are virtually unlimited. After that, the use of electrospun nanofibers as a scaffold for TFC (thin-film composite) membranes in pressure- and osmotic-membrane processes is discussed. The use of electrospun nanofibrous membranes in the thermally-driven MD (membrane distillation) process for water treatment, as well as performance improvement schemes [12] (Fig. 6; Tables 2 and 3).

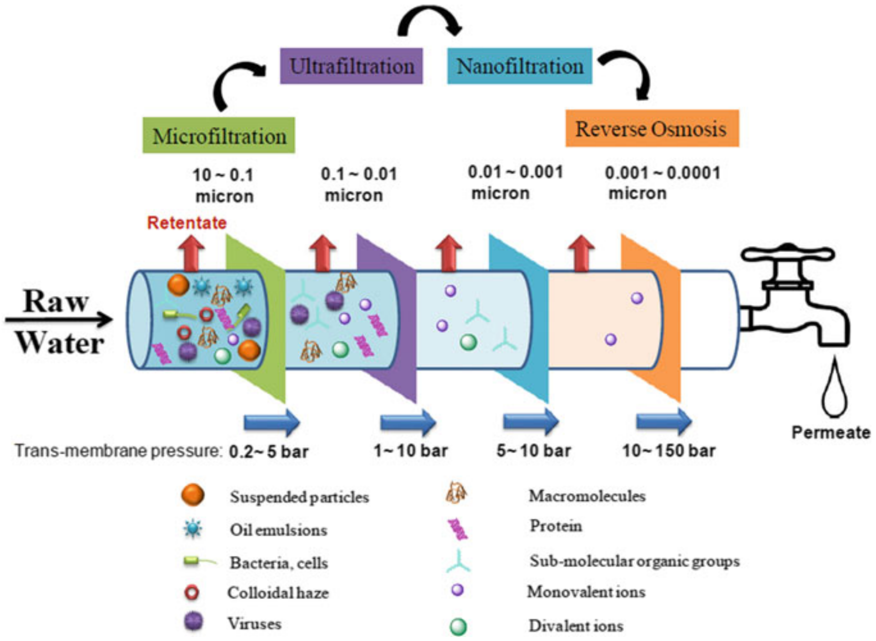

Fig. 6 Schematics of membrane water treatment system (Adapted from [73])

6 Conclusion

With the rapid increase in population, increased industrialization, urbanization, and vast agriculture techniques, the demand for clean and safe water is increasing over the world. Water is currently being decontaminated and purified using a variety of procedures. Manufacturing plants, refineries, and industrial effluent wastewater is typically treated at the on location sites. Biological waste treatment plants separate waste matter by using biological materials and bacteria. On the other hand, physical waste treatment plants treat wastewater using synthetic responses in the same way that physical processes do. Physical wastewater treatment plants are commonly used to treat wastewater from factories, industries, and manufacturing organisations. While biological treatment systems are ideal for treating wastewater from households and business premises. Mechanical methods are used as a preliminary stage of wastewater treatment. The various types of membrane technology will play an increasingly essential role in water and wastewater control in industry. Polymeric membranes are employed on an industrial scale for water desalination and wastewater treatment due to their ease of manufacture and fascinating separation performance. An improvement of the NF and RO performance in the removal of heavy metals could be achieved by incorporating nanomaterials. Water flux and heavy metal rejection can both be improved with nanocomposite membranes. Electrospinning is a versatile

Table 2 Some features of pressure-driven membranes (adapted [36])

Membrane process	Particle size (nm)	*MWCO (kilo Dalton)	Retained diameters (μm)	Pressure required (bar)	Membrane Type	Average permeability (L/m^2 h bar)	Solutes retained
Microfiltration	100–10,000	100–500	10^{-1}–10	1–3	Porous, asymmetric or symmetric	500	Suspended particles (bacteria, fat, oil, colloids, organics, microparticles)
Ultrafiltration	1–100	20–150	10^{-3}–1	2–5	Micro porous, asymmetric	150	Macro and micromolecules (proteins, pigments, oils, sugar, organics, microplastics)
Nanofiltration	1–10	2–20	10^{-3}–10^{-2}	5–15	Tight porous, asymmetric, thin film composite	10–20	Divalent cations and anions, lactose, sucrose
Reverse osmosis	<1	0.2–2	10^{-4}–10^{-3}	15–75	Semi porous, asymmetric, thin film composite	5–10	Monovalent ions and all contaminants

* MWCO = Molecular weight cutoff

Table 3 Advantages and disadvantages of membrane-based technologies

Sl. No.	Membrane based processes	Advantages	Disadvantages
1	Microfiltration (MF)	• It is capable of removing impurities from water without the use of harsh or costly chemicals • Its larger pore size makes it excellent for a 'first pass' filtration [4]	• Its enormous pore size makes it impossible to distinguish tiny materials from water [18]
2	Ultrafiltration (UF)	• It removes all particulates as well as any microbes that may have contaminated the water • There are no chemicals employed in the process, no pollutants are emitted into the environment [13] • It requires less operating pressure and uses less energy than nanofiltration or reverse osmosis	• Soluble materials will not be filtered • The odor of the water still remains the same • Neither humans nor animals should drink the water produced during this method. This is because the method does not separate solubles, which could be damaging to our health [107]
3	Nanofiltration (NF)	• The hard water is cleansed of viruses, organic components, and valence ions. It is an efficient method for softening hard water • Salt content and dissolved matter content (TDS) in brackish water are reduced; heavy metals, nitrates, and sulphates are reduced [55]	• Soluble elements cannot be separated from the water • Higher energy consumption than UF and MF (0.3–1 kWh/m^3) • Some extremely polluted waterways require pre-treatment [90] • Nanofiltration membranes cost slightly more than reverse osmosis membranes [26]

(continued)

Table 3 (continued)

Sl. No.	Membrane based processes	Advantages	Disadvantages
4	Reverse osmosis (RO)	• Pollutants such as lead, pesticides, fluoride, pharmaceuticals, arsenic, and other contaminants can be removed from water using reverse osmosis devices, making the human body sick. Lead poisoning can result in brain damage and anaemia [17] • A semi-permeable membrane is used in the RO water purification process to extract pollutants from water, leaving it clean and pure for drinking. Its high-pressure technique contributes to the purification process as a positive feature	• While a RO water purifier removes dissolved contaminants, it also removes natural minerals like iron, magnesium, calcium, and sodium, which are necessary for human health and can lead to a mineral shortage. Water becomes de-mineralized as natural minerals are eliminated, affecting the taste and making it bland [106] • RO water purifier does not kill waterborne disease-causing bacteria and viruses. There high probability that microorganisms can pass through RO membrane [111]
5	Nanocomposite membranes	• The advantages of this separation method are high removal capacity, operational flexibility, and cost-effectiveness [82] • They're lighter than traditional composites because they can achieve high levels of stiffness and strength with significantly less high-density material [120]	• Due to their intrinsic hydrophobicity, they are prone to fouling • They also have a low chlorine resistance [77]
6	Electrospun nanofiber membrane	• Nanofiber membranes with a large surface area have several advantages over cast film [113] • Fibers with diameters size of nanometer to few microns; relatively inexpensive technique; high aspect ratio; enhanced mechanical properties	• They undergo several difficulties in making a large volume of scaffold [51]

technology that makes producing nanofibers facile. Nanofiber membranes (ENMs) have gotten a lot of interest because of their large specific surface area and excellent pore interconnectivity, and they appear to be very promising for wastewater treatment. In any case, by enhancing the pore size, porosity, and mechanical strength of ENMs, various problems should be considered and overcome. As a result, the application of membrane technology for wastewater management appears to be highly promising and could have a great future, but a serious and focused effort by the scientific community and government agencies is required.

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Chapter 3
Polymeric Nanocomposite Membranes for Treatment of Industrial Effluents

Aisha Zaman, Adrija Ghosh, Sumon Santra, Jishnu Chakraborty, Jonathan Tersur Orasugh, and Dipankar Chattopadhyay

1 Introduction

Since the origin of this earth, all organisms including mankind are dependent on water. However, the progress of lifestyle, advancement in science and technology, and growing industries have led to an unfair distribution of the very limited fresh water sources among various segments of society. Millions of people mostly in developing and underdeveloped countries do not have access to potable water [1]. Moreover, the generation of large volumes of wastewater is unavoidable with the escalating demand for water in the industrial, agricultural, and domestic sectors. To compensate for this water scarcity, the used water must be treated, replenished, and reclaimed thereby fulfilling the water usage necessities of the ever-increasing population. Hence, the cost of freshwater generation has constantly been on the path of an upsurge. Water filtration has become a multi-billion-dollar industry that is

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only growing with the alarming concerns about contaminants in water and decline in safety and cleanliness in easily available existing water resources. Membrane technology, though not a new technique, has emerged with extensive application in water treatment and desalination for domestic as well as industrial water supply and effluent treatment. Various water treatment facilities use membrane separation and membrane filtration including membrane-based hybrid technologies to clean surface water, groundwater, and wastewater in order to produce safe and hygienic water for drinking domestic and industrial use. This chapter gives an overview of the membrane process used for water remediation highlighting the employment of various polymeric membranes for the same along with existing challenges, emerging approaches, and future prospects.

2 Membrane Technology for Water Remediation

Membrane technology is a broad term that encompasses a wide range of scientific and engineering approaches for characteristic separation processes in various fields. The common factor in these processes is the use of a thin membrane for the separation of gas or liquid streams [2]. Membrane separation can be achieved via rejection or transportation of substances, components, chemical or microbial species through a semi-permeable or selectively permeable membrane. Owing to its multi-disciplinary characters, the capability of producing high-quality products and agility in system designing, membrane technology, has wide application in various industries such as food processing, bioprocessing separation, refining, and purification of products of pharmaceutical, biotechnological, beverages, food, metallurgy industries including water treatment [3].

Some of the advantageous features of the membrane separation process which often brands it as more preferred and suitable towards water treatment in comparison to other conventional methods are listed below:

- Clean technology
- Low energy consumption
- Continuous separation at mild operating conditions
- Possibility of adjustable membrane properties
- Leeway of hybrid processing with other techniques
- Easy upscaling

Membrane Separation, therefore, has the potential to give strong competition to the various existing water remediation processes and can easily replace conventional methods, such as chemical treatment processes, distillation, filtration, ion exchange, etc. [4]. However, just like any other process, membrane separation has its demerits such as concentration polarization, low selectivity, flux, membrane lifetime, and membrane fouling. Studies are being conducted to overcome these challenges, more about the challenges and the advanced and emerging approaches to tackle them have been discussed in Sects. 3 and 5 below.

2.1 *Types of Membrane Process in Water Remediation*

As mentioned above membrane process can have different approaches towards the separation of molecules and particles. Based on the different types of driving forces the process of movement of media through a membrane can be categorized as follows:

- Equilibrium based membrane processes
- Non-equilibrium-based membrane processes
- Pressure driven process and
- Non-pressure driven processes

The pressure-driven membrane processes also known as membrane filtration are the most widely accepted and employed membrane processes in the field of water treatment [5]. These processes can concentrate or separate pollutants by means of hydraulic pressure applied with filters with different pore sizes.

2.1.1 Pressure Driven Membrane Filtration

Membrane filtration is a characteristic pressure-driven separation technique that applies a membrane for mechanical and chemical filtering of particles and molecules of various sizes. The membrane filtration process has different levels based on their pore sizes and hence can be classified as microfiltration (MF), ultrafiltration (UF), nano filtration (NF), and reverse osmosis (RO) [2] as depicted in Fig. 1.

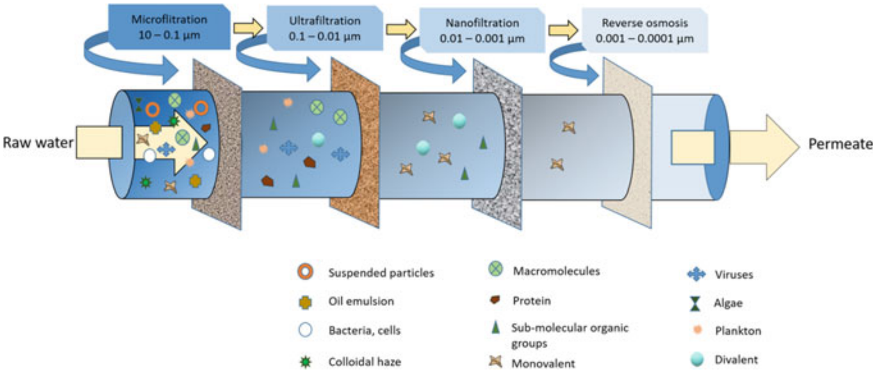

Fig. 1 Types of membrane filtration based on pore size

Microfiltration

Microfiltration is a low-pressure-driven separation process applied to eliminate particles with an average molecular weight of 400 k Dalton. The pore size of a microfiltration membrane ranges from 0.1 to 1.0 μm. It is mostly applied for concentrating and separating macromolecules, suspended particles, and colloids from an aqueous solution [6]. Microfiltration filters membranes are usually made of organic materials, such as various polymers like poly-ethylsulfone and polypropylene. It can also be made of inorganic materials, such as ceramic, glass, or sintered metal membranes [7].

Ultrafiltration

Ultrafiltration (UF) is a pressure-driven technique that applies hydrostatic pressure and concentration gradient to force water through a semi-permeable membrane, thereby leading to the separation of particles ranging from 0.1 to 0.01 μm. UF has gained wide acceptance and popularity owing to its capability to remove upto 100% pathogens including viruses and bacteria, most organic materials, particulates, even various salts, and low molecular weight particles. Therefore, nowadays "molecular weight cut-off" (MWCO) is best used to describe a UF membrane. MWCO is referred to the specific molecular weight at which upto 90% of the molecules are retained by a UF membrane. The UF technology is commonly applied for secondary and tertiary filtration stages in water treatment facilities, different industries such as food and beverage, paper pulp mill, etc. for removing turbidity causing particles and recycling of wastewater.

Nanofiltration

Nanofiltration (NF) is another pressure-driven membrane tool used for removing solutes and ionic molecules with a molecular weight typically ranging from 200 to 1000 g mol^{-1}. The pore size of NF membranes is typically on the scale of 1–10 nm and are employed to remove microbes, turbidity, the fraction of dissolved salts, and hardness. The application of NF membranes has been extended to the separation of molecules from organic solvents [8], and hence has a great potential in the refining and pharmaceutical industries. When it comes to the treatment of water NFs can be easily applied for cleaning surface water, groundwater, wastewater, and pretreatment for desalination as well. It is also used in the production of drinking water [9].

Reverse Osmosis

Reverse Osmosis or RO technology is one of the most powerful tools for water purification. In RO water purification systems, hydraulic pressure is applied to overcome the osmotic pressure thus forcing the solvent from a region of high solute concentration to a region of low solute concentration through a partially permeable membrane and hence the name reverse osmosis. This results in the retention of ions or large molecules on the pressurized side whereas the smaller solvent molecules freely pass through the membrane and are collected downstream. The pore size of the RO membranes can vary depending on the desired production rate for pure water on a daily or even an hourly basis. The commonly used RO membranes are generally composed of semi-permeable polymeric ultra-thin films made of polyamides, polysulfones, cellulose acetate, etc. RO technology is extensively used in drinking water purification systems, large-scale production of potable water, sea water desalination, in industrial sectors for removal of suspended as well as dissolved solids and microorganisms [10].

2.1.2 Non-pressure Driven-Forward Osmosis

When Forward Osmosis or FO is defined as a non-pressure driven process, it implies that FO does not require hydraulic pressure gradient, instead, it occurs with the help of natural osmotic pressure along a concentration gradient. When the osmotic pressure gradient between the feed and draw solutions is positive and has the same hydrostatic pressure, the water is forced through the membrane from the feed to draw the solution while the contaminants are retained in the feed stream [11]. FO is widely applied for product concentration in food and beverages industries, for wastewater concentration facilitating zero-liquid-discharge-waste disposal. In FO-based hybrid techniques for water treatment, FO is often applied as a pre-treatment footstep, while RO and NF are used for water recovery and regeneration [12]. FO is also emerging as a potential applicant for direct desalination of seawater [13].

3 Polymers: Ideal Material for Membrane Fabrication

The functional element of any membrane filtration system is the membrane. Membranes can be prepared from organic or inorganic materials. Ceramics, zeolite, sintered metals, and oxides such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), zirconia (ZrO_2), etc. are common examples of inorganic membranes used for water filtration [14]. While the organic materials used for membranes are mostly carbon-based and polymeric in nature, polymeric membranes have some leverage over inorganic membranes and therefore are the most preferred option for the membrane material. The advantages of a polymer as a suitable material for the membrane are shown in Fig. 2.

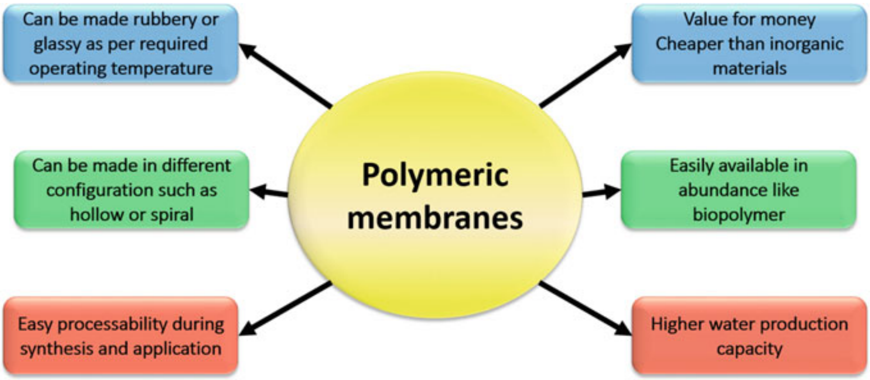

Fig. 2 Advantages offered by a polymeric membrane for water purification application

As polymeric materials are more flexible and easier to handle, it is often the first choice for preparing a membrane for filtration. Various polymers are applied as the functional membranous layer in all types of filtration methods mentioned above, namely MF, NF, UF, and RO. Some of the most common polymers that are potentially applied for membrane filtration are cellulose acetate, polyamide (PA), polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyacrylonitrile (PAN), polymethacrylic acid (PMAA) and polyaniline nanoparticles (PANI). However, polyethersulfone amide (PESA) is a new addition to the above list and there are many more polymeric materials that are being explored for their potential as a membrane candidate [15]. The nature of the polymer being used in membrane filtration is very critical as it plays the most significant role in determining the quality of the permeate generated and the overall cost of production of water. Appropriate selection of the polymer for a specific type of membrane filtration can ensure overcoming some major challenges such as the need for frequent membrane replacement and excessive energy consumption.

For enhanced performance, the polymeric membranes are often modified either chemically or by the addition of inorganic additives or blended with another suitable polymer. For instance, in order to achieve better strength in a highly porous membrane, polyvinylidene fluoride PVDF matrix was reinforced with polytetrafluoroethylene (PTFE) particles thereby reducing surface tension and increasing contact angle resulting in narrow pore size distribution and hence better strength [16]. The introduction of inorganic additives such as TiO_2 or SiO_2 helps improve hydrophobicity. Hydroxyl-rich silica particles were incorporated in a PVDF flat-sheet membrane to regulate its porosity and pore size. With increasing silica content, lower permeate flux, and a reduced rate of mass transfer between solvent and non-solvent was achieved. Moreover, the contact angle of PVDF was also increased [17]. Another successful way of enhancing membrane hydrophobicity is the addition of perfluorinated polymers. Blending perfluorinated polymers to PVDF or application of copolymers such as poly vinylidene fluoride-co-hexafluoropropylene PVDF-HFP can offer to be potential base materials for desalination membranes [18]. The incorporation of the hexafluoropropylene (HFP) monomer in the PVDF backbone resulted in lower crystallinity which in turn considerably enhanced the amorphous phase content [19].

3.1 Polymers for MF

MF membranes are generally applied for membrane distillation (MD), MBRs, OMBRs, and wastewater treatment. The integration of TiO_2 in MF membranes has emerged as a viable membrane separation technique. PES and PVDF membranes incorporated with were TiO_2 nanoparticles show a decrease in membrane porosity and an additional capability to degrade various pollutants like textile dyes, pharmaceutical compounds, and pesticides [20]. Although MD is easy to implement it has not yet achieved popularity at an industrial scale due to the major issues of MF membrane fouling and low flux. Recently studies have shown that surface modification of DCMD membranes by tetrafluoromethane (CF4) plasma resulted in a superhydrophobic membrane with increased flux and high salt rejection as compared to the virgin membrane [21]. Other studies have indicated that the introduction of grapheme oxide (GO) in MF membranes can effectively reduce membrane fouling. Owing to its hydrophilic nature and high negative zeta-potential arising from its functional groups, it can augment permeation through the membrane and obstruct fouling by reducing microbial biofilm formation [22].

3.2 Polymers for UF

PS, PES, PSF PEG are the polymers broadly employed for UF membranes. Although PS and PES have good mechanical properties, strong chemical stability, and a wide range of pH operations, their applications are imitated due to their hydrophobicity [23]. Most other polymers such as PVDF, PVC, and PMAA used in UF membranes throw challenges by being naturally hydrophobic. This can result in a decline of flux and buildup of organic materials favoring microbial growth followed and fouling and membrane failure subsequently. Hence modification of the membrane to increase surface hydrophilicity becomes necessary [24]. Reports from the past and recent studies have shown that the addition of nano-structured inorganic particles has helped reduce hydrophobicity by increasing surface hydrophilicity and flux rate [25]. The terminal silanol (Si–OH) groups on mesoporous silica particles (MSP-1) were reported to induce hydrophilicity in polysulfone PSF membranes [26]. Grafting of (2-hydroxyethyl methacrylate) (P(HEMA)) on TiO_2 nanoparticles followed by impregnation into PSF membranes reportedly showed superior hydrophilicity along with elevated flux rate and better antifouling properties when compared with pristine

PSF and TiO_2 [11]. Another study showed that coating PVDF UF membrane with dopamine solution facilitated the attachment and homogenous distribution of TiO_2 particles on its surface. This significantly improved hydrophilicity resulted in high flux and low fouling ratio [27].

3.3 Polymers for NF

Most NF membranes are composed of PI, PA, PVA, and PAN polymers. PI membranes show instability in polar solvents, chlorinated solvents, and in the presence of strong amines and strong acids or bases. Modification of such membranes via cross-linking is opted to increase chemical resistance. Poly-arylene ether ketone (PAEK) is another polymer suitable for NF membranes as it has high resistant to various solvents and strong acids and bases owing to its low degree of sulfonation. However, (PAEK) has a low permeability hence its separation performance was subjected to testing in dimethylformamide (DMF) and tetrahydrofuran (THF), and improved results were obtained [28]. A Polyamide NF membrane with a high level of pore size uniformity for the separation of sub angstrom scale molecules was prepared. The angstrom scale pore size was achieved by surfactant-assembly regulated interfacial polymerization (SARIP). The self-assembled surfactant network aided in faster and homogeneous dispersion of amine monomers on the solvent interface during polymerization, thereby producing an active layer of polyamide with consistent and precise sub-nanometre, angstrom scale pores [29].

3.4 Polymers for RO

As discussed, earlier RO is so far the best and most widely accepted technology for producing potable water. The most common polymers used for RO membranes are cellulose acetate (CA) and polyamide (PA). CA is opted for its natural availability and biodegradability, though PA is preferred due to its capability of stable performance under a wide range of pH as well as high temperatures. However, PA is susceptible to chlorine attack due to its amine group, which needs to be prevented by an additional de-chlorination step [30]. To avoid this issue of chorine attack any additional step, copolymers such as poly-arylene ether sulfone (PAES) which are resistant to chlorine attack due to the absence of any susceptible amide linkage are also widely used as RO membranes [31]. Disulfonated PAES co-polymer thin films were synthesized with a controlled degree of sulfonation and molecular weight achieved by the application of Meta-aminophenol. This was followed by further reaction with acryloyl chloride to attain acrylamide terminated PAES oligomers, which were then subjected to UV radiation for cross-linking. The final copolymer thin film was seen to have a smooth surface thereby encouraging high water passage and relatively reduced uptake and swelling [32]. In a recent study, the PA membrane for RO was modified with GO and poly acrylic acid (PAA) to enhance antifouling and anti-scaling properties. The resultant PAA modified GO coated RO membrane exhibited improved hydrophilicity and surface smoothness with a mere reduction of permeate flux by only 3%.

3.5 Nanocomposite Membranes

Polymer-based nano-composite membranes are chemically engineered materials which often contain target specific nanoparticles dispersed in the membrane matrix. Such nanocomposite membranes are extensively used for water treatment, solvent nano filtration, gas separation and many other operations. The type of nano fillers or nano particles used in nanocomposite membranes can be organic, inorganic, biomaterial or even a hybrid component. As per the requirement, the configuration of the nanocomposite membrane can be a flat sheet like or hollow fiber type. Based on the preparation technique the nanocomposite membranes can be classified into two major categories that are thin film nanocomposites and blended nanocomposite membranes.

3.5.1 Thin Film Polymer Nanocomposite Membranes

Thin film polymer nanocomposite membranes or TFC are achieved by either direct deposition of the nanoparticles on the membrane surface or by encapsulation of the nanoparticles within the membrane via interfacial polymerization. Direct deposition can be done by dip coating method where the nanoparticles self assemble to form a thin film on the surface of the membrane, or nanoparticles can be introduced onto a prepared membrane surface by pressure application [33]. Graphene oxide, silica, zeolite, silver, carbon nanotubes, titanium dioxide, are some common nanoparticles that are used as fillers in TFC membranes. Such membranes with nanoparticle incorporation offer various advantages such as high thermal stability, mechanical strength, selective permeability, hydrophilicity and resistance to extreme pH levels etc. However leakage of nanoparticles during high pressure filtration may become a challenge, but that too can be overcome by chemically modifying the particles to facilitate surface functionalization [34]. Hence such TFC membranes have gained high interest among researchers as well as industrialists. Fabrication of Polyethersulfone (PES) based thin film membrane with surface coated TiO_2 nanoparticles using PVA and glutaraldehyde as additives were reported in a recent study [35].

3.5.2 Blended Polymer Nanocomposite Membranes

In this type of membrane preparation nanoparticles are first mixed with polymer and dispersed in the casting solution before the membrane is casted. Such membranes are hence commonly called nanoparticles entrapped membranes. In this method the homogeneous dispersion of nanoparticles in the polymer matrix is an important factor. Agglomeration of nanoparticles is a common issue observed during the fabrication of nanoparticle entrapped membranes. This problem mainly arises due to the incompatibility between the inorganic and organic components, where interfacial tension also plays a major role in dispersion. These issues can cumulatively result in improper or heterogenous dispersion of the nanoparticles in the polymer matrix thus causing agglomeration. Application of dispersion agents to bind the inorganic nanoparticles to the organic polymer matrix is one way of overcoming this issue. Another technique to play down the agglomeration challenge is the surface modification and functionalization of the nanoparticles [34]. Jafar et al. prepared a TiO_2 nanoparticle entrapped PES membrane by dissolving TiO_2 in DMAc using PVP as additive [35].

4 Preparation Approaches Towards PM

Various techniques are applied for the preparation of polymeric membranes as well as the polymeric nanocomposite membranes. Some popular methods are discussed below.

4.1 Electrospinning

Electrospinning works on the basic principle of movement of liquid under the influence of electrostatic field forming nanofibres. This phenomenon was first observed by William Gilbert in 600. Since then, this electrohydrodynamic technique has evolved over the years to become the cheapest and most hassle-free method for the fabrication of nanofibers without self-assembly [36]. Electrospinning was first commercialized by application in air filters.

The electrospinning apparatus involves the use of a syringe in which the polymeric solution to be electrospun is poured. The syringe is suspended upside-down, and a metallic collector is laid under it. Subsequently, a high electric field is created between the syringe and the collector by charging the polymeric solution through the application of high voltage on it. This results in the formation of a droplet in the tip of the syringe. As the applied voltage becomes strong enough to overcome the surface tension of the droplet, it converts into a jet forming the ‘Taylor cone’. While the jet progresses towards the collector plate, it endures bending instabilities along with the evaporation of the solvent. This results in the formation of fibrils with a smaller diameter and longer length [37]. The nonwoven fibers are assembled in the collector plate (Fig. 3).

Yin et al. [38], synthesized sulfonated polyethersulfone nanofibrous membrane through the process of electrospinning. The pore size and distribution were

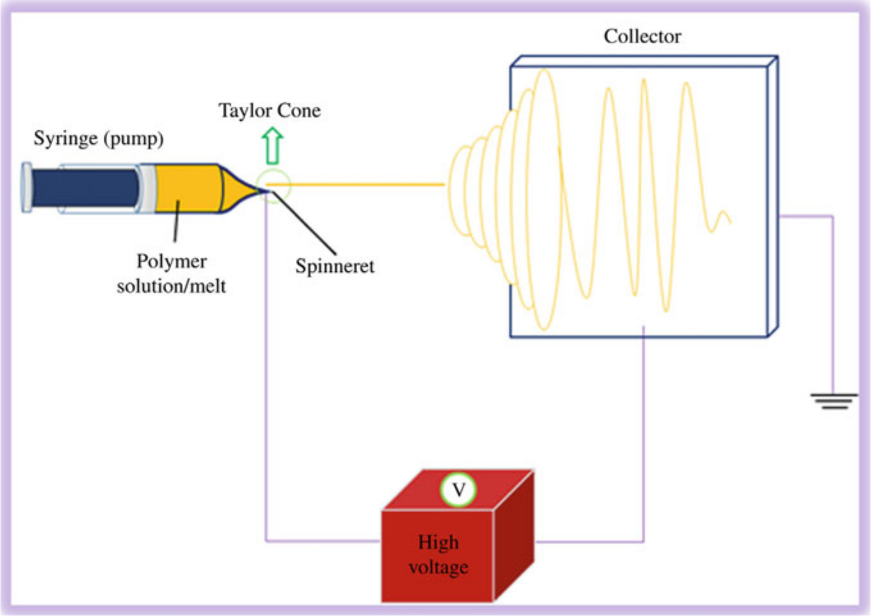

Fig. 3 Schematic representation of electrospinning technique. Reproduced with permission from Orasugh et al. [39], Elsevier

immensely influenced by the diameter of the fiber which in turn affects the adsorption of dyes and heavy metals. The membrane exhibited a flux of 320 L/m^{2}h against nanoparticles, methylene blue, and Pb (II).

4.2 Track Etching

The track etching technology involves the use of nuclear tracks for the fabrication of porous membranes. Polycarbonate track membranes were first commercialized in the 1970s.

There are a few methods to generate tracks in foils in order to transform them into porous membranes. Latent tracks can be produced by irradiating fragments from the fission of heavy nuclei on the film. A collimator is generally used in this process. Particles penetrating the film may rupture the polymer chain leaving behind damaged tracks. Another method involves the use of ion beams from accelerators. The damaged areas of latent tracks are eradicated and converted into hollow channels by the method of chemical etching [40].

Korolkov et al. [41] prepared poly(ethylene terephthalate) (PET) track-etched membranes and modified them by soaking in trichloro(octyl)silane for ameliorating its hydrophobic nature. The membrane was used for the separation of oil–water emulsion where chloroform–water and cetane–water were used as models for testing. Membranes having a pore diameter of 350 nm exhibited flux of 305 and 75 mL/m^2 h for chloroform–water and cetane–water respectively. Yeszhanov et al. [42] synthesized hydrophobic track-etched membranes by graft polymerization of triethoxyvinylsilane and covalent binding with perfluorododecyltrichlorosilan. The membrane was used for direct contact distillation of water containing carbendazim. It showed a flux of 214 g/m^2 h.

4.3 Sintering

Sintering is a technique that is used to synthesize polymeric membranes from powders of polymer or inorganic materials. This technique involves compression and heating of the desired particles below the melting point, stimulating them to stick together. Pores are generated in between the stuck particles which have a size just as the size of the particles. Polymers that can be used for sintering techniques include polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE) [43].

Huang et al. [44] electrospun PTFE/poly (tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)/poly (vinyl alcohol) (PVA) ultra-fine fibers on a porous supporting tube. It was subsequently sintered to produce PTFE/FEP porous membranes. The membranes had the potential to separate water–oil emulsions and had a flux of 134 L m^{-2} h^{-1}.

4.4 Phase Inversion

Phase inversion is a versatile technique for preparing polymeric membranes of various pore sizes. In this technique, a polymer soluble in a solvent transform from a fluid state into a solid state under optimized conditions leading to the formation of membranes. Morphology of the prepared membranes depends upon the operating conditions, mostly on the rate of elimination of the solvent and velocity of phase separation. Phase separation can either be non-solvent induced or thermally induced.

Wang et al. [45] synthesized polyethersulfone (PES)/graphene oxide (GO) membranes by using the phase inversion technique and DC electric field. The prepared membrane was used for the elimination of methyl red. It had a high flux of 289.63 Lm^{-2} h^{-1} which is about double the pristine PES. Durmaz et al. [46] fabricated cellulose and cellulose acetate membranes via phase inversion using 1-ethyl-3-methylimidazolium acetate and dimethyl sulfoxide (DMSO). Wet cellulose membranes showed decreased elimination of Bromothymol Blue with an increasing amount of DMSO solvent. On the other hand, dried cellulose membranes showed similar performances in rejection of Blue Dextran and Bromothymol Blue.

4.5 Stretching

This technique is used for making polymeric membranes from semi-crystalline polymers. Pores are produced in the membrane at high temperatures due to stretching perpendicularly to the arrangement of crystallites. The crystallites are arranged in the direction of extrusion.

Li et al. [47] studied and optimized the stretching conditions required for the formation of hollow PTFE membranes. The authors concluded that the membranes synthesized at low stretching temperature and high stretching ratio exhibited high flux and rejection as a result of high porosity and regulated size of pores. Ji et al. [48] prepared poly(vinylidene fluoride) (PVDF) hollow fiber membranes through the process of melt-spinning and stretching. The synthesized membrane was used for the elimination of SiO_2 and active sludge. It exhibited a rejection of 99.99% and lowered turbidity. Table 1 summarizes all the methods that were discussed in the previous sections and their merits and drawbacks.

5 Membrane Antifouling Approaches

For the past few decades, scientists are seeking for developing membranes having potential antifouling properties. Fouling is a major problem arising from various interactions occurring between membrane surface and foulants. The types of interactions happening between foulants and membrane are shown in Fig. 4 [56].

These foulants get attached to the surface of the membranes, as a result, it blocks or narrows down the membrane pores. As a result of which the efficiency of the membranes decreases. In general, the foulants that have less size than the membrane pore tends to narrow the membrane pores either by blocking the pore or by getting adsorbed on the surface of that membrane. Different types of membrane fouling are shown in Fig. 5. However, the particles having larger sizes tend to form the cake layer upon mixing with other particles on the membrane surface [57]. The cake layer is considered as permanent membrane fouling which is very difficult to clean. At present, the target is to design materials having antifouling as well as antibacterial properties to increase the longevity of the membrane. Various materials have been reported to show antifouling characteristics in an application. These are mainly implemented against microbial, organic, and inorganic fouling.

Table 1 Different methods used for membrane preparation and their applications

Technique	Pore size	Application	Merits	Demerits	References
Sintering	0.1–10 µm	Microfiltration	High temperature resistant, chemical resistant	A large amount of material is required, high energy cost, high capital cost	[43, 49]
Track-etching	0.02–10 µm	Ultrafiltration, microfiltration	Controlled pore size, density	Comparatively low porosity, non-uniform surface charge and shape	[40, 50]
Stretching	0.1–3 µm	Microfiltration	High porosity, large scale production, available in commercial modules	Production of thick membranes, restricted to semi-crystalline polymers	[43, 51]
Phase inversion	From dense to few microns	All fields	Versatile membrane structures and thickness, Less compressible	Availability of suitable solvents, environmental hazards	[52, 53]
Electrospinning	From ten nanometer to several micrometers	All fields	High porosity, high surface-to-volume ratio, light weight	Difficult to handle due to charge accumulation, small scale production, salt retention	[54, 55]

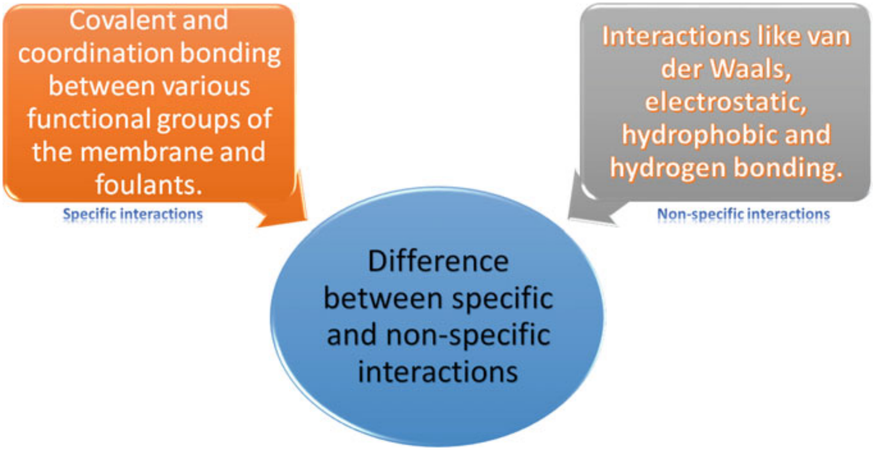

Fig. 4 Basic difference between specific and non-specific interactions

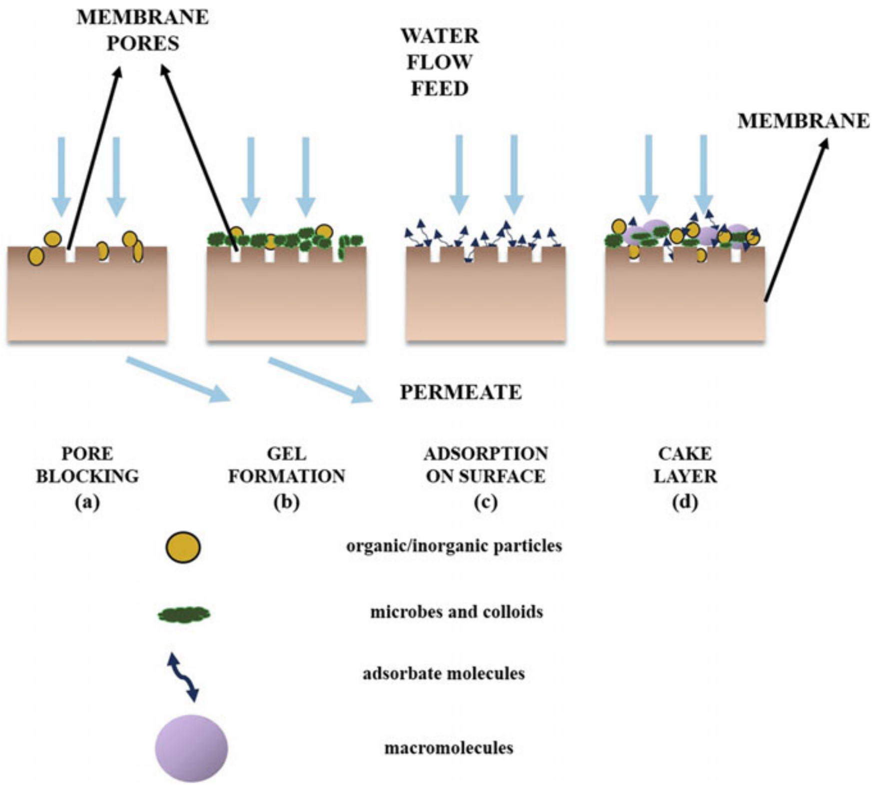

Fig. 5 Types of membrane fouling based on causing agent

5.1 Microbial Mediated Antifouling

Fungal, bacterial, and algal growth on the surface deposition the surface of the membrane has a huge impact on its efficiency. As a result of their growth biofilm formation occurs on the membrane surface and ultimately results in membrane fouling [58]. The physical structure of a biofilm is like that of a gel and has slimy and adhesive characteristics, so it is very difficult to clean them off the membrane surface. It has been reported that this biofilm must be detected in the earlier stage as with the cake layer formation the difficulty in removing them increases [59].

To reduce these types of complications various antifouling membranes are being developed to deal with fungal, bacterial, and algal growth. Similar to the work by Shen et al. who created a surface modified TFC membrane, the membrane was developed by surface ionization with various metal ions. It is reported that due to surface modification of the TFC membrane it showed better anti-adhesive and antibacterial properties compared to ordinary TFC membranes. Polyethyleneimine and N-containing organic phosphonic acid in the membrane resulted in better anti-adhesive properties against bovine serum albumin. And silver atoms attached with the membrane provided anti-bacterial properties against S. aureus and E. coli bacteria [60]. Besides the use of metal ions for the prevention of biofilms different photocatalyst materials (TiO_2, ZnO, and CuO) are also used in the membranes for the photocatalytic degradation of bacterial growths [61]. A work by Damodar et al. reported that polymer membranes grafted with TiO_2 show high antibacterial properties against *E. coli.* [62]. Similarly, it has been reported that N-Halamine materials can improve the antibacterial property of the membrane against *Escherichia coli* and *Staphylococcus aureus.* In 2013 by the use of the same material N-Halamine Yu et al. developed SiO_2@N-Halamine Polyethersulfone hybrid membrane which had showed improved antibacterial and organic antifouling properties [63].

This is the antifouling approach utilized to protect the membranes from fouling caused by a fungus, bacteria, and algal growth. But not only by surface modifications but membranes can also be saved from fouling by applications of various cleaning procedures. This includes applying various chemical treatments and washing methods.

5.2 Inorganic/Organic Antifouling in PMWR

Inorganic fouling refers to fouling caused by the deposition and blocking of membrane pores by inorganic precipitates like metal hydroxides. Formation of scaling due to change in pH. A list of inorganic fouling causing agents is mentioned in Table 2. However, organic fouling is caused by the accumulation of natural organic matter (NOM), polysaccharides, polyoxyaromatics, proteins, organic dissolved components, etc. [58]. Scale formation is a major cause of inorganic fouling. This mainly happens due to crystallization and particulate fouling. Precipitation of ions on the membrane surface causes crystallization whereas deposition by convective transportation of colloidal particulate matter on the membrane surface causes particulate fouling [64].

Various antifouling approaches are constantly being studied to produce modified membranes (microfiltration, ultrafiltration, nanofiltration, forward osmosis, and reverse osmosis). In this surface modification is an important process to reduce fouling. Some of the methods to modify membrane surface include the use of blends, grafts, coating, etc. There are several reports on this, like surface modification of polyamide membrane by nanoporous titanate nanoparticles for water source having a high quantity of organic, inorganic foulants, and brackish water [65]. In a study, surface modifications were done using a polyelectrolyte coating upon a nanofiltration membrane. With the implementation of such modifications, various surface properties like hydrophilicity and roughness were improved and led to enhanced the antifouling nature [66]. Hydrogel membranes are made of hydrophilic polymers and have a wide range of applications in water treatment, desalination, etc. [67]. Hydrogel membrane can be used to treat high concentrations of organic pollutants present in water bodies. Qin et al. prepared a forward osmosis membrane with an ultrathin hydrogel layer which exhibits high antifouling properties against organic foulants

Table 2 List of common inorganic fouling agents

Inorganic fouling agent	Sources
Cations	Fe^{3+}, Mg^{2+}, Al^{3+}, Ca^{2+}
Anions	$CO_3{}^{2-}$ Source = $CaCO_3$, $MgCO_3$
	F^- Source = FeF_3, AlF_3, CaF_2, MgF_2
	OH^- Source = $Mg(OH)_2$, $Ca(OH)_2$, $Fe(OH)_3$
	$PO_4{}^{3-}$ Source = $Ca_3(PO_4)_2$, $AlPO_4$, $FePO_4$, $Mg_3(PO_4)_2$
	$SO_4{}^{2-}$ Sources = $MgSO_4$, $CaSO_4$
Salts	$Fe(OH)_3$, $FePO_4 \cdot 2H_2O$, $Mg_3(PO_4)_2$, $Al(OH)_3$, $MgCO_3 \cdot 3H_2O$, $AlPO_4$, $Ca_3(PO_4)^2$, $CaSO_4$, $CaCO_3$,

such as protein, oil, humic acid, and alginate. It is reported that this antifouling property of this FO membrane is due to high hydrophilicity and low roughness. As a result of this property, foulants can be easily removed from the membrane surface by simple physical cleaning methods rather than the use of chemical methods of cleaning [68]. The blending method is a simpler process to fabricate new materials. There are several works in which nanoparticles such as carbon nanotube, ZnO, ZrO_2 Al_2O_3 were used to blend with other materials to obtain new membranes [69–71]. It is said in the microbial antifouling section the prepared SiO_2@N-Halamine Polyethersulfone hybrid membrane has organic antifouling and is also able to prevent microbial fouling prepared by blending with SiO_2@N-Halamine using the phase inversion method. As a result of this, the membrane showed both antifouling and antibacterial properties [63].

5.3 Bio-enzyme Antibacterial Mediated Antifouling

For the past decade, various bio-enzymes have been targeted for use in membrane modifications. Enzymes are preferred as they are easily biodegradable and thus do not possess a threat to environmental pollution. In a work, Nady et al. presented a membrane with enzyme-catalyzed surface modification. Here the surface of a Polyethersulfone (PES) membrane is modified using phenolic acid (enzyme–substrate). One of the major drawbacks of the PES membrane is fouling due to various proteins. The main purpose of this enzyme surface is to act as a protein repellent and thus act as an antifouling membrane [72]. Membranes used in filtration are generally cleaned using various chemicals. Many enzymes have been reported to be effective in cleaning membranes of foulants with the additional use of other chemicals. Yu et al. found that α-amylase, lipase, cellulase, and protease cannot solely be used to

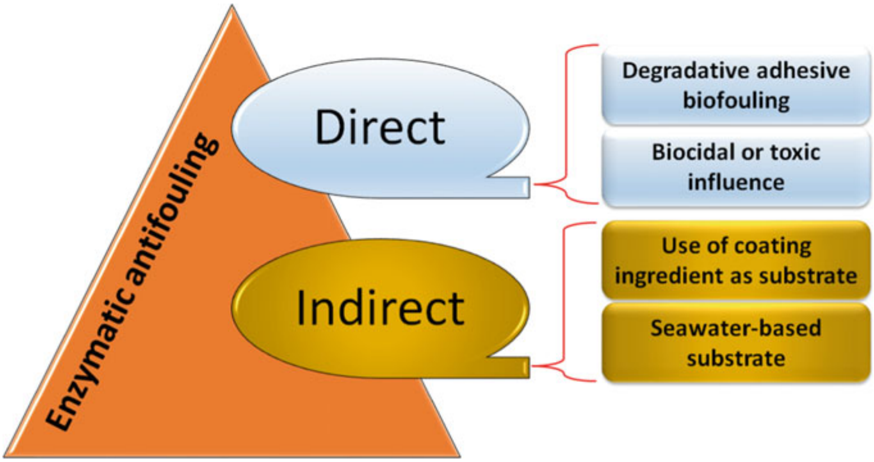

Fig. 6 Categorization of enzymatic antifouling

remove foulants but when used together with other chemicals like Citric acid and NaOH effective cleaning was done [73]. In the present day, researchers are constantly trying to prepare advanced membranes having the self-cleaning ability to minimize the chances of fouling. In a work, pancreatin was covalently immobilized on the PES membrane. It was found that on adjusting pH and temperature (protease, lipase, and amylase) the bio-enzymes present in pancreatin can actively degrade the fouling layer formed on the membrane surface [74]. In general, there are two methods in enzyme-based membrane antifouling (direct and indirect) as shown in Fig. 6. Here the enzyme-based coating is one of the important methods to prevent fouling. In a work, protease enzyme has been used to prepare an antifouling coating on the membrane which can readily prevent fouling due to proteins [75]. Not only in the case of prevention of proteins, but enzyme-based coatings have also proven effective against microbial fouling. The coating containing starch, glucoamylase, and hexose oxidase is able to produce hydrogen peroxide gas enzymatically. As a result of which there has been a significant decrease in the formation of the bacterial biofilm [76]. In another work, Subtilisin is immobilized in maleic anhydride copolymer thin film as an enzyme coating. The enzyme coating was successful in preventing the growth of the green alga Ulva linza and the diatom Navicula perminuta on the membrane surface [77].

5.4 Surface Roughness Mediated Antifouling PMWR

By the study of the surface of various membranes, it has been possible to understand the relationship between fouling and roughness of membrane surfaces. For this, surface structure of different membranes is analyzed with the help of atomic force microscopy. This characterization helps to find out how smooth or rough the surface of membranes is.

Multiple research works have confirmed that membrane fouling increases with the roughness of the membrane surface [78, 79]. By the use of the static adhesion test, it has been found that nanosized particles adhere more to the rough membrane surfaces than smooth surfaces [80]. In one of the works, Woo and his research group studied the antifouling property of a microfiltration membrane having a smooth surface and compared it with that of a similar membrane having a rough surface. Both the membranes did have similar pore size distribution and average pore size. But it was found that the final fluxes of the membrane with a smooth surface are about 4.98% higher than that of the membrane with a rough surface [81].

6 Polymeric Membranes for Effluent Treatment in Different Industries

A huge amount of water is required in different industries where various types of contaminants are directly discharged into the water. As a result, contamination of fresh water is a major concern for its significant contribution to the pollution of water. Due to the direct discharge of toxic pollutants in the water, the chemical oxygen demand (COD) is rapidly increasing which causes harmful effects on natural water bodies. The color and odor of water are also changing because of various dyes, hazardous organic and inorganic substances, untreated water, raw materials are continuously mixing with the fresh water in nature. So, to remove the pollutants and reduce the contamination level, the treatment of water is very important. Among various techniques of wastewater treatment membrane technology is very much popular because this technique is very economic and convenient to install and use [82, 83].

6.1 Food Industries

Different types of harmful effluents are generated in various steps of a food industry system. Food production, processing, transportation, and storage are directly or indirectly had an impact on water pollution or any other environmental pollution. Many harmful contaminates from dairy industries, fruit processing industries, meat industries are directly mixed with fresh water. In addition to that, if the discharged industrial water is not treated properly, there is a significant loss of biomass and valuable nutrients [84]. Fruit and vegetable food processing industries contain solid waste such as rinds, seeds, skins from different organic raw materials. Meat, poultry, and seafood industries discharge skeleton waste, animal fat, blood, eviscerated organs into the water. Beverage and fermentation industries wastewater contains various materials

Table 3 Membrane processes used in various industries

Membrane approach	Solutes held	Diameters of retained particles (μm range)	Food industry-based effluents treatment utilization
MF	Bacteria, colloids, grease, fats, organic microparticles, oil, etc.	10^{-1} to 10	Beverage, cereal, diary, oil, etc.
UF	Oils, pigments, proteins, sugar, etc.	10^{-3} to 1	Beer, cereal, diary, fish, meat, oil, vegetables, wine, etc.
NF	Divalent cations and anions, lactose, sulfates, pigments, sodium chloride, sucrose, etc.	10^{-3} to 10^{-2}	Beverage, diary, meat canning, olive oil, etc.
RO	Inorganic ions, salts, etc.	10^{-4} to 10^{-3}	Fish, diary, meat, vegetables

used in the fermentation process. Waste streams of dairy industries contain waste milk which eventually degrades to form lactic and formic acids [82].

Membrane technology can be used to remove pollutants from food processing industrial wastewater. Depending upon the pollutant materials microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) techniques can be applied. After removing the contaminants from wastewater, the fresh water and removed compounds can be recycled once again which can reduce the cost of processing and water consumption [85]. The application of various membranes to various food industries is shown in Table 3.

6.2 *Pharmaceutical Industries*

Nowadays health protection is a major concern due to the rapid increase of diseases all over the world. In the past few years, rapid industrialization of pharmaceutical manufacturing industries led to the rapid development of the country, but a concurrently huge amount of water pollution also occurred for this reason. Recently, the pharmaceutical industries are among the top five industries in the global economy in addition to that it is one of the major sources of water pollution. A large amount of water is required for various processes in these industries such as production, processing, formulation, cooling, etc. These numerous processes generate a large amount of wastewater in which a high concentration of toxic, organic, and inorganic compounds are present. This wastewater contains steroids, hormones, drugs, antibiotics, lipid regulators which can harm various water bodies and the overall environment. The COD (chemical oxygen demand) of pharmaceutical wastewater is very high which can disturb the ecological balance. Much attention should be paid to removing these pollutants so that we can reutilize the wastewater and reduce the health hazard by eliminating the pharmaceutical contaminates [86]. Different major pollutants from various pharmaceutical industries and their BOD and COD have been shown in Table 4.

Traditional methods are unable to eliminate all the pharmaceutical pollutants so, membrane technologies can be a very good alternative that can erase contaminates from water. But individual technology can't remove all compounds, so membrane technology can be combined with conventional technology and by this hybrid process pollutants can be removed efficiently and economically. Depending upon the pore size, membrane composition, driving force, and membrane composition, different types of the membrane can be used such as MF, UF, NF, RO membrane, etc. [95]. The pore size of MF and UF is greater than the size of contaminants for this reason these membranes are not frequently used. NF and RO membranes are used for this purpose which have low pore size [96]. NF/RO membranes are extensively used for

Table 4 Major pollutants from different pharmaceutical industries and their BOD and COD

Pharmaceutical industry	COD (mg/l)	BOD (mg/l)	Major pollutants (mg/l)	References
Antibiotic producing industry	12,500 ± 1070	9400 ± 980	Butyl acetate 1500 ± 350 Methylene chloride 500 ± 98	[87]
Herbal pharmaceutical industry	5000 ± 80,000	–	Lignin 450 ± 8500	[88]
Chemical synthesis pharmaceutical industry	40,000 ± 60,000	–	–	[89]
Bulk drug pharmaceutical industry	13,000–15,000	7000–7500	Antipyrene 5–10 Carbamazepine 10–15 1-bromonapthalene 5–10 dibutyl phthalate 30–40	[90]
Bulk drug manufacturing industry	34,400 ± 2000	22,000 ± 1200	–	[91]
Antibiotics waste from manufacturing and equipment cleaning industry	16,547 ± 1827	10,184 ± 2574	Triethylamine 9872 ± 2142	[92]
Antibiotic waste	34,348 ± 1425	–	–	[93]
Chemical synthesis pharmaceutical industry	20,000–230,000	–	Etodolac 50–215	[94]

the removal of antibiotics from waste water [96]. For the last two decades, membrane bioreactors are used extensively because it is economically beneficial and it has immense sludge retention time (SRT) [97].

6.3 Textile Industries

Textile industries are considered as one of the largest industries worldwide. The growth of textile industries caused some accidental effects on the environment and water pollution is most significant among them. Textile industries require a huge amount of fresh water as a result various contaminants are directly discharged into this. It is reported that if textile industrial wastewater is not treated properly, it can cause serious environmental issues. The untreated or incompletely treated wastewater can be very harmful to water bodies and terrestrial life. Various types of organic compounds, heavy metals, inorganic salts are used in textile industries and dyes are considered as a major contaminant among them. The pollutants related to these industries decrease oxygen concentration and block the water permeability through the water which totally imbalance the water ecosystem [98]. It has high COD, low BOD/COD ratio, high total dissolved solids (TDS), high pH, high turbidity, and high salinity [99]. In Table 5 characteristic of wastewater which is taken from various steps of the textile industry is shown in detail.

Membrane technologies are extensively used for textile wastewater treatment. Mechanical, chemical resistance, thermal stability, pore size, materials are basic parameters to select a membrane that can give maximum removal percentage and have minimum fouling behavior. Membrane technologies are advantageous because the toxic chemicals can be recovered and reuse of these can reduce the cost of processing [82]. The microfiltration technique is often used for the removal of colloidal and suspended dye particles from water, but this technique can’t be used as an independent technique to erase all the effluents because toxic compounds and complexes are not removed by the MF membrane. UF membranes are rarely used for these types of water treatment because the molecular weight of the dye complexes is much lower than the molecular cutoff of the UF membrane, but it can be used as a pretreatment before carrying the water to other membrane techniques. We can get a very good quality of treated water by using the nanofiltration membrane and NF membranes are very advantageous because they have high solvent permeability, are convenient to use and have good chemical cleaning capability which suggests that they can be used as a mainstream technique for textile waste water treatment [101]. RO membranes are used for recovering macromolecules and ionic compounds from textile industrial waste water [102]. Various kinds of integrated or hybrid processes are also used to minimize the contamination level of textile wastewater [103].

Table 5 Characteristics of textile wastewater obtained from different stages of textile processing. Reprinted with permission from Dasgupta et al. [100]. Elsevier

Characteristics	Scouring	Bleaching	Mercerising	Dyeing	Composite	Discharge limit into public sewage Bureau of Indian Standards (BIS-3306–1955)	Maximum permissible limit for water reuse
pH	9–14	8.5–11	8–10	1.5–10	1.9–13	5.5–9.0	6.5–9.2
TDS (mg/L)	12,000–30,000	2500–11,000	2000–2600	1500–4000	2900–10,000	2100	–
TSS (mg/L)	1000–2000	200–400	600–1900	50–350	100–700	100	–
Color	–	–	Highly colored	Strongly colored	Strongly colored (>14,000 Pt–Co units)	Colorless	Colorless
BOD (mg/L)	2500–3500	100–500	50–120	100–400	50–550	30	–
COD (mg/L)	10,000–20,000	1200–1600	250–400	400–1400	250–8000	250–500	–
Chlorides (mg/L)	–	–	350–700	–	100–500	600–1000	600
Sulphates (mg/L)			100–350		50–300	1000	400

6.4 Leather Industries

Tannery industries are one of the oldest and largest industries that have huge potential for employment, growth, and exports to foreign countries [104]. Different types of goods are produced in those industries such as leather garments, footwear, and leather accessories like bags, wallets, belts and among them, footwear is most important as it consumes more than half of total leather production [105]. But these industries release a huge amount of hazardous compounds which direct mix with fresh water. These effluents from leather industries are classified as a critical environmental hazard because of the high toxicity of the substances which include inorganic and organic dissolved matters, sulfide, chromium, lead ions and other heavy metals, chlorine, ammonia, and other various pollutants [82]. These pollutants can cause skin cancer, ulcer, and other critical diseases which have a high mortality rate. Various characters of textile/leather industry wastewater vary with every step of leather manufacturing, and it is shown in Table 6. In Table 7, various contaminating hazardous metals and their percentage are shown.

Treatment of these effluents is very important to save the ecosystem and the overall environment. Various techniques such as adsorption, coagulation, flotation, electrochemical processes are available but membrane technology is a wildly accepted and popular technique for the treatment of leather industrial, and tannery waste water because of its high efficiency, low cost, and eco-friendliness [82]. MF, UF, NF, RO techniques are used independently or in an integrated hybrid process. Depending upon contaminations which membrane can be used is determined. Tannery industry wastewater treatment contains three steps, first is primary or chemical-physical treatment in which sedimentation, sludge separation occurs. The second step is secondary or biological treatment in which recycling of sludges and their separation take place. And the final step is tertiary treatment and in this step filtration, redox processes are done [106]. Biological treatment is done by UF membrane which is coupled with a bioreactor. RO membranes are also used to reduce the salt content of wastewater. Besides these techniques hybrid membrane processes are used in which a conventional technique is combined with a membrane technique or a membrane technique is coupled with other membrane techniques.

6.5 Petroleum Industries

Different sections of petroleum industries include natural gas production, production of gas to a liquid, liquefied natural gas, and production of oils. These production units consume a huge amount of fresh water and discharge wastewater which contains various effluents. The waste water is produced either during the production of hydrocarbon which is a result of oil and gas dispersion or when it is applied at different components to control the process such as cooling or oil processing [106]. The wastewater of petroleum industries mainly contains oil, grease, organic matters

Table 6 Characteristic of leather industry wastewater at various steps of processing (Mean composition and volume percentage of various wet operations in a leather industry). Reprinted with permission from Cassano et al. [106]. Elsevier

Parameters	Soaking		Liming		Deliming-bating		Pickling	Chromium tanning	Dyeing, fat liquoring, retanning		Other effluents
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
pH	6	10	12.5	13	6	11	4	3.2	4	10	–
Temperature (°C)	10	30	10	25	20	35	–	–	20	60	–
Sedimentable materials (mg/l)	100	250	300	700	50	150	20	45	100	500	–
Total suspended solids (mg/l)	2300	6700	6700	25,000	2500	10,000	380	1400	10,000	20,000	–
BOD_5 (mg/l)	2000	5000	5000	20,000	1000	4000	100	250	6000	15,000	–
COD (mg/l)	5000	11,800	20,000	40,000	2500	7000	800	400	15,000	75,000	–
Chromium(III) mg/l	–	–	–	–	–	–	–	4100	0	3000	–
Sulfides (mg/l)	0	700	2000	3300	25	250	–	–	–	–	–
Chlorides (mg/l)	17,000	50,000	3300	25,000	2500	15,000	8950	2000	5000	10,000	–
Oils and fats (mg/l)	1700	8400	1700	8300	0	5	–	–	20,000	50,000	–
Chlorinated solvents (mg/l)	–	–	–	–	0	2500	–	–	0	250	–
Surfactants (mg/l)	0	400	0	300	0	500	–	–	500	2000	–
Discharge water on total volume (%)	18		12		22		2	3	38		5

Table 7 Elements present in a leather industry wastewater and their approximate percentage

Sl. No.	Element	Proportion (%)
1	Ca	62.46
2	Si	9.770
3	Fe	8.851
4	Cr	6.770
5	Mg	3.730
6	Al	2.800
7	S	2.110
8	Ti	0.808
9	K	0.455
10	P	0.444
11	Sr	0.161
12	Cu	0.083

like hydrocarbons such as paraffin (methane, ethane, propane), naphthene (dimethyl cyclopentane, cyclohexane), aromatics such as benzene, toluene, xylene, etc. and naphthenic acids that are also present at significant amounts [107, 108]. Petroleum industry wastewater is rich in organic pollutants and oil. So, it is difficult to treat this water and remove all the effluents [109]. The chemical characteristics of produced water in a gas and oil field are shown in Table 8.

MF membranes are used as a pretreatment process to increase the effectiveness of UF, NF, or RO techniques. Oil removal can be done by using the UF process along with the MF process, but one disadvantage of this process is that UF membranes are very susceptible to fouling. So, to overcome this problem the membrane surfaces are made hydrophilic, and the surface roughness is reduced. NF and RO membranes are used for this water treatment purpose [110].

Table 8 Typical chemical characteristics of produced water. Reproduced with permission from [110]. Copyright Adham et al. [110] Elsevier

Parameter	Oil field [111, 112]	Gas field [113]	SAGD [114]	Coal bed methane field [115]
TDS, mg/L	247,000	5200	<10,000	2510
Sodium, mg/L	69,160	1030	3000	1350
Chloride, mg/L	152,750	2300	4800	62
TOC, mg/L	500–2000	500	430	2
HCO_3, mg/L	310	–	1400	1700
pH	5.6	4.3	8.8	8.4

7 Challenges and Outlook

According to reports, most nations have environmental legislation limiting oil concentration in final wastewater discharge to 10–15 mg/L [116]. Membrane fouling reduces the membrane's lifespan as well as its performance in terms of water flow, permeability, and oil rejection. Membranes with a high hydrophilic property are advantageous for treating greasy wastewater. Most earlier research used hydrophilic membranes rather than hydrophobic membranes because this encourages high water flow performance. Furthermore, the hydrophobic membrane has a significant oleophilic leaning property [116]. Both the hydrophobic and oleophilic wetting qualities of the membranes reject water molecules while allowing oil molecules to flow through, resulting in oil fouling on and inside the pores. Permeation occurs when oil droplets pass through a porous medium.

This layer cake creation causes membrane obstruction, which reduces membrane permeation performance and eventually prevents water molecules from passing across the membrane. Apart from oil molecules, oily wastewater also contains other contaminants such as protein. This impurity may contribute to a higher likelihood of membrane fouling.

Because of the intricacy of the materials used in MMM manufacturing, the presence of inorganic nanoparticles as addition may provide a challenge. This issue hampered the creation of a homogeneous dope solution and resulted in the aggregation of additives.

In the structure of the membrane, because there is a barrier obstructing the water molecules from smoothly passing across the membrane, agglomeration would lower the effective contact area and water flow performance.

According to Garca-Ivars et al., the size and shape of the nanoparticles play an essential impact on their wetting capabilities and dispersion. Nanoparticles less than 100 nm have a harder time settling in dope solutions than macroparticles [117]. Spherical nanomaterials, on the other hand, are preferred over polyhedral nanoparticles because they have fewer contact points between particles, which prevent agglomeration and aggregation. Aside from that, nanoparticle agglomeration may only result in nanoparticle leakage, since the nanoparticles prefer to permeate alongside the feed permeation.

The creation of membranes formed from expensive materials such as PAN and nanoparticles, from an economic standpoint, remains a hurdle to their practical deployment. As a result, using low-cost materials and a basic procedure is a possibility.

Furthermore, carbon-based compounds such as carbon nanotubes (CNTs) and graphene are among the most widely used materials because they improve membrane hydrophilicity and oleophobicity. Aside from material selection, there are a number of other aspects to consider when calculating total operating and maintenance costs for the entire membrane treatment process. Membrane replacement, chemical, energy, labor, and so on, as well as maintenance, should all be considered. According to

Ersahin et al., the membrane system's significant contribution is endowed by chemical consumption, labor service, and energy consumption, which accounted for 35, 22, and 17% of the overall expenses, respectively [118]. Reduce the number of membrane cleanings to reduce chemical use.

It is not, however, impossible to design and manufacture lab-scale membranes for industrial uses. It is critical to have a thorough grasp of chemical compositions and reactions in order to build membranes with the desired properties. As a result, more work will be necessary to develop high-quality membranes comparable to current technology.

8 Conclusion

Membrane biofouling is one of the most significant challenges to membrane-based separation's long-term durability. As a result, in membrane technology for water and wastewater treatment, the development of anti-biofouling expertise is critical. Early initiatives focused on developing hydrophilic membranes with anti-adhesion properties to reduce surface biofouling. However, due to continual bio-adsorption, development, and regeneration of bacteria on polymer membranes, this is insufficient to manage biofouling over a long-term operation.

Current research is beginning to focus on the construction of antibacterial membranes by combining and surface functionalizing biocidal nanoparticles with polymers. Various antibacterial agents, including inorganic, organic, and enzymatic-based compounds, have been used for membrane functionalization to achieve this goal, with promising results.

In general, metal-based nanoparticles and carbon-based nanomaterials are regarded as potential options for inorganic biocides due to their strong antibacterial efficacy, high stability, and commercial availability. Furthermore, such materials can provide membranes with other desirable features such as a smooth, hydrophilic surface, resulting in increased membrane fouling resistance.

Nonetheless, the inorganic filler's poor compatibility with the organic membrane remains a technical challenge. It is hypothesized that organically decorated inorganic nanoparticles improve interface adhesion within polymeric matrices, which also applies to membranes with a thin polymer-based active layer.

Despite the strong antibacterial activity provided by these nanomaterials, issues such as the release of (heavy) metal ions that cannot be rejected by membranes and nanomaterial leaking from antibacterial membranes remain.

This must be thoroughly investigated when employing multifunctional nanomaterials to make antibacterial changes. Furthermore, future studies should focus on good control of the release rate, with the goal of successfully inactivating bacteria strains and extending the validity time. Due to the limited lifespan of antibiofouling capabilities, which is closely linked to the slow dissolution of biocides from membranes, using antibacterial membranes in realistic operational settings is still a big difficulty. To improve the antibacterial durability of the modified membranes, significant efforts should be made to build long-lasting antibacterial membranes. The practical application of these antimicrobial membranes in real-world situations needs to be investigated further. In this context, tracking the detection of released antibacterial agents is useful for better understanding antibacterial efficacy and resistance.

Surface modification and immobilization of NPs onto larger-size supports are currently being used to control the release profile of biocides as well as boost metallic nanoparticles' stability within the membrane matrix. Furthermore, the size and morphology of inorganic biocides can be tweaked to improve the membranes' overall effectiveness.

Advanced organics with specific chemical structures have evolved as new antimicrobial ingredients for membrane modification, in addition to inorganic antibacterial NPs. Although the inclusion of organic bacterial agents into the polymeric membrane is conceivable, the membrane's operational stability, particularly towards membrane disinfectant, remains a difficulty.

Surface grafting by polymerization is a promising method for firmly anchoring organic biocides to membrane surfaces against bacterial activation.

However, the high cost and stringent laboratory conditions play a big role in deciding whether or not to use organic compounds as a bactericidal agent. Biocatalysts antimicrobial agents, on the other hand, provide a safe, effective, and environmentally friendly way to control microbial activity on membrane surfaces. However, due to a dearth of inexpensive enzymes and the instability of free enzymatic reactions, this area of research is still in its early stages. As a result, current research is focused on using cutting-edge enzyme immobilization techniques, such as metal–organic framework encapsulation, to enhance the stability and recyclability of enzymes.

As antibacterial surface design advances, a smart antibacterial surface technique based on 'death release' cleverly merges the dual functions of antibacterial and antimicrobial surfaces.

In comparison to typical antibiofouling surfaces with a single purpose, such as antiadhesion or bactericidal capabilities, this proposed new technique has advanced rapidly in the previous five years. For the design of smart antimicrobial surfaces, function switching that is controlled by internal or external stimuli is critical. These principles and methodologies are promising for designing the antibacterial surface of polymeric membranes, aiming for a robust and long-term antibiofouling performance, despite the fact that such smart antibacterial surfaces are only widely used in clinical applications.

Despite significant advances, there are still a number of unresolved concerns with antimicrobial membranes. The following are some of the issues that need to be addressed. (1) To date, most antibacterial changes have been limited to a lab scale.

Because of the rigorous preparation conditions and high cost of nanomaterial functionalization, scaling up modification procedures is difficult. Furthermore, research on the actual usage of antibacterial membranes in realistic situations has been rare, implying that there are still some information gaps to fill in order to produce nanocomposite antibacterial membranes for industrial water treatment. (2) Membrane antibacterial activity assay: Because most current researchers continue to employ a static antibacterial assay approach based on traditional antibacterial agent tests, the results may fail to predict antibacterial membrane performance in a real-world dynamic water filtration process. (3) Membrane filtration behavior: antibacterial drugs can be added to improve bacterial resistance. This, however, may affect membrane filtering performance such as water flux, salt rejection, and operational stability.

To preserve or improve membrane filtration performance following antibacterial treatment, a lot of effort should be put into controlling the membrane structure. (4) Antibiofouling membranes: the actual relationship between membrane biofouling and bacterial fouling in long-term operation is yet unknown. Despite the fact that the connected bacteria are inactivated by the antibacterial membrane, the released intracellular material may supply appropriate substrates for subsequent bacterial colonization, resulting in severe membrane fouling. We believe that the creation of an anti-fouling membrane with an antibacterial function will accelerate the development of antibacterial membranes and, in turn, lead to the development of a high-efficiency anti-biofouling membrane for water treatment.

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Chapter 4
Polymeric Nano-composite Membranes for Waste Water Treatment

Venkatalakshmi Jakka and Shubhalakshmi Sengupta

1 Introduction

Environmental pollution due to anthropogenic reasons have resulted in wide spread health hazards to living organisms. Release of toxic chemicals, solid wastes, dyes, oils etc. in the water bodies have the potential to pollute the soil and water of a wide area. Thus, for providing a solution for this problem, treatment of waste water before discharge from industries, municipalities are being carried out in most of the countries. Various processes involving physical separation of pollutants, chemical treatments and bioremediation techniques are involved in waste water treatment. Various adsorbent materials are nowadays used for this purpose. Polymers and its composites belong to a group of materials having wide applicability. Various polymers and its composites specifically reinforced with nano fillers like nano-clay [55], graphene [78], carbon nanotube [91], nano-cellulose [38], nano-silica [9] have been used for this purpose. In this chapter we will discuss about polymer nanocomposite and their application in their treatment of waste water.

1.1 Polymer Composites

In our today's world polymers and its composites find wide usage owing to their economic viability, durable and lightweight structure over metals and ceramics. Therefore, the reinforcing of polymers with various inclusions (fibers, whiskers, particles etc.) is the process to improve their mechanical properties [34].

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Now a days, various reinforcing agents are used in polymers for making polymer composites with tailor-made application potential. Apart from particle reinforcement, fibre reinforced polymer (FRP) composites have various desirable properties like corrosion resistance, high mechanical strength along with resistance to environmental degradation [68]. Thus, these polymer composites with their varied properties have found their usage in industries such as automobile, aerospace, construction, biomedical, mechanical and marine [10, 58, 88].

1.2 Classification of Polymer Composites

In general, composite materials are classified based on the type of filler reinforcement. The polymer composites have the matrix comprising of polymers and reinforced with filler material of various types (particle, fibre, sheets, fragments, whiskers etc.) [2]. Classification of composites based on their on their filler reinforcement is represented in Fig. 1.

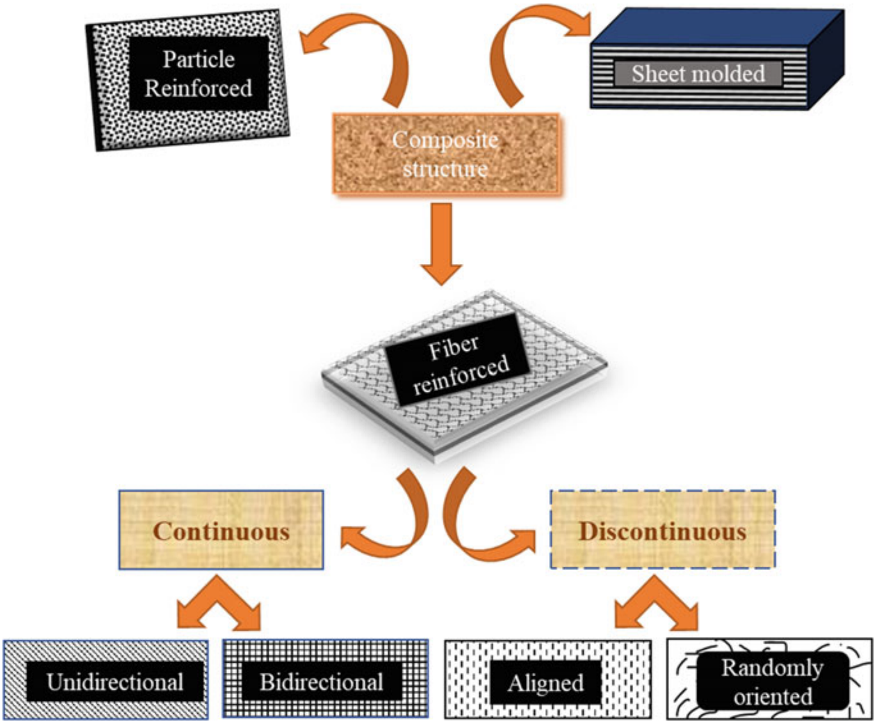

Fig. 1 Classification of composites (Reproduced from Rajak et al. [68] (open access journal))

1.2.1 Fibre-Reinforced Composites

In case of fibre-reinforced composites (FRC) different types of composites can be formed depending on the length of the fibres. Use of long fibres produces continuous composites, whereas short fibre reinforcement results in discontinuous composites. Hybrid-fibre reinforced composites have more than one type of fibre reinforced in them.

The characteristics and behaviour of the composites depend on the arrangement of the fibres and the way they are oriented [56, 62]. These fibres can be placed either be unidirectional or bidirectional in the case of continuous fibres. In case of the continuous ones they do have the required length for load transfer and reduce the brittleness of the matrix. Fibres can be natural or synthetic. Palm, rice husk, coir, banana, cotton, luffa, flax, hemp etc. are examples of natural fibres used commonly for polymer reinforcement and basalt, glass, Kevlar etc. are examples of synthetic fibres [67, 71].

1.2.2 Particle-Reinforced Composites

Particle reinforced composites (PRC) have less material strength and resistance to fracture when compared to FRC but are more cost effective and possess isotropic properties. [8, 49]. PRCs are used for many applications especially as construction materials, in manufacturing automobile parts etc. [30].

1.2.3 Sheet-Moulded Composites

The sheet moulded composites (SMCs) are fabricated by compressing the sheets together through the process of compression moulding. The laminate contains layers which increase the buckling stability with increase in the number of layers [50]. SMCs are employed in automotive body parts, where the large structural components are used [57].

1.3 Manufacturing Methods

The types of filler and matrix used for the fabrication of polymer composites and the desired properties determine the manufacturing process involved in the manufacturing process. Various manufacturing techniques are involved in reinforcing fibres and fillers in the polymers. It generally involves two steps. In the first step, Manufacturing/preparation of the fibre/filler is preformed and in second step, matrix material is reinforced with these fillers/fibers [68]. Various manufacturing processes are present for fabricating both thermoplastic and thermosetting polymer composites. This includes open moulding, injection moulding, paltrusion, compression moulding, resin transfer moulding, vacuum-assisted resin transfer moulding etc. Apart from these polymers composite membranes can be synthesized by solution casting, electrospinning etc. methods [32].

1.4 Applications of Polymer Composites

Polymers and its composites have wide range of applications. These polymers can be used as a matrix or filler or both in making various materials. Some of these materials have for mechanical applications where the use of reinforced polymer composite materials results in high rigidity and strength, light weight, better corrosion resistance and enhanced fatigue strength [52]. Owing to their varied properties these composites are also used extensively in the automobile industry [72, 84]. Polymers and their composites are extensively used in making automotive parts like tires, belts etc. They are also used in manufacturing of aircraft parts [59]. Again fibre glass matrix composites are widely used in marine transportation purposes. Use of polymer composites reduces the weight of the materials considerably. For example, the telescopic cylinder made of the polymer composite observed 50% weight reduction in the total hydraulic system used in dump truck for soil material transportation [74]. Similarly, low weight carbon fibre-reinforced silicon carbide (C-Si) composites are used for making emergency brakes in cranes, large vehicles and high-speed trains [63]. Again, flax fibre (70%) and carbon fibre (30%) were used for frames of bicycles get weighed just 2.1 kg. Automobile body parts such as dashboards, engine hood and storage tanks are made of reinforced natural fibre like flax, hemp, jute and ramie [3]. Polymer matrix composites are also widely used manufacturing medical devices. Scanners, surgical tools, lenses, implants, prosthetics etc. are made from biocompatible polymer matrix composites [88]. Polymer matrix composites are also used in manufacturing electrical materials like panels, switchgears, insulators and connectors. Even fire resistant materials are also made by using Phosphate reinforced inorganic polymer composites [17]. Apart from these polymers matrix composites are also used for making sport equipment, protective gears, industrial machine parts and in various house building construction materials [11, 64].

The polymer composites having nano-fillers have also found certain newer areas for their use. They are used as suitable food packaging materials, in tissue engineering (e.g. scaffold formation) etc. They are also used in textile industry for making UV protection clothing. They also have application in energy storage as they are used in making solar cells. Some polymer nanocomposites have use in electromagnetic interference (EMI) shielding purposes. As environmental protection is the need of the hour, polymer nanocomposite membranes are now being used for filtration, adsorption purposes for purifying water and waste water [14]. In this chapter, such use of polymer nanocomposite membranes for waste water removal and other water purifying methods have been discussed.

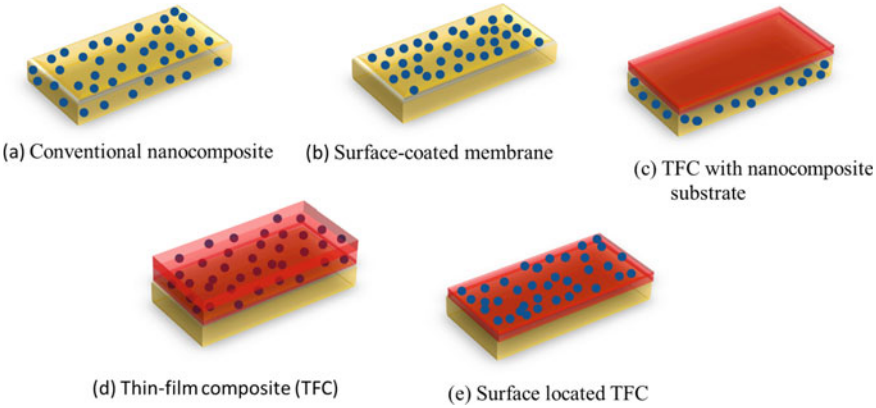

Fig. 2 Polymer nanocomposites types

2 Polymer-Nanocomposites

Reinforcement of polymer matrices with nanofillers (particles/fibres having a size range from 1 to 100 nm) imparts various unique structural, mechanical and thermal properties to it. Thus, use of nano-technology in synthesizing polymer composite membranes improves its various properties including young's modulus and tensile strength [83]. Depending upon the structural morphologies of the membrane and position of the nano-filler onto the matrix surface various types of such composites are fabricated and named accordingly as surface located membrane, conventional nanocomposite thin-film composites (TFC), TFC with nanocomposite substrate and also surface coated TFC [65, 87] These different types of composites are shown schematically in Fig. 2.

Thus, different types of polymer nanocomposite membranes are fabricated with tailor-made properties for applications in a wide spectrum of engineering needs. One such area of its wide applicability is the field of waste water treatments.

3 Polymer Nanocomposites for Water Treatment

Research on polymer nanocomposites has given various materials with applications in the field of adsorption and removal of heavy metals, dyes and toxic pollutants [5]. Various types of polymer nanocomposites exist which are able to treat waste water. Carbon-based, clay-based polymer composites are mainly used for this purpose [44, 47, 60, 81, 82].

3.1 Polymer-Carbon Composites

Carbon-based polymer nanocomposites are used as adsorbent materials owing to the distinct properties of carbon in nanoscale. Enhancement in mechanical properties, electrical conductivity and thermal stability can be achieved by using carbon-based nano-fillers in polymer composites. Different carbon nanomaterials are present depending on their shape and geometrical structures. Carbon-based materials like activated carbon, carbon nanotubes, carbon mesopheres, graphenes are used primarily for water treatment purposes. Polymer-carbon composites have high solubility in aqueous medium, higher surface area, enhanced mechanical strength and thermal stability. These properties make them suitable for waste water treatment purposes [5].

In recent study, carbon-polymer nanocomposites were fabricated by adding ultrathin single walled carbon nanotubes (SWCNT) in Au nanorods/polyisopropylacrylamide-co-acrylamide) for synthesizing SWCNT nanoporous membrane which can be used for separating oil from oil-in-water nano emulsions. Owing to their hydrophilicity with underwater oleophobicity and nono pore size they are able to achieve 99.9% efficiency in removing oil [31]. The scheme of their preparation of this nanoporous membrane is given in Fig. 3.

In another study, the carbon nano composite membrane was synthesized by using functionalized multiwalled CNTs (F-MWCNT) with ultra-porous poly(sulfone) (PSf) along with a selective layer of modified pebax. Pebax consists of softer polyether (PE) and harder polyamide (PA) segments. This polymer nanocomposite was used to separate oil from the water–oil system. The polymer nanocomposite system removed oil efficiently. It was observed that 0.5 wt% of the filler led to

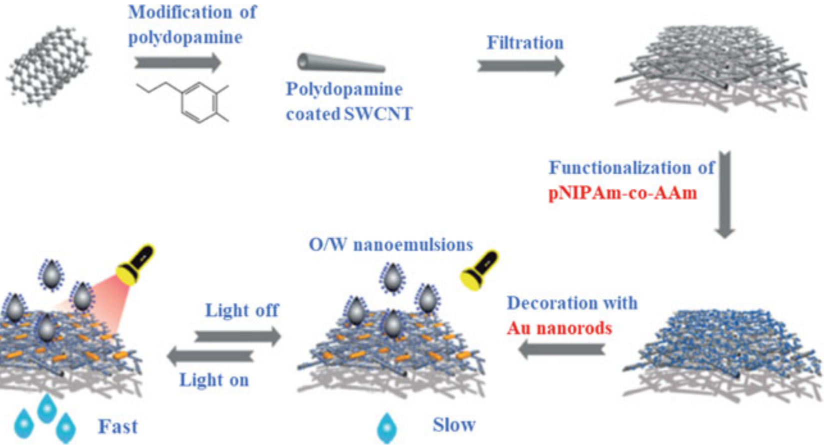

Fig. 3 Schematic illustration of synthesis of singled-walled CNTs incorporated copolymer membrane of poly(N-isopropylacrylamide)-co-(acrylamide) and their use in oil removal from water–oil mixture (Reproduced with permission from Hu et al. [31])

increased permeation by three times which was reduced by increasing of F-MWCNTs amount. It was observed that the oil rejection capacity of the membrane increased from 91.40 to 99.79% when the amount of F-MWCNTs was increased by 2.0 wt%. These results showed that CNTs known for their anti-fouling and self-cleaning properties are also capable of efficiently removing oil from the oil–water mixture when filled in a suitable polymer matrix system [69].

As seen in the previously mentioned study, the CNTs used in CNT-based composites required surface improvement for absorbing organic pollutants especially organic dyes. In another study multi-walled carbon nano tube was incorporated in polydopamine (PDA)-Poly(sodium-p-styrenesulfonate hydrate) (PSPSH) composite which was prepared using a combination of mussel inspired chemistry and Single-Electron Transfer Living Radical Polymerization (SET-LRP). In first step, PDA was coated on the Surface of CNT based on the mussel-inspired chemistry method of synthesis. In the second step, amidation and esterifcation reactions were carried out using CNT-PDA and 2-bromo-2-methylpropionyl bromide by SET-LRP method. This polymer nanocomposite showed an adsorption capacity of 174 mg g^{-1} for absorbing methylene blue dye [85]. The treatment of water by CNT-based polymer composites including desalination and water purification is given in Table 1.

Another carbon material having varied application and used as filler is graphene (Fig. 4). It is a two-dimensional carbon-based material. Graphene and its derivatives owing to their enhanced chemical and physical properties have been used extensively as an advanced membrane for wastewater treatment. One of its derivatives graphene

Table 1 Carbon-based polymer nanocomposites and their use in water remediation

Sl. No.	Type of carbon filler materials used	Method of synthesis/fabrication	Salts/dyes/contaminant removal from water	References
1	Sulfonated (MWCNT)-poly(piperazine amide)	Interfacial polymerization	$MgCl_2$, $MgSO_4$, Na_2SO_4, NaCl	[91]
2	Carboxylated (MWCNTs)-polyamide	Blending	Salt/BSA (bovine serum albumin)	[77]
3	MWCNTs with ZnO-polyethersulfone	Blending	Direct red 16 dye	[94]
4	Carboxyl MWCNTs with polyimide	Crosslinking	Rose bengal dye	[22]
5	GO-polysulfone	Blending	Bovine serum albumin	[78]
6	Ag-GO-poly (vinylidene fluoride)	Blending	*Escherchia coli* rejection	[21]
7	CNTs with iron oxide	Doping	Sodium alginate removal	[1]
8	Polyamine functionalized GO	Blending	Bovine serum albumin	[89]
9	Reduce graphene-NH_2-polyamide	Interfacial polymerization	Na_2SO_4, $MgSO_4$, NaCl, $CaCl_2$	[41]

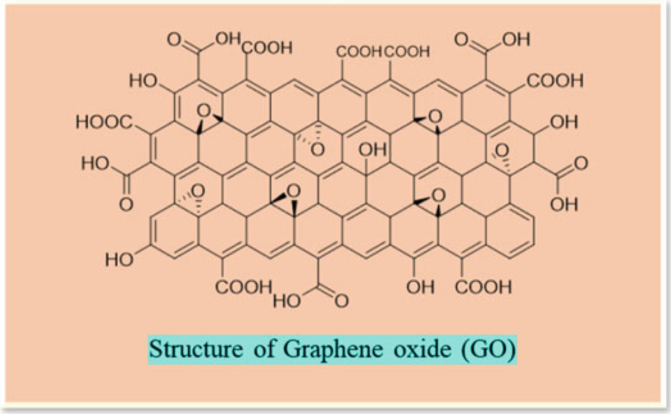

Fig. 4 Structure of graphene oxide

oxide (GO) is functionalized with oxygen containing functional groups. Hence, GO holds an amphiphilic character, hydrophilicity and large surface area and is used as an effective nanofiller for preparation of polymer nanocomposites [37, 43]. This filler also imparts selectivity, antibacterial and antifouling properties [42, 90]. Moreover, GO combines with Metal and metal oxides to form GO-based nano composites such as GO-Ag, GO-Cu etc. resulted extraordinary antibacterial property [15, 16, 41, 48]. Some examples of the GO-based composites used for water treatment (including water purification and desalination usage) are given in Table 1. These nanocomposites can be incorporated in polymer matrices for use as an adsorbent in water treatment [12]. Development of high performance membrane for water treatment was found when GO was incorporated as a filler in the polyethersulfone (PES) membrane. Improved water flux, salt rejection, heavy metal and dye removal were observed [53].

Some of the examples of carbon-based polymer nano composites were given in Table 1.

3.2 Silicon-Based Polymer Nano Composites

Silicon is one of the most abundant elements on the earth's crust. It exists in nature as sand, glass, clay etc. Silicon in general is incorporated as a nanomaterial in composites. Polysiloxane, polysilsesquioxane and polysilane are different silicon materials based on their structural properties formed from nano-silica [9]. These materials have high and low temperature resistance, corrosion resistance, low surface tension, and water repellent nature owing to the arrangement of silicon and oxygen atoms in an alternating pattern [19]. Polyhedral oligomeric silsesquioxanes (POSS) contain nanocubic organic–inorganic hybrid structure with eight organic groups surrounded by an Si–O–Si core. Therefore, POSS was referred as one of rapid most extensive designed silsesquioxanes [29]. Hybrid materials of silicon polymers that accompanied multifunctional properties have extended potential applications in wastewater treatment material manufacturing [36]. Polydimetylsiloxane (PDMS) is the most well-known example of silicon polymer, form organosilane alcohol terminated oligomers in the presence of moisture. The PDMS sponge removed the toxic azo dye Rhodamine B (RB) in water. In the presence of sun light, it removed 80% of RB dye whereas, nearly 50% of RB dye adsorption took place in the dark [28]. Functionalization of poly siloxane and polysilsesquioxane is a very convenient process and it is easily compatible with other materials. Owing to its porous structure and large surface area, it is widely developed for advanced oil–water separation flux and adsorption of ions. The synthesized blocky and porous nanoparticles (POSS nano hybrid) were found to remove methyl orange dye [45]. Moreover, silicon-based-materials reduce or degrade the halogen pollutants due to their strong electron reduction potential. They photo-catalytically degrade organic pollutants by combining with strong oxidative materials [24]. Different silicon reinforced polymer nanocomposite materials (including aerogels and sponges) used for waste water treatment are given in Table 2.

3.3 Polymer–Polymer Nano Composites

Polymer–polymer composites are also used for wastewater treatment. Polymer–polymer composites put forwarded for modulating the adsorptive properties via surface functionalization, cross linking and blending. One of the main advantage of these composites were simple preparation and removal of pollutants with its high adsorption capacity. Electrospun nanofiber synthesized from co-polymers styrene and acrylonitrile was surface functionalized and used for adsorption of the basic violet dye (adsorption capacity of 67.11 mg/g in 30 min) [20].

One of the well-known example polymer–polymer composite was synthesized by using cellulose isolated from the agriculture waste which acts as an extremely efficient polymer composite which was grafted with monomers 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of a crosslinker used for dye removal. Figure 5 showed scanning electron microscopy images of untreated and surface functionalized cellulose. This surface functionalization helped the cellulose-composite in the removal of the anionic (Congo red) and cationic (malachite green and crystal violet) dyes from industrial water at pH 2.2 and 7.0 in the time period of 8 h and 90 min, respectively [38].

Table 2 Silicon-based polymer nano-composites for water treatment

Sl. No.	Silicon containing materials	Preparation method	Contaminant removed from wastewater	References
1	L-sodium alginate/cellulose aerogels	Surface modification	Toluene	[86]
2	Silane(Si)-(melamine–formaldehyde)-(dodecyltrimethoxysilane) sponge	Surface modification	n-Hexane	[92]
3	Kaolin-modified hydrophobic melamine sponge	Surface modification	Dichloromethane	[82]
4	Polyhedral oligomeric silsesquioxane (POSS)-polyamide nanofiltration membranes	Phase inversion	$HASO_4{}^{2-}$, $SeO_3{}^{2-}$	[27]
5	Fe_3o_4@poss-sh	Chemical modification	Ag^+, Hg^{2+}, Pb^{2+}	[25]
6	Silsesquioxane-disulfide-linked polymer	Chemical synthesis	Methylene blue, reactive blue, crystal violet (CV)	[44]
7	Hybrid fluorescent porous polymer	Chemical synthesis	Reactive blue, Congo red	[40]

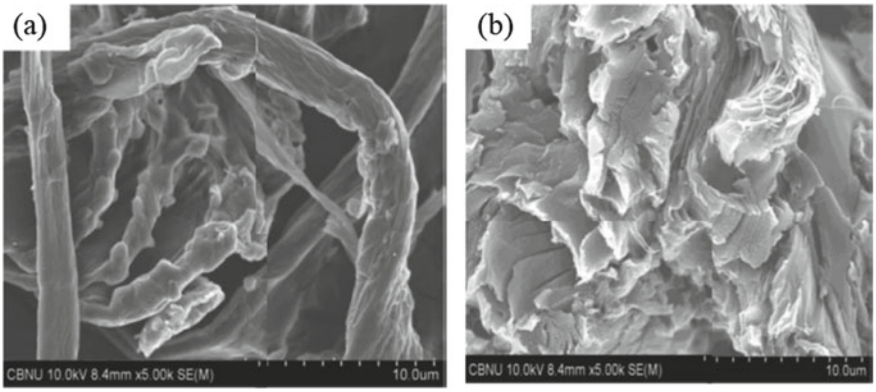

Fig. 5 SEM images of cellulose **a** before and **b** surface Functionalization of cellulose (Reproduced with permission from Kumar et al. [38])

Like cellulose, nanocellulose is also extensively used in polymer matrices to form polymeric membrane for waste water removal [33, 35, 66]. Recently a study showed that nanocellulose filled poly vinyl alcohol (PVA) composites could effectively remove fluoride from water. Thus, cellulose nanocomposites membranes could be used effectively for deflouridation purposes [13].

3.4 Polymer-Clay Composites

Clays are low cost adsorbents which are used avidly for removal of pollutants from water. Different types of clay minerals are available for this purpose. Some of the commonly used ones are montmorillonite, halloysite, vermiculite, mica and kaolinite [39, 54]. These adsorbents are mainly dependent on the surface area, porosity, and particle size. But poor water wettability and pH dependence were the limitations of the clay materials. These drawbacks were overcome by combining with polymer resins to form polymer–clay composites which were used in further applications in wastewater treatment plant in many industries [76].

Clay-based polymer composites are divided into three main types. Intercalated-nano composites are formed when polymer chains enter crystalline silicate layers. In the second type the crystalline silicates fail to phase separate then they are known as microcomposites. Again if the clay layers are separated by 1 nm size, then they are known as exfoliated nanocomposites [6]. The Clay–polymer nanocomposites (CPN) were synthesized by using different polymers like polyurethanes, Polystyrene, poly vinyl chloride (PVC), epoxies and chitosan etc. These synthesised CPN were showed vast possible applications mainly waste water treatment to remove inorganic materials like metal and metal ions, which are dangerous to the environment and humans due to their carcinogenic nature [23]. For instance, in situ polymerization of monomer methyl methacrylate with bentonite clay, iron oxide nanoparticles formed the magnetized-CPN which had an adsorption capacity of 113 mg/g of Cr(VI) [75]. Therefore, in situ polymerization of organo-bentonite and polyacrylonitrile composites also act as adsorbents and had a removal efficiency of 99.8% for Cu(II), 98.9 for Zn(II) and 97.4% for Cd(II) respectively at pH 6.0 [4].

Again, kaolinite modified with PVA was found to adsorb Pb(II) and Cd(II) with adsorption capacities of 56.18 and 41.67 mg/g, respectively. CPN successfully removed dye molecules of crystal violet, methylene blue and malachite green through intraparticle diffusion mechanism with higher removal efficiency of 94, 97, and 98%, while MMT and chitosan biopolymer removed the Congo red with the adsorption capacity of 46.9 mg/g [79]. The removal efficiency of different clay polymer nanocomposites is given in Table 3.

4 Conclusion

Polymers and their composites have unique tailor made properties which cater towards various environmental applications. Water conservation and reutilization is the need of the hour owing to the huge depletion and pollution of our water resources. Polymers and their composites have applications in diverse fields. One such application of polymeric composites is in the area of waste water treatment and water purification. Nowadays, there are various nanomaterials present which owing to their physical and chemical properties can be used as adsorbents for water remediation purposes. But, their use in large scale operations or in reactors sometimes requires their incorporation in stable, water absorbing matrices. Polymers with it's varied characteristics in many cases have proven to be a suitable matrix for such purposes. Natural polymers like cellulose, chitosan or synthetic ones like poly vinyl alcohol have been used in these regards. Various polymers with filler incorporations have been synthesized from their monomers by various polymerization techniques to form such polymer nanocomposites. These polymer nanocomposites have been studied most in the form of membranes for their water remediation processes. These membranes have the potential to remove all types of water contaminants and hold a bright future for their application in sewage treatment plants worldwide in the near future.

Table 3 Polymer-clay nanocomposites for pollutant removal

Target pollutant	Adsorbent	Maximum adsorption capacity (mg/g) or percent removal %	pH/Temperature (°C)	References
Pb (II)	CTS–Al-pillared MMT nanocomposite	99.5%	6.5/25	[18]
	Xanthated–bentonite nanocomposite (as an inorganic polymer)	99.9%	5/25	[26]
Cr (III)	Alginate–MMT nanocomposite	~100%	6/–	[95]
	Chitosan/attapulgite	27.03, 46.08, 65.36 mg/g	5/25, 35, 45	[95]
Cu (II)	Chitosan–Al-pillared MMT nanocomposite	96%	6.5/25	[18]
	Polyacrylic acid/bentonite	222.22 mg/g	–	[7]
	Cellulose-graft-polyacrylamide/hydroxyapatite	175 mg/g	7/–	[70]
Fe (III)	Alginate–MMT nanocomposite	~100%	6/–	[73]
Methyl orange	MMT/layer double hydroxide	88%	–	[93]
Methylene blue	Chitosan-g-poly (acrylic acid)/MMT	1859	6.5/–	[80]
	MMT/layer double hydroxide	74%	–	[93]
	Kappa-carrageenan-g poly (acryl amide)/MMT nanocomposite hydrogels	322.0	–	[51]
Mn (II)	Alginate–MMT nanocomposite	~100%	6/–	[73]
Crystal violet	Kappa-carrageenan-g-poly(acrylamide)/sepiolite nanocomposite hydrogels	47.0	10/ambient temp	[51]
Congo red	Chitosan/MMT	54.42 mg/g	4/30	[79]
Cr (VI)	Chitosan and nanoclay	357.14 mg/g	–	[61]
Azo dye	Chitosan/bentonite	323.6 mg/g	2/20	[46]

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Chapter 5
Membrane-Based Technologies for Industrial Wastewater Treatment

Ankita Vinayak, Neha Rathi, Poonam Kushan, Swati Sharma, and Gajendra B. Singh

1 Introduction

Rapid industrialization and urbanization have resulted in inextricable water consumption and wastewater generation. Simultaneously, a continuous supply of freshwater is another major inevitable component of human life, as most of the activities of mankind are water-dependent. Natural water resources are not sufficient to meet the water needs of the ever-increasing population. Limited water resources and water scarcity have increased the need to treat industrial wastewater to make it useful. Effectively treated wastewater can greatly supplement natural water resources [23]. Currently, various treatment methods such as coagulation, filtration, flocculation, and biological processes are being used to treat wastewater. Water reuse technologies and desalination are some other approaches used to overcome the demand for freshwater [61]. However, there is a need to improve existing technologies for the effective treatment of highly contaminated wastewater. In recent times, membrane technology has emerged as one such advanced and promising approach for the remediation of wastewater. It offers several benefits such as improved selectivity, increased life span, low cost, easy accessibility, environment friendliness, and able to exhibit excellent mechanical, chemical, and thermal stability [63]. Moreover, membrane technology eliminates the need for any harsh chemicals or harmful products during the water treatment process.

Being simple and cost-effective in nature, membrane technology plays an important role in seawater desalination, and the treatment of drinking water and industrial wastewater. The major force responsible for separation via membrane is pressure. Based on pressure-driven forces, pore size, and mechanism, membranes are categorized as ultrafiltration, microfiltration, nanofiltration, and reverse osmosis [87].

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Based on the composition, membranes are classified as inorganic and organic (polymeric) membranes. Both inorganic and polymeric membranes are extensively used for the treatment of industrial wastewater [41]. Inorganic membranes such as silica and zeolite membranes are used for water treatment technologies. These membranes are highly resistant to environmental conditions, but difficulty in handling, high cost, catalytic nature, and poor size control make them less efficient for wastewater treatment [91]. In contrast, polymeric membranes are considered as favorable and superior membranes for wastewater applications because they are highly adaptable, stable, and resistant. The membrane properties such as pore size, monomers, additives, casting condition, and concentration can be controlled in polymeric membranes [51, 91]. Various naturally occurring and chemically synthesized polymers are employed for the fabrication of polymeric membranes. Salahi and co-workers assessed the treatment of Tehran refinery oily wastewater using cross-flow membrane filtration [71]. The performance of five different polymeric membranes of polysulfone and polyacrilonitrile including ultrafiltration and microfiltration was compared and evaluated. Among all, the polyacrilonitrile (100 kDa) ultrafiltration membrane was found to be suitable and effective for the reduction of turbidity, TSS, oil grease content, and TDS of oily wastewater [71]. The chapter tends to discuss various polymeric membrane materials, industrial wastewater, sources of wastewater generation, and its toxicity on plants, animals, and humans. The possible ways of wastewater treatment through polymeric membrane-based technologies are also discussed.

2 Industrial Wastewater

A huge amount of water is used as raw material for various industrial applications. Industrial processing releases a large volume of effluent, rich in various dissolved and suspended solids, into the water bodies, termed industrial wastewater [59]. The composition of industrial wastewater depends on the type of industry and product processing. Common pollutants found in industrial wastewater are heavy metals, pesticides, chemicals, salts, oil, free radicals, and other by-products (Fig. 1) [5, 74, 81]. Broadly, based on the nature of pollutants, industrial wastewater is divided into organic and inorganic industrial wastewater [32]. Effluent from industries such as textile, pharmaceutical, brewery, tannery, cosmetics, leather, food, organic dyestuff, and oil refineries contain organic wastewater. These industries mainly use organic raw materials for chemical reactions which ultimately release organic contaminants into wastewater such as phenols, herbicides, and hydrocarbons [96]. For instance, the brewery industry—one of the important components of a country's economy—releases a large number of organic contaminants. Brewery wastewater is generated by the use of various substrates such as yeast, grains, sugars, salts, and solids during the manufacturing phase [12]. In addition to the manufacturing steps, these contaminants also build up during filtration, washing, cleaning, and downstream. Due to the consumption of freshwater during various wet processing operations, the textile industry is also considered a major creator of industrial wastewater. On average,

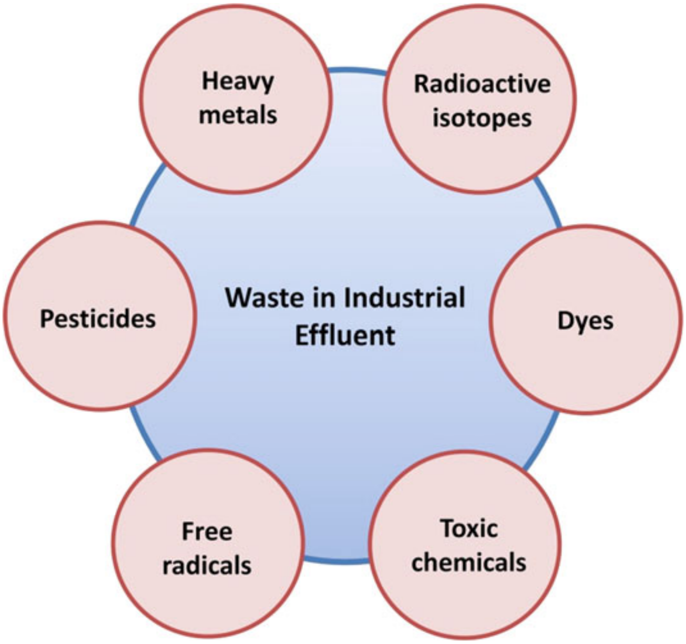

Fig. 1 Various types of pollutants in industrial wastewater

the textile industry consumes 200 L of water for the processing of 1 kg of fabric. According to reports, the textile dyeing industry alone releases 17–20% of industrial wastewater [35]. The discharged effluent contains chemicals such as salts, surfactants, alkalis, oils, dyes, hydrogen peroxide, and starch [82–84, 89]. Depending upon the type of processing and application, the concentration of contaminants may vary in mill effluent. Diverse forms of organic contaminants are contributed by food industry effluent which includes fruit, vegetable, meat, seafood, and dairy sectors. Food industry waste is generated in three forms—solid, semi-solid, and liquid. Solid waste consists of bread, vegetable residue, soybean, inedible dough, fruit pulp, and peel. Liquid wastes are generated due to the consumption of water during food processing such as cleaning, cooking, temperature control, and transportation. The liquid effluent is composed of organic matter, fats, oils, suspended solids, and various forms of nitrogen [4]. Both solid and liquid wastes are rich in cellulose, lignin, starch, and sugars (mainly glucose and fructose). The high load of organic contaminants and suspended solids in effluents elevates BOD and COD levels, subsequently posing a threat to aquatic flora and fauna [40]. The inorganic pollutants of industrial effluent mainly include toxic non-biodegradable metals such as cadmium, arsenic, lead, chromium, and mercury. Significant amounts of toxic heavy metals are released from various industries such as paint, mining, electroplating, tanneries, and alloy industries [56]. Hang and group [33] studied the characteristics of sediments of electroplating plants for the accumulation of heavy metals. The results showed high content of copper, zinc, manganese, chromium, and nickel in sediments near the site of a plant [33]. In another study, Bhutiani and co-workers [16] studied the quality of groundwater in industrial areas of North India. The percentage of five heavy metals—chromium, cobalt, iron, zinc, and nickel—was assessed in groundwater locations in and around Integrated Industrial Estate (IIE) Haridwar. The presence of cobalt, iron, zinc, chromium, and nickel, beyond permissible limits, was reported in more than 90% of the samples collected.

3 Toxicity of Industrial Wastewater

The presence of toxic contaminants in industrial wastewater is deleterious to both the environment and living beings. Industrial effluents damage the aesthetic quality of water, and also negatively affect aquatic organisms. Waste seepage into agricultural land and groundwater alters plant growth and enters the food chain which eventually affects animals and humans [5, 82]. Heavy metals and dyes are considered as major persistent pollutants of discharged effluent [14, 15, 83, 84]. Both are reported to be carcinogenic, mutagenic, and teratogenic. Intake of these toxic contaminants causes detrimental health issues such as organ damage, reduced development, and growth [5]. Most of the pollutants are recalcitrant, poorly degradable, and even during treatment get transformed into another toxic form. For instance, heavy metals such as zinc, cadmium, nickel, and cobalt released in effluent accumulate in parts of plants, ultimately affecting human health like various metabolic pathways and functions [56]. Cadmium is a non-essential toxic heavy metal, which poses considerable toxic effects on the human organ system. Intoxication of cadmium induces epigenetic mutations in DNA expression, apoptosis, and oxidative stress, and can damage the skeletal system, liver, cardiovascular system, and kidney [28]. Adimalla and Wang [3] conducted a study to evaluate the toxicity of heavy metals on human health. Toxicity was assessed in terms of various parameters such as lifetime cancer risk, hazard quotient, geo accumulation, and ecological risk index. Results indicated that metals such as nickel, lead, zinc, arsenic, and copper were within permissible limits while the concentration of chromium was higher than the recommended limit in most of the soil samples. Lifetime cancer risk index was also higher in the case of arsenic and chromium, indicating the carcinogenic risk of metals [3]. Thus, intake of toxic heavy metals poses several risk complications in adults and children.

4 Polymeric Membrane-Mediated Industrial Wastewater Treatment

The harmful impact of industrial wastewater raises the imperative need to find better treatment methods. Industrial effluents can be effectively treated with polymeric materials. These materials can be used as filters, flocculants, composites, and membranes for processes such as filtration, flocculation, oxidation, adsorption, and biological and chemical treatments. Membranes assembled with renewable resources such as alginate, cellulose, gum, pectin, and chitosan are more sustainable than conventional ways as they are greener, biocompatible, easy to use, non-toxic, and biodegradable (Table 1).

Table 1 Biopolymer-derived materials and their application in wastewater treatment

Biopolymer	Biopolymer-based modified material	Applications	References
Cellulose	Cellulose acetate/polybenzoxazine cross-linked electrospun nanofibrous membrane	Separation of organic micro-contaminants	[26]
	Superhydrophobic block copolymer on the cellulose membrane	Separation of water from oily/particulate phases	[43]
	Jute cellulose nanowhiskers coated on PAN ES fiber mats	Industrial wastewater treatment	[19]
	Cellulose voronoi-nanonet membranes	Removal of sub-micron-size contaminants (pathogenic microbes)	[78]
	Titanium-doped activated carbon cellulose	Crystal violet and methyl violet removal	[53]
	CA/MOFDPC membrane	Removal of methylene blue, recyclable	[77]
	Magnetic partially carbonized cellulose nanocrystals	Pesticide removal, recyclable	[90]
	Macroporous Cu-MOF@cellulose acetate membrane	Pesticide removal	[2]
	Bacterial cellulose membrane modified with EDTA (BCM@APTES-EDTA)	Removal of radioactive isotope—Sr (II)	[22]
	DA@PDA composite nanofiber membrane	Adsorption of methylene blue	[21]

(continued)

Table 1 (continued)

Biopolymer	Biopolymer-based modified material	Applications	References
Chitosan	Anti-bacterial chitosan/zinc phthalocyanine fibers	Reduction of 4-nitrophenol, methyl orange, congo red	[9]
	Chitosan film cross-linked with epichlorohydrine, modified with MIL-125-NH_2	Removal of radioactive iodine	[25]
	CS/PVA modified using polyethyleneimine	Removal of Ni^{2+}, Cu^{2+}, Cd^{2+}	[70]
	Chitosan nanofibrous membrane	Adsorption of acid blue 113	[48]
	Cellulose/chitosan nanofiltration membrane	Retention of methyl orange, methyl blue, salts	[88]
	Graphene oxide nanoribbons/chitosan composite membrane	Removal of radioactive uranium	[36]
Alginate	Porous calcium alginate membrane	Removal of methylene blue	[50]
	Nanofibrous alginate membrane coupled with nanowhiskers	Removal of chromium and 10–100 nm-sized contaminants	[58]
	Sodium alginate-based nanocomposites membrane	Isopropanol removal	[52]
	Bentonite/alginate adsorbent	Removal of heavy metals and dyes	[10]
	Hybrid membrane of sodium alginate and graphene oxide	Great pervaporation ability	[18]
	Nanocomposites of sodium alginate and zinc oxide	Removal of Congo red, methylene blue dye	[24]
	Silica-alginate hybrid membrane	Removal of cadmium	[13]
	Alginate-based attapulgite foams	Removal of heavy metals	[86]
	Alginate nanofiber membrane	Adsorption of methylene blue	[85]
	Metal oxide framework of sodium alginate and $Ca(NO_3)_2$	Removal of tetracycline pollutant	[98]

(continued)

Table 1 (continued)

Biopolymer	Biopolymer-based modified material	Applications	References
Guar gum	Hybrid membranes using polyvinyl chloride and guar gum	Reduction of membrane fouling	[7]
Pectin	Iron-loaded pectin hydrogels	Separation of arsenic	[45]
	Pectin-based interpenetrating membrane	Removal of methylene blue	[39]
Gelatin	Gelatin-based nanocomposites with carbon nanotube and magnetite nanoparticles	Adsorption of methylene blue and direct red 80	[69]
	Gelatin-based encapsulation matrix	Adsorption of reactive red 195A	[17]
Pullulan	Pullulan-based polyacrylamide hydrogels	Removal of cationic and anionic dyes	[68]
Zein	Zein-based SiO_2/zein/PAN nanofibers	Separation of oil/water contaminants	[79]
	Zein/nylon 6 nanofiber membrane	Removal of cadmium	[11]
Polyvinyl alcohol	Chitosan/PVA/zeolite composite membrane	Removal of nickel, ferrous, chromium	[31]

4.1 Cellulose-Based Membranes for Wastewater Treatment

Cellulose is the most abundant organic polymer, made up of repeating units of D-glucose produced by plants, certain algae, bacteria, and fungi. Glucose units in cellulose are bound together by glycosidic linkages. Hydroxyl groups in cellulose are the point of modification because they are reactive and provide hydrophilicity to the cellulose [34]. Conventionally, cellulose has been used in the form of wood, plant fibers, cotton, etc., until the elucidation of the polymeric structure of cellulose. Typical properties like chirality, hydrophilicity, chemical variability, and degradability make cellulose membrane (CM) the best alternative for non-biodegradable petroleum-based polymer films [42]. The CMs have been modified to make them antifouling membranes for oil/water separation and for filtering waste and thiol-based odorant materials. In one research study, the hydrophilic nature of CM was changed to hydrophobic using the technique reversible addition-fragmentation chain transfer and a copolymer poly{[3-(trimethoxysilyl) propyl acrylate]-block-myrcene} synthesized on it by "grafting-from" procedure [43]. The result demonstrated that myrcene in CM blocked thiol contaminants resulting in a pleasant odour and was also able to separate organic micro-contaminants from water.

Fabrication of cellulose-based absorbent membranes from inorganic industrial wastes as raw materials can be a cost-effective approach for the removal of organic pollutants. Recently, Maqbool and group [53] prepared three nanomaterials, i.e., NCel (Nanocellulose), Ti-ACNs (Titanium-Doped Activated Carbon Nanostructures), and a combination of both Ti-AC-Cel-NC (Titanium-Doped Activated Carbon Cellulose Nanocomposite) from organic and inorganic industrial waste. Ti-AC-Cel-NC showed efficient removal of pollutants like crystal violet and methyl violet via surface adsorption and photocatalysis. The increased surface area and homogenous Ti-ACN distribution with nanocellulose give polymer structures a four-fold higher efficiency for dye removal [53]. Heavy metals such as titanium, iron, aluminum, and copper can be effectively removed from industrial wastewater by converting them into metal salts, which will ultimately reduce environmental pollution. Tang and co-workers [78] reported the synthesis of cellulose voronoi-nanonet membrane possessing small and uniform pores, tightly bonded with NMF substrate. Non-solvent induced phase separation method was used to form a microfiltration membrane exhibiting high porosity, high rejection efficiency, ultrathin thickness, good interconnectivity, and excellent permeation flux at low pressure. The membrane could intercept submicron particles of nearly 0.3 μm with rejection efficiency $>99.80\%$ and showed outstanding antifouling function [78]. Heavy metal ions like Pb(1l), Zn(1l) could be removed from wastewater through a combination of ion-exchange methods and electrostatic attraction. Alpha zirconium phosphate nanoparticle (α-ZrP-n) solutions were coated on cellulose membranes to form an α-ZrP-n membrane which possesses a strong negative charge. Efficiency of the pristine membrane and α-ZrP-n membrane was compared and was found that the mechanical strength of pristine was 3.4, and 4 MPa that of α-ZrP-n. However, the removal efficiency for metals Cu (II), Ni (II), Zn (II), and Pb (II) did not increase with the increase in the concentration of α-ZrP-n [38]. Radioactive isotopes ^{90}Sr, ^{60}Co, and ^{137}Cs have high solubility and long half-lives. Exposure to radionuclides can lead to serious health issues. Adsorbent membranes of chitosan, nano zeolite, and cellulose are used for the removal of radioactive metals from wastewater as they are affordable, biodegradable, and easy to use. Using (3-aminopropyl)triethoxysilane (APTES—a cross-linker), the bacterial cellulose membrane was modified with EDTA to remove Sr^{2+}. In a separate study, a three-layered bacterial cellulose membrane "@APTES-ethylene diamine tetra acetic acid" (BCM@APTES-EDTA) having nanofibers of size <100 nm was synthesized. The maximum adsorption capacity of the membrane was 44.86 mg/g. FTIR and XPS spectra of BCM@APTES-EDTA showed its active participation in the adsorption of Sr^{2+} [22].

Being a major industrial pollutant, various membrane-based approaches are reported for the treatment of dye-containing industrial effluent. In [30], Gopakumar and colleagues conducted a study, for the adsorption of positively charged crystal violet (CV) dyes and Fe_2O_3 using an adsorbent material prepared from cellulose nanofibers (CNFs). Meldrum's modified cellulose nanofiber-based PVDF nanofibrous membrane was prepared using Meldrum's acid using a nonsolvent-assisted methodology. It was the first report on nonsolvent-assisted surface modification of cellulose. To increase the temperature tolerance of polymeric nano-porous membranes, there is a need to enhance the thermal properties of membranes. As mechanical properties of cellulose acetate membranes can be modified by inorganic nanomaterials such as nanofiller, the adsorption and thermal properties of the pristine cellulose acetate (CA) membrane were increased by cross-linking it with polybenzoxazine (BA-a). It was performed by varying the concentrations of CA and BA-a in an electrospinning solution and adding CTR (cross-linking agent) into CA10/BA-A5 mixture which had a high BA-a level. Treatment with polybenzoxazine changed properties of membranes like low water absorption, high glass transition temperature, and near-zero volumetric, making it a potential candidate for fabrication at the nanoscale [26]. Cellulose membranes have been modified through various approaches such as deacetylation and polymerization for better surface properties. In a study, a modified version of deacetylated cellulose acetate (DA) nanofibrous membrane showed 8.6 times higher adsorption capacity than DA nanofibers [21]. DA nanofiber's surface was coated with uniform polydopamine to form a composite nanofiber, i.e., deacetylated cellulose acetate polydopamine (DA@PDA) by electrospinning method. The morphology of DA@PDA membrane, its surface chemistry, adsorption mechanism, and effects on methylene blue were also studied. In another study, cellulose acetate filter paper together with titanium dioxide supported the formation of nanocomposites (AgCAF and $AgTiO_2$) and *Duranta erecta* leaf extract was used as a reducing agent. The impregnation method was used for the synthesis of material, and the applicability of catalysts was tested on a methyl orange dye and nitro compounds like 4-NP (4-nitrophenol), 2-NP (2-nitrophenol), trinitrophenol, and 2-NA (2-nitroaniline). Prepared nanocomposites AgCAF and $AgTiO_2$ proved to be excellent catalysts with high stability, easy recovery, and excellent adsorbent for dyes [8].

There are several methods for removing pesticides from wastewater for example photocatalytic degradation, bioremediation, and adsorption. Adsorbents like activated carbon, quartz, and gold nanoparticles are used for the removal of organophosphorus pesticides, however, they have applicability limitations due to cost and compatibility. In comparison, porous membranes have advantages like recyclability and better adsorption. MOF (Cu-BTC@CA) membrane was prepared with different ratios of Cu-BTC to evaluate the adsorption efficiency of dimethoate. Porous CA membrane was synthesized and further Cu-BTC was in situ prepared using a CA membrane. An increase in adsorption capacity from 207.8 mg/g (with CA) to 282.3–321.9 mg/g (with Cu-BTC@CA) was observed [2]. Cu-BTC@CA membranes showed recyclability and efficient pesticide removal. In another study, microcrystalline cellulose was treated with sulfuric acid and loaded with Fe_3O_4 nanoparticles to form MPC-CNC (Magnetic partially carbonized cellulose nanocrystals). MPC-CNC was used to extract 5 triazinse (prometryn, terbutryn, simazine, ametryn, and atrazine), 5 triazoles (triadimenol, triadimefon, myclobutanil, epoxiconazole, and tebuconazole), and herbicides. Fe_3O_4/CNCs showed 90% pesticide adsorption from contaminated water [90]. Even after 9 cycles, the adsorption efficiency of nanocrystals was maintained and had a strong anti-interference ability.

4.2 Chitosan-Based Membranes for Wastewater Treatment

The second most abundant biopolymer after cellulose is chitin, which is present mainly in the exoskeleton of arthropods, crustaceans, and to a lesser extent in fungi. Chitosan is synthesized by hydrolysis of N-acetyl groups of chitin under alkaline conditions. It is soluble in organic acids with a pH of less than 6 but insoluble in water and organic solvents [27]. Chitosan is biodegradable, less toxic, and an economical material, however, it possesses low thermal stability, low porosity, and poor mechanical strength. To increase the functionalization of chitosan, certain modifications like alkylation, acylation, oligomerization, phosphorylation, and enzymatic modifications are carried out. Cross-linking of chitosan using reagents such as glyoxal and glutaraldehyde is often performed to increase their mechanical strength. Chitosan gel beads, films, fibers, nanoparticles, and membranes are synthesized for various industrial applications such as drug delivery, food industries, cosmetics, tissue regeneration, and wastewater treatment [55, 62].

Chitosan-based materials and membranes are commonly used for the removal of contaminants from industrial wastewater. Removal of pollutants such as radioactive waste through chitosan materials is mainly due to adsorption because it is cost-effective, selective, easy to operate, and requires less energy. Certain pre-treatments are performed for the synthesis of effective chitosan membranes to increase the adsorption capacity. Graphene is one such widely used material for the preparation of nanomaterials due to its high surface area, electrical conductivity, and good mechanical strength [44]. Hu and group [36] reported the encapsulation of chitosan (CTS) into graphene oxide nanoribbons (GONRs) to form GONRs/CTS composite membranes. The incorporation of CTS increased the adsorption sites on GONRs. X-ray diffraction, Fourier transform infrared spectroscopy, and SEM were used for the characterization of GONRs/CTS composite membranes. Adsorption through the modified membrane was rapid, spontaneous, pH-dependent, and endothermic, following the pseudo-secondary kinetics and Langmuir models. The adsorption capacity of GONRs/CTS was found to be 320 mg/g, and it could remove uranium-containing radioactive wastewater [36]. Being a highly stable structure, cross-linked chitosan metal–organic framework (MOF’s) composites are used for the removal of radioactive metals such as iodine. El-Shahat et al. conducted a study on the removal of iodide using modified chitosan films. Chitosan was cross-linked with epi-chlorohydrin and then covalently modified with MIL-125-NH_2. The adsorption capacity of cross-linked chitosan membrane for iodide was found to be 399.68 mg/g, suggesting it to be a better adsorbent for industrial pollutants [25]. Another research study reported the preparation of chitosan microspheres using the process of emulsion polymerization, for the removal of iodine. FTIR, SEM, BET, and TGA were used to study the pH, recyclability, and adsorbent dosage of chitosan microspheres. Results showed that the adsorption capacity of I^- was 0.8792 mmol/g and microspheres performed best in the pH range of 4–10. Chitosan microspheres were able to regenerate for 5 cycles while maintaining high efficiency. Thus, microspheres are found to be a promising tool for the removal of iodine from nuclear waste [93]. Heavy metal removal was also studied by CS/PVA, synthesized using polyethyleneimine (PEI). PEI has a large number of amine groups, and its blending with CS/PVA results in increased adsorption sites, ultimately increasing its adsorption capacity. However, excess PEI has reversible effects like decreased membrane porosity and efficiency. Results showed that the removal efficiency of the formed membrane for Ni^{2+}, Cu^{2+}, and Cd^{2+} was more as compared to activated carbon. ΔG and ΔH negative values showed spontaneous and exothermic adsorption. Also, the regeneration and recyclability of the membrane in the EDTA solution were successful [70]. In 2017, Ali and research group prepared zero-valent metal NPs, using pellets—chitosan/zinc phthalocyanine (CS/ZnPc, and chitosan membrane. 5 wt% of ZnPc was dispersed in CS solution to synthesize pellets of ZnPc-CS composite fibers. For developing metallic and bimetallic zero-valent NPs, ZnPc-CS was used as a host material and for adsorption of metal ions, it was kept in 0.1 M metal salt solution. Metal NPs were loaded onto ZnPc-CS composite fibers, and pellets were formed via water-based in situ preparation. FE-SEM, XRD, and FTIR confirmed the presence of metal nanoparticles on composite fibers. Prepared composites were found to be excellent catalysts for the reduction of 4-nitrophenol, congo red, and methyl orange. Recyclability, high anti-bacterial activity, ease to use, and low cost make them a potential tool for wastewater treatment [9]. Chitosan nanocomposites are also commonly employed for the removal of dye molecules from wastewater. Through the process of adsorption nanocomposites like CS/Polyaniline/CdS, CS/PVA/ZnO, CS/SiO_2/CNT, CS/lignin/titania, CS/Bio-silica was formed for the removal of Reactive Blue-19 [67], Acid Black-1 [46], Direct Blue-71, Reactive Blue-19 [1], Brilliant Black [54], and Acid Red 88 [76], respectively.

The electrospinning method was used to prepare chitosan nanofibrous membranes exhibiting an average diameter of 86 ± 18. The membrane was able to adsorb acid blue 113 dye, exhibiting an adsorption capacity of 1377 mg/g, higher than the chitosan microscale sample having only 412 mg/g adsorption capacity. Adsorption behavior was found to fit with the Langmuir isotherm model and followed pseudo-second-order kinetics. Chitosan membrane showed potential in the long-term treatment of wastewater as it was showing good regeneration capacity even after 4 cycles [48]. Chitosan-TiO_2 nanocomposite (CTNC) was prepared by sol–gel method for selective removal of Rose Bengal dye. Rose Bengal dye used to treat eczema and psoriasis is a contaminant and in high concentrations, it causes blistering, itching, or redness on the skin. Mesoporous nanoparticles facilitate dye uptake in the cavities of prepared CTNC imprinted polymer. The membrane showed effective removal of dye with good recyclability and stability [6]. Similarly, for the removal of copper ions, chitosan grafted porous poly L-lactic acid (P-PLLA) nanofibrous membrane was developed using polydopamine (PDA). The p-PLLA fibers were collected as nanofibrous membranes after being electrospun. P-PLLA, PDA was used in uniformity to enhance the stability, performance, and coating of membranes. P-PLLA membranes have a high surface area and PDA, and chitosan has abundant amino groups which resulted in the efficient removal of copper (Cu^{2+}) ions [99].

4.3 Alginate-Based Membranes for Wastewater Treatment

Alginate is a linear anionic copolymer with irregular units of β(1–4)-linked mannuronic acid and α (1–4) guluronic acid, bound by glycosidic bonds. It is derived from various sources of brown seaweeds such as *Ascophyllum nodosum, Macrocystis pyrifera,* and *Sargassum* spp. using Na_2CO_3 to yield sodium alginate [65, 80]. Alginate is an eco-friendly, stable, non-toxic, non-immunogenic, biodegradable polymer exhibiting water permeability potential. These properties enable alginate to be used in textile industries, food industries, and biomedical fields for various applications. Most importantly, alginate is used for the removal of synthetic dyes, nanoparticles, and heavy metals from wastewater, which is extremely toxic to the environment and living organisms. Adsorption of contaminants is conferred to the presence of the carboxylic group which runs along the polymeric chain of alginate [10, 60, 66].

With certain pre-treatment and modifications, alginate membranes can be efficiently exploited for remediation purposes. Li and co-workers [50] fabricated a porous sodium alginate membrane using the freeze-drying method in which sodium ions are replaced by calcium ions via cross-linking reaction. Modified calcium membrane was utilized to remove dyes from wastewater released by paper, textile, cosmetics, and food industries. Newly formed calcium alginate membrane provides active sites, which are easily accessible for ion diffusion and better adsorption of toxic dye molecules. The adsorption potential of the membrane was assessed for the removal of methylene blue dye from wastewater at various abiotic parameters such as contact time, temperature, pH, and dosage. Results showed that a modified calcium alginate membrane can be effectively employed for the removal of methylene blue dye from industrial wastewater at optimum conditions [50]. Another approach for modification of alginate membranes is coupling with nanowhiskers of maize cellulose. They act as a barrier layer for selective filtration in ultrafiltration or microfiltration. Sodium alginate is initially blended with polyethylene oxide, washed repeatedly using $CaCl_2$, and prepared for final layering on a stalk of maize nanowhiskers. The resultant membrane completely removed contaminants based on their size; filtered molecules were then retained on the interconnected structure of the membrane for final adsorption [58]. In another approach, the membrane of calcium alginate is modified to filter out dyes and cadmium ions from wastewater using kaolin powder. The powder easily gets dispersed into water, facilitating filtration of pollutants by alginate membrane through the formation of stable suspension [95]. Alginate membranes can be used in the form of nanocomposites with appropriate pore-sized nanoparticles. The compatible properties of both nanoparticle and polymeric host matrices such as their flexibility, adsorption properties, chirality, anti-microbial properties, and eco-friendly nature make them a potential tool for wastewater treatment [94]. Heteropolyacid structures have hydrated protons which offer increased hydrophilicity and selectivity for water molecules and hence can be incorporated into the sodium alginate membrane forming a nanocomposite membrane. The membrane can be further used for the separation of contaminants from industrial wastewater. Isopropanol is extensively applied in various industries such as a cleansing agent in electronic industries, for solvent extraction, and for the manufacture of acetone and hydrogen peroxide. Isopropanol removal from industrial wastewater becomes difficult as it forms azeotrope at 12.2% in discharged effluent. Different concentrations of heteropolyacids—6, 8, and 10 wt%—were used with sodium alginate for membrane formation which was then tested for pervaporation segregation ability. The nanocomposites with 6 wt% heteropolyacids showed the highest selectivity for isopropanol sorption from wastewater [52]. Additionally, nanocomposites can also be formed by the electrospun method which allows easy fabrication of nanoparticles of interest with alginate without requiring many pre-treatments. Fabrication using the electrospun method was performed by Dodero et al. [24] to obtain nanocomposites of zinc oxide and sodium alginate for the removal of congo red and methylene blue. Dyes are released in excess amounts from the textile, printing, pharmaceutical, and plastic industries. The dye-containing water is lethal to the environment due to the carcinogenic and mutagenic nature of dyes. Apart from being a cost-effective and easy approach to nanocomposite production, electrospun using zinc oxide offers the advantage of the anti-bacterial property that allows the reuse of nanocomposite membrane. Results of the study indicate a similar affinity of both dyes toward nanocomposite membrane even though both the dyes had different chemical structures and bind at the same binding sites of nanocomposite membranes [24]. Interpenetrating polymeric network or IPN is another type of composite system for the adsorption of heavy metals and dyes from wastewater. In one research report, Al-Sakkari et al. [10] prepared beads of bentonite/alginate by ionotropic gelation as an adsorbent for dyes and heavy metals. The resultant beads could be reused multiple times for the separation of methylene blue from a sample of industrial wastewater. Real wastewater from the tannery industry was tested to examine the potential of beads. Results showed complete removal of heavy metals and up to 40% removal of dyes using IPN [10]. Recently, graphene oxide-polymer hybrid membrane has drawn attention because of their great applicability in pervaporation and water purification. Water purification is conferred to the presence of transport channels in the membrane of graphene oxide which helps in selective penetration. Hybrid membranes of sodium alginate can be prepared with pristine graphene oxide and reduced graphene oxide against an ethanol/water mixture. The hybrid membrane has the advantage of antifouling properties and enhanced water flux for ultrafiltration. The membrane was then tested for water permeation, and results indicated the optimal pervaporation ability of pristine graphene oxide at 2.0 wt% and that of reduced graphene oxide at 1.6 wt% with separation factors 1559 and 1566, respectively [18]. Another hybrid using an alginate/ceramic membrane was formed for the removal of cadmium, a lethal persistent metal ion from wastewater that can cause blood and skeletal damage in living organisms. Using ceramic membranes with alginate adds the benefit of high throughput results at low pressure. Membrane modification begins by first modifying all three commercially available membranes of silica (pore size 1), zirconia (pore size 3), and alumina (pore size 10) with alginate of different sources. Commercially available alginate from *Macrocystis pyrifera* source was used for silica along with zirconia and that extracted from the source *Laminaria digitate* was used for alumina. Following this, an aquatic solution (0.2% w/v) of both types of alginates was made and added to the pores of the microporous silica, zirconia, and alumina membranes. In certain cases, alginate leach into the effluent, to prevent this epoxy-silane is used as a cross-linking agent improvising the binding ability of a metal to the membrane. Silica-alginate-modified hybrid membrane showed the best metal removal ability from all three hybrid membranes [13].

The practical use of sodium alginate becomes costly at a large scale, and it also exhibits low mechanical strength. To overcome these barriers, attapulgite, having two layers of Si–O tetrahedron and one layer of (Al, Mg, Fe)–O–OH octahedron, is used in association with sodium alginate. Attapulgite is basically immobilized on a sodium alginate membrane resulting in the formation of floatable attapulgite foams. These attapulgite foams efficiently removed heavy metals from a sample of wastewater and could also be reused [86]. Since the benefits of alginate membranes in dye removal are numerous, Wang and co-workers [85] investigated other samples such as seawater, and highly acidic and highly alkaline solutions, to assess the effectiveness of alginate in dye removal. Three different varieties of nanofiber membranes were made using alginate via the electrospun method. In addition, these three nanofiber membranes were produced by three different cross-linking approaches, namely calcium chloride cross-linking, glutaraldehyde vapor cross-linking, and trifluoroacetic acid cross-linking. It was performed to establish any possible relation between cross-linkers and efficient adsorption rate under various environmental conditions. To test the cationic dye adsorption abilities of these nanofiber membranes, methylene blue dye was used as a model dye. Overall, the optimal adsorption performance of all three nanofiber membranes was observed in the pH range of 4–10. Among all, glutaraldehyde vapor-linked nanofiber membranes showed excellent results in both alkaline and seawater conditions [85]. Further, Zhuang and group [98] used another single-step modification approach for the utilization of alginate membrane in wastewater treatment. Highly porous metal–organic frameworks of alginate and $Co(NO_3)_2$ are prepared in a single step to target tetracycline pollutants. Initially, diffusion of tetracycline is fast and then gradually it reaches equilibrium in 16 h. On the whole, the membrane showed great adsorption ability and reusability [98]. A limitation, viz. fouling of membrane hampers their long-term applicability and prevents their reuse. It mainly occurs due to the accumulation of oily contaminants in the pores of membranes, which in turn requires some physical or chemical cleaning, leading to an overall increase in operational cost and declining the efficiency of wastewater treatment.

Alginate when used as membrane coating enhances membrane survival in harsh conditions as well as shows great antifouling results, serving as an ideal material for industrial wastewater treatment [37].

4.4 Other Organic Materials-Based Membranes for Wastewater Treatment

Apart from cellulose, chitosan, and alginate, several other biopolymeric membranes are known which exhibit varying adsorption potential for the treatment of industrial wastewater. Guar gum, consisting of linear chains of D-mannopyranosyl along with D-gal-actopyranosyl, is a natural, biodegradable, mucoadhesive, water-soluble polysaccharide; it is obtained from guar beans endosperm. In recent years, guar gum is commonly employed in wastewater treatment due to its sustainable, antibacterial, inexpensive, eco-friendly, and non-toxic nature [7, 60]. In 2017, Paixão and colleagues used guar gum to separate oily contaminants, which are discharged in huge amounts from petroleum industries. The oily stock solution is mixed with guar gum and boric acid, leading to the shrinkage of guar gel with time. It results in leaving oil and grease content in the supernatant, indicating the excellent effective abilities of the guar gum membrane in separating oil-contaminants from water [64]. Membrane fouling, commonly observed with membrane filtration during wastewater treatment, was reduced due to the presence of guar gum in ultrafiltration membranes made of polyvinyl plastic. Thus, guar gum can improve the quality and efficiency of ultrafiltration membranes prepared from waste plastic for wastewater treatment [7].

Pectin is another naturally occurring finest biopolymer, found abundantly in the walls of higher plant cells. Like other biopolymers, pectin also possesses excellent properties such as being biodegradable, non-toxic, easy to access, and of low cost [57]. It is extracted from various biowaste materials like orange waste, mango peels, citrus limetta, and pineapple peel. Repeating units of D-galacturonic acid are bound via α-(1–4) glycosidic bonds to form hetero-polysaccharide pectin. These can be modified to form pectin beads, hydrogels, adsorbents, and IPN and then employed for wastewater treatment [20, 49]. In one study, pectin hydrogel potential for the adsorption of dyes and metal ions from industrial wastewater was assessed. Pectin hydrogel loaded with iron efficiently separated arsenic from industrial wastewater. Similarly, pectin hydrogel made by acrylic grafting of pectin membrane to form a pectin/cellulose bead can remove cadmium, copper, and ferric metal ions from industrial wastewater [45]. Since pectin membrane has the potential to remove different heavy metal ions from wastewater, it depicts a good binding affinity of pectin for various pollutants in industrial wastewater which can be further utilized to remove toxic dyes. In 2020, Ilgin conducted a study using semi-IPN of pectin membrane which was formed by the free radical polymerization method. Electrostatic attraction between the cationic group in dye with an anionic group of pectin membrane hydrogel is the key factor in the removal of dye molecules from industrial wastewater [39].

Gelatin is the most abundant protein found in animals. The linear polypeptide gelatin is formed by the hydrolysis of collagen. Owing to its biocompatibility, cheap availability, non-toxicity, and biodegradability, gelatin is commonly used for wastewater treatment. Gelatin-based membranes require simple equipment, less energy, and offer high permeability and selectivity [47, 92]. Gelatin membrane along with carbon nanotube and nanoparticles of iron oxide was used to prepare nanocomposites for the adsorption of cationic and anionic dyes, namely methylene blue and direct red 80, respectively. The study showed excellent adsorption by gelatin membrane-based nanocomposites for both dyes [69]. The results of the study are supported by the work of Bilal and co-workers in 2016, where they used gelatin membrane as an encapsulation matrix for the enzyme manganese peroxidase and cross-linker glutaraldehyde. Reactive red 195A was used as a model dye, and it was observed that gelatin membrane-based hydrogel could decolorize dye up to 90% within 5 h [17]. Similarly, hydrogels of polyacrylic acid and hydrogels of polyacrylic acid/attapulgite, grafted using gelatin membrane, could efficiently adsorb malachite green as well as orange G dye from industrial wastewater [97]. A limitation while working with gelatin was observed, as it undergoes dissolution in an aqueous solution which can be prevented by cross-linking gelatin with chitosan using a genipin cross-linker. A modified gelatin membrane can be used to separate oily effluents of industrial wastewater [92]. Pullulan is a microbial exopolysaccharide synthesized by *Aureobasidium pullulans* in either maltotriose or maltotetraose polymeric chain form. Linkage at (1–>4) as well as (1–>6) positions in pullulan can be altered to modify its flexibility, and solubility and is utilized in various chemical, pharmaceutical, and food industries [75]. In one research study, pullulan was used as a flocculant, making use of its positive charges and thermoresponsive chain that enhances its flocculation efficiency. Polyacrylamide hydrogels were synthesized by pullulan grafting and porogen calcium carbonate via the free radical polymerization method, for the efficient clean-up of cationic and anionic dyes from industrial wastewater [68]. Similarly, pullulan derivative microspheres of P-g-pAPTAC were used as an adsorbent for acid orange, methyl orange, and azocarmine B. Other pullulan derivatives such as P-g-pNIPAAm, P-g-pAPTAC1, P-g-pAPTAC2, and DMAPA0.16-P have been used as a flocculant in clay and pesticide removal from industrial effluent with varying removal efficiency [29].

Zein is a plant protein obtained from corn and has amphiphilic properties. It is mainly used for the separation of oil contaminants from industrial effluent, as other membranes require external stimuli in the form of pH, light, temperature, and electric field to switch wettability for efficient adsorption of oil contaminants. Since zein has both hydrophilic and hydrophobic domains, and less effort is required to enhance the overall efficiency of oil contaminant separation from industrial wastewater [73]. Zein membrane is fabricated to form two membranes of SiO_2/zein/PAN nanofibers, pre-wetted with water and oil before initial separation to observe its water and oil removal abilities. Both membranes showed 99.99% separation efficiency, and the experiment was repeated for about 30 cycles to monitor membrane fouling. Results showed excellent reusability due to the superoleophobic property of the zein membrane underwater [79]. Similarly, Ansari and group [11] fabricated a zein/nylon 6 membrane for chromium removal from industrial wastewater [11]. Apart from the above-mentioned polymeric materials, polyvinyl alcohol (PVA) membranes offer benefits such as non-toxicity, significant film-forming abilities, good optical activity along with mechanical strength, reusability, and easy preparation. Synthetic production of PVA is performed by saponification or transesterification and cross-linking before its use in water treatment to retain its structure as well as mechanical properties [72]. Habiba and group [31] fabricated PVA with chitosan and zeolite to form a composite membrane of chitosan/PVA/zeolite nanofibers using the electrospun method. The membrane was stable in different media (acidic and basic) and was efficient in the removal of chromium, nickel, and ferrous ions from industrial wastewater at low concentrations only. Fouling of the membrane, which becomes a major issue while working with a membrane-based water clean-up system, was also minimized because of the anti-fouling abilities of the PVA membrane [31]. The use of polymeric membranes for wastewater treatment in various industrial sectors is shown in Fig. 2.

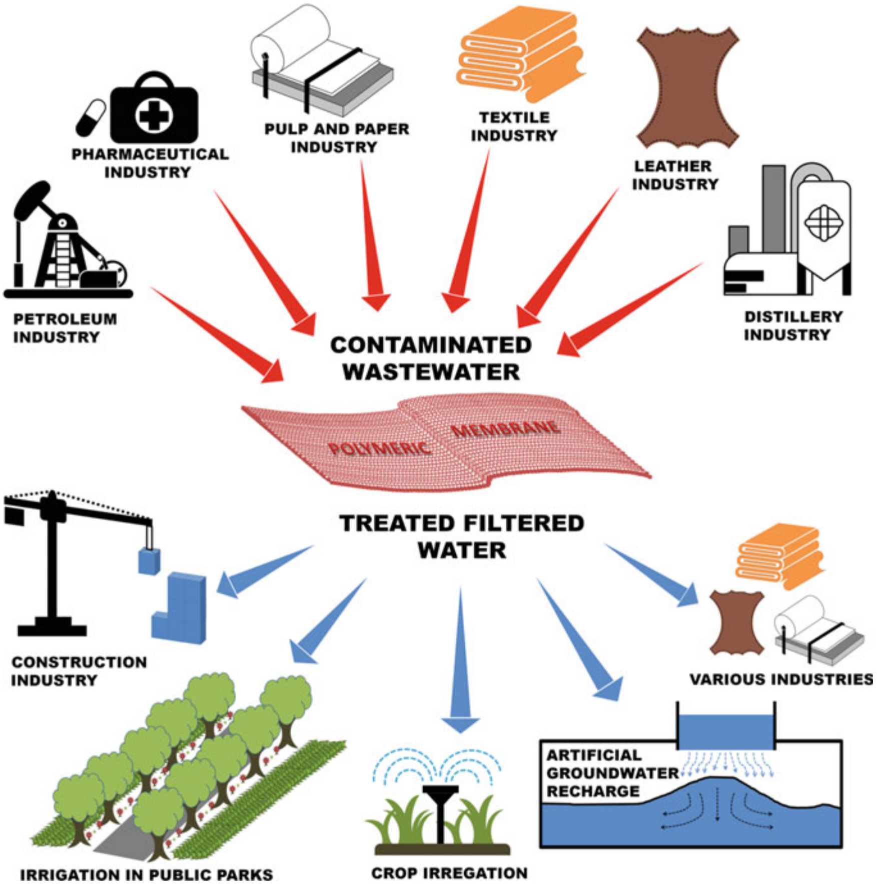

Fig. 2 Application of polymeric membrane in industrial wastewater treatment and reuse of treated water in various sectors

5 Conclusions

The increasing human population and dwindling water supply have made the treatment of industrial wastewater an important component of sustainable management. Recently, membrane technology for microfiltration, nanofiltration, and ultrafiltration of industrial wastewater has gained momentum. It has utmost importance to provide a sustainable and potable water supply for several industrial processes. Various types of membranes are used for the removal of organic and inorganic contaminants from wastewater and to render potable reuse of water. Being an eco-friendly and biocompatible alternative, biopolymers such as alginate, chitosan, and cellulose are increasingly employed for the fabrication of membranes. Biopolymer-based membranes offer a range of advantages such as functionalization, hydrophilicity, and chemical, mechanical and thermal stability. Membrane properties like pore size, strength, permeability, wettability thickness, and roughness can be altered to enhance the wastewater remediation process. Several enhancements are required to overcome challenges such as membrane fouling, membrane resistance, capital, and energy requirements encountered during membrane technology. Technological advancements including electrodialysis, forward osmosis, bioreactors, and integration with nanotechnology can pave the way for the better execution of wastewater industrial plants using polymeric membranes. In-depth studies for the membrane coatings, materials, better composites, and multilayers will assist to achieve the wastewater remediation goal. To facilitate the practical application of membrane technology, membrane industry guidance and standards are also required for the fabrication of efficient membranes. Synthesis of potential membranes will allow the implementation of methods for the improved treatment of industrial wastewater. The combination of membrane technology processes with other methods such as fuel cells will make a remediation process more sustainable and feasible. Such improvements in membrane technology will contribute to overcoming conventional shortcomings and will help in dealing with complex industrial wastewater contaminants in a better way. At this stage, more research and investigations are required to achieve the sustainability aspect of membrane-based technologies for industrial wastewater treatment. New developments are expected to accelerate technology from lab scale to pilot scale for practical, real wastewater treatment.

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Chapter 6
Membrane Bioreactor: A Potential Stratagem for Wastewater Treatment

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1 Introduction

Technology and procedure for wastewater treatment have evolved a lot since last century. One of those advanced approaches is membrane bioreactor (MBR) technique. A membrane bioreactor can be defined as a chamber especially designed for small-scale biochemical transformation combined with a process assisted by membrane according to Environmental Protection Agency (EPA). This MBR technique has become a preferable choice over the conventional municipal wastewater treatment commonly known as Activated sludge process (ASP) as it has overcome several drawbacks of conventional system, such as requirement of large space for secondary clarifier, excess sludge production, limitation regarding removal of recalcitrant, etc. Basically, MBR is a combination of conventional activated sludge system and solid/liquid separation using membrane filtration in a single set-up. In the 1930s, the standard method of wastewater management was biological treatment. Biological treatment can basically be reclassified as aerobic and anaerobic methods. Both of these methods were used to treat domestic as well as industrial wastewater. Recycling and reuse of wastewater for a secondary purpose is on high demand as water consumption is increasing by leaps and bounds worldwide and the quantity of portable water is getting reduced gradually. Simultaneously, the demand for fresh water for maintaining the growth of population is getting higher [29].

Different parts of Europe, Africa, Asia, South America and even Australia have been identified as water scarcity zone. On the other hand, there are some marked

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regions where though water supply is adequate but quality of water is poor, with high salinity, nutrient eutrophication, contamination with heavy metals, etc. The best solution in this situation is the application of MBR [28].

Several organic and inorganic soluble particles get converted into NH_4^+, CH_4, NO_3^-, NO_2^-, H_2O and simpler biological particles. After removing the soluble biodegradable matter, the formed biomass is separated from the liquid and effluent is produced and then solid–liquid separation takes place [58]. Membranes of MBR are generally made up of cellulose or polymer and can prevent the passage of microorganisms. In general, two configurations are most commonly used for MBR applications, one is either hollow fibre forming or flat plates [59]. Besides that, other configurations are submerged MBR, Hollow fibre model, side stream model, etc. Most of the MBRs require a certain degree of pumping and make the water flow through the membrane properly (EPA). A number of processes have been developed for membrane separation such as ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), electrodialysis, etc. These names are varies depending on the various ranges of separation from 0.1 to 1000 nm. Several advantages are associated with MBR technology, such as high-quality effluent, volumetric loading rate is also high, hydraulic retention time is relatively short, solid retention time is comparatively lower and the most important amongst them is less sludge production. Another useful output is simultaneous nitrification and denitrification in long sludge retention time (SRT). One advantageous point here is elimination of secondary clarifiers. In correlation with that, thus reduction in plant area requirement is another prominent advantage. Concentration of bacteria, total suspended solids, biological oxygen demand (BOD) and phosphorus are comparatively low in MBR and these effluents can be discharged readily or can be reused, that can be explained by Environmental Protection Agency (EPA). In spite of having a number of plus points, some factors are considered as major drawbacks of the MBR process. MBR system is not as much efficient in the removal of dissolved wastewater as removing solid material. The second one is membrane fouling that creates problem by reducing membrane performances. High capital and operation cost are other disadvantages in the maintenance of MBR. Environmental Protection Agency (EPA) said that energy cost is also high in controlling bacterial growth. Pore narrowing, cake formation and pore clogging are considered as membrane fouling. These foulants may be organic or inorganic. The crucial factors responsible for membrane fouling are membrane character, biomass character and operating condition [29]. However, there are still some solutions to prevent membrane fouling like addition of coagulant, quorum quenching etc. All the obstacles mentioned above are associated with a wide range of applications of MBR. Besides wastewater treatment, MBR can be used in a number of ways such as water recycle, food processing, production of biofuel, in pharmaceuticals, etc. [27]. This chapter considers a detailed description of MBR system, process, application and all the pros and cons of its application.

2 Membrane Material and Types

A membrane is a material more permeable to some compounds (either chemical or physical) than others, which means this allows the separation between two or more components. Hence, it is perm selective and this selectivity, not always, though mostly is based on pore diameter. For example, microfiltration (MF) is lesser selective than nanofiltration (NF). Perm selectivity let the separation of retentate (components which are rejected by the membrane) and permeate (components which are passed through the membrane), shown in Fig. 1.

Most of the very common filtrations used to treat wastewater are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Fig. 2). Unsurprisingly, the most selective amongst these are the RO filter, in which the selection of the components can be as minute as 1 nm in diameter and the membrane can even reject monovalent ions like Na^+, Cl^-, etc. [30].

Apart from these above-mentioned pressure-driven processes, other membrane technologies are also there, including both extractive (i.e. the extraction of some of the selective constituents) and diffusive (i.e. the introduction of selective components) approaches. Electro-dialysis (ED), bring the most common of them, is a process where an ion-exchange membrane is used to separate ions based on different ionic charges, ionic sizes and charge densities of the solute ions [30].

No matter what the process is, the membrane used in MBR is always subject to some limitations, and of them, membrane fouling is definitely the major one, occurs due to the tendency of some particles from rejected retentate to accumulate on the membrane surface (i.e. blinding) or within membrane surface (i.e. pore plugging/pore restriction). Apart from this, clogging (filling of membrane channels) is another threat which hampers MBR performance due to the weak hydrolytic force of the feed water [30].

In any membrane bioreactor, the membrane must have the mechanical stability to withstand the constant flow of water. Though, metallic membrane serves the purpose here most supremely, still its use is very rare in MBR. Most of the membranes used are anisotropic in nature, meaning a membrane with more minute porosity is used over a

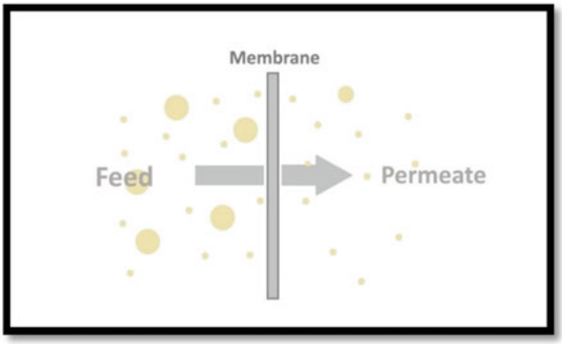

Fig. 1 Separation of feed water through membrane

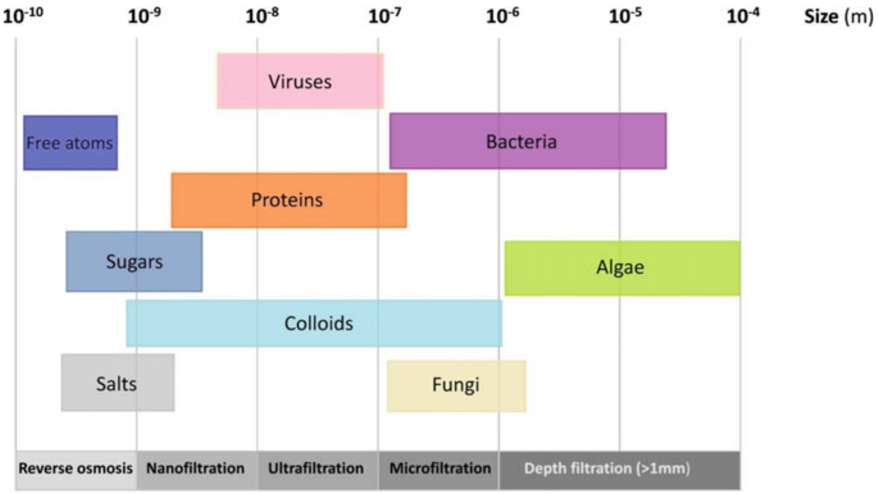

Fig. 2 Perm selectivity of different membranes used in MBR

less selective but more mechanically stable membrane. For this extra selective layer, the most preferable choices are polymeric and ceramic membranes, coupled with the fact that they are thermally and chemically resistant too. The only matter of consent, perhaps, is the hydrophobic natures of the polymeric materials, which is susceptible to all the hydrophobic matters passing through, hence are threat to membrane fouling. To avoid this, an extra coating of hydrophilic layer is essential by using techniques such as plasma treatment, chemical oxidation and organic chemical reaction or grafting. Some of the common forms of polymers being used are polyvinylidenedifluoride (PVDF), polyethylene (PE), polysulfones (PSFs), polyethylsulphone (PES), polytetrafluoroethylene (PTEE), polypropylene (PP) and cellulose acetate (CA) [4, 30].

Composition of the polymer solution and membrane preparation process ultimately determines membrane characteristics. The different methods of preparing a ideal membrane for MBR plants can be through any of the following:

(1) **NIPS**: Non-solvent induced phase separation (NIPS) is a membrane fabrication process where the membrane is prepared via introducing different solvents (of different solubility) to a particular polymer, in other words, here, membrane is prepared on account of the varying solubility of polymers with respect to different solution. The two solvents, which are used are known as 'non-solvent' and 'solvent' of poor and good solubility respectively to the polymer. First, the good solution is mixed with the polymer, followed by the introduction of the non-solvent into it via an injection nuzzle. This will lead to the formation of pores onto the membrane, i.e. the result of the diffusion into the non-solvent by the good solvent solution. Finally, the polymer is washed well, dried and hence ready for its application. Here, the outer and inner pore diameters of the membrane are highly determined by the size of injection nuzzle [5].

(2) **MSCS**: Melt-Spinning and Cold-Stretching (MSCS) method includes stretching of the membrane sheet, that results in lengthening and creating various pores in the amorphous (interlamellar) membrane structure in a temperature, i.e. less than Tm (melting temperature) and higher than TG (glass temperature) [6]. Major difficulty in this method is to control the pore diameter, therefore stretching ration (R) becomes a crucial factor, which can also be defined by $R = V_1/V_2$ (where V_1 = Extrusion speed and V_2 = take-up speed) [53].

(3) **TIPS**: Another important method for preparing polymeric membrane is through thermally induced phase separation (TIPS) developed first in the 1980s. Here, the membrane is formed by extracting thermal energy from a homogenous solution through phase separation technique. Membranes obtained from this method can be of very narrow diameters, therefore provide better performance [60].

3 Membrane Bioreactor (MBR)

3.1 Configuration of Membrane Bioreactor

Membrane bioreactor is a hybrid system of filtration process (through artificial membranes) along with their biodegradation (by microorganisms); hence, this includes two main phases, i.e. selective transport as well as catalytic properties [44].

- **Membrane configuration**: To form a proper set-up for any MBR, it is important to form a module which promotes high turbulence of the feed water and which is easy to clear. Perhaps this is the reason why the orientation of the membrane is crucial. Based on their geometry, a membrane can be either planar or can be cylindrical. The most commonly used membrane configurations of MBR are Plane/Frame model (FS), Hollow fibre (HF) and Multi-Tubular (MT) are presented in Fig. 3a–c.
- **Bioreactor configuration**: Bioreactor in a tank containing microorganisms helps in the degradation of the biological waste. In an MBR, this may contain the membrane within it (if iMBR) or outside it (if sMBR) shown in Fig. 4. Inside the tank, aerobic treatment is performed, which however demands high energy, and also increased the maintenance cost of MBR plan [6]. However, the emission of greenhouse gases like nitrous oxide moderates the purpose of environmentalism.

The variety of microorganisms used in a bioreactor include bacteria, protozoa, metazoa, algae, fungi and filamentous bacteria. However, over 90% of them used in an MBR to treat municipal waste are bacteria. Most often they are in aggregated forms, forming clusters, chains or pairs, though can live as single cells also. They rely mainly on carbon sources, electron donors or acceptors for their metabolism. The tendency of their microorganisms to accumulate over the membrane surface is the reason of forming biofilms which reduce MBR performance [6].

Mechanically, MBR configuration can be classified into two types based on the membrane position:

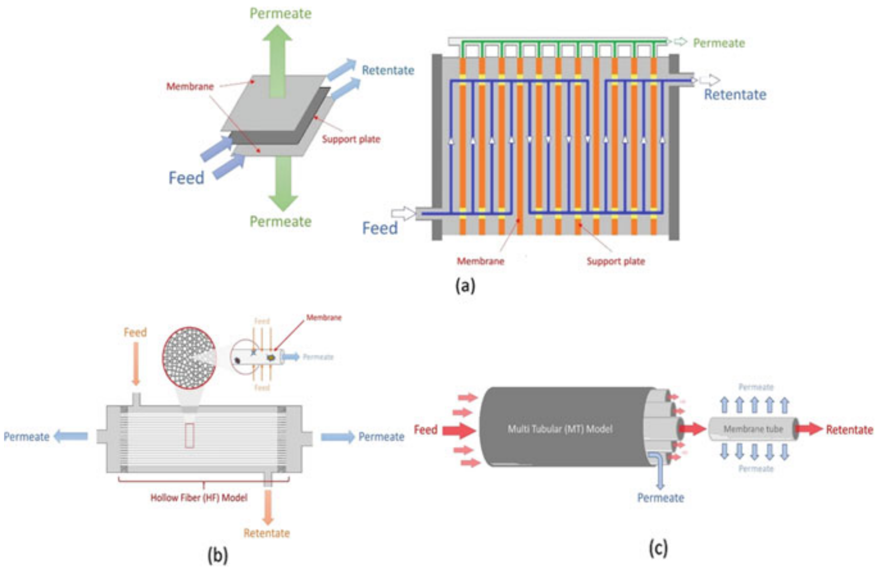

Fig. 3 Different membrane configuration: **a** FS, **b** HF and **c** MT

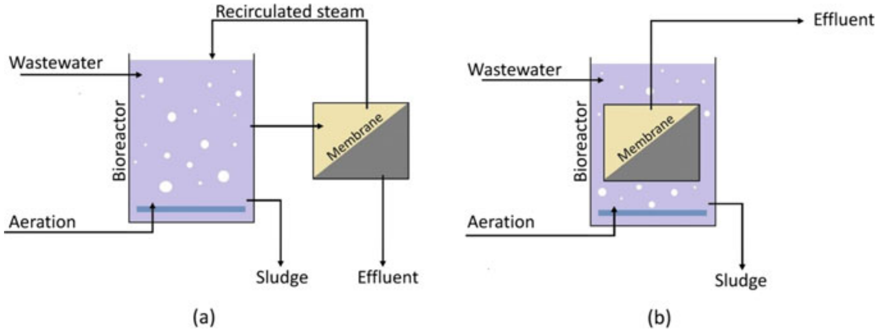

Fig. 4 Configuration of **a** sMBR and **b** iMBR

a. **Immersed Membrane Bioreactor (iMBR)**: If the membrane is placed inside the biological reactor, then the extraction of the permeate is towards the permeate side using the suction pressure of water and/or by the static head pressure of water at the retenant side. Undoubtedly, this is the more common configuration for treating municipal wastewater, majorly because of the extra effort required for pumping in sMBR [55].
b. **Sidestream Membrane Bioreactor (sMBR)**: Here, the membrane is placed separately, outside the reaction tank, hence, transmembrane pressure or TMP is required at a much higher rate to generate permeate water [32]. Perhaps this is

the reason why membrane separation here is performed through pressure-driven filtration [49].

For the treatment of municipal wastewater, iMBR seems to be more preferable over sMBR, because the aeration which is provided for the bio-organisms also doubles up the benefit of providing resistance to the immersed membrane against fouling. The specific aeration demand (SAD) per unit membrane area in a particular time interval is what serves as the key operating parameter here (in $Nm^3/m^2.h$) [49]. Whilst, the shear of pressure over the membrane surface is carried out through pumping, in case of sMBR. Here, a cross-flow of water or air is required to the prevent fouling effect; hence, the determining parameter is cross-flow velocity (CVF) [32]. One downside of pumping is that it generates shear stress to the microbial flocs, and with that reducing microbial activity [49]. A brief comparison between iMBR and sMBR is given in Table 1.

- **Aerobic and anaerobic membrane bioreactors**: Aerobic treatment in wastewater reclamation is used since a long, the major energy and cost investment

Table 1 Comparison between iMBR and sMBR

Serial no.	Parameters	iMBR	sMBR
1	Membrane position	Membrane is placed inside (immersed) the bioreactor tank	Membrane is placed outside the aerobic tank
2	Membrane type	For iMBR, flat sheet (FS) or a hollow fibre (HF) type of membrane module is used	Multi-Tube (MT) module is useful for a sMBR plant
3	Energy consumption	Requires lower energy than that of sMBR	sMBR required higher energy as an additional pumping is required to pass the feed water through the membrane
4	Cleaning and maintenance	iMBR offers a lower cleaning frequency as the membrane is itself cleaned by the aeration generated for the bio-organisms inside the bioreactor tank, though, occasional backwash is needed	Whilst, in order to prevent membrane fouling in sMBR, various strategies such as cross-flow of air or water and/or backwash techniques are applied alongside chemical treatments
5	Applications	Suitable for large-scale applications (such as in municipal programmes) for its comparatively low cost and energy demands	This is important in small-scale but higher strength applications as this can handle higher MLSS concentration. Therefore, suitable in treating industrial wastewater

reducing the wider application of MBR technology. Hence, in recent years, some strategies are applied to reduce energy as well as for cost-cutting issues. For example, the ammonia-N-based aeration strategy has shown a major reduction in aeration and therefore the reduction in energy consumption rate [6]. Also, the reduction in aeration has a direct impact on the reduction of greenhouse gas (GHG) emission.

According to a classic review article in Selangor, Malaysia, it has been determined that, in the treatment of effluent with a COD (Chemical Oxygen Demand) content lower than the amount of 1000 mg/l, aerobic processes are supremely useful, but to treat a higher pollutant where the biodegradable COD content is over 4000 mg/l, anaerobic processes are preferable [11].

In anaerobic treatment, the biogas which is renewed from the decomposed organic matter itself is used to treat wastewater and, finally, the nutrients are used as fertilizer. This treatment is applied with the membrane technology to develop anaerobic MBR (AnMBR) (Fig. 5). Normally, the biogas which is generated from the decomposition of waste material is methane-rich. A classical aerobic MBR differs from that of an AnMBR in numerous aspects shown in tabular form (Table 2), ranging from cost to build-up time [40].

Based on operating conditions, AnMBR can be one of the followings [14]:

a. **CSTR (Completely stirred tank reactor) AnMBR**.
b. **UASB (Up-flow anaerobic sludge blanket) AnMBR**.
c. **AFBR (Anaerobic Fluidized bed membrane bioreactor) AnMBR**.
d. **JFAB (Jet Flow Anaerobic bioreactor) AnMBR**.

Fig. 5 Configuration of anaerobic MBR

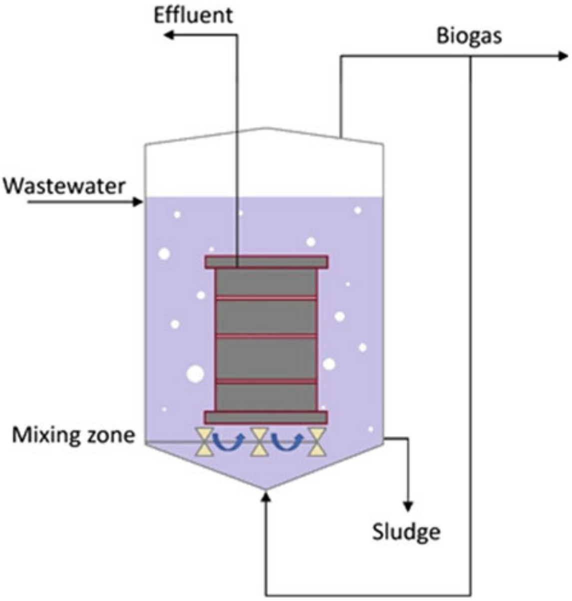

Table 2 Difference between aerobic MBR and anaerobic MBR

Aspects	Aerobic	Anaerobic
Energy consumption	High	Low
Maintenance cost	High	Low
Quality of the effluent	Excellent	Moderate
Sensitivity to temperature	Less sensitive	Highly sensitive
Odour problems	Less	High
Start-up time	15–30 days	60–100 days

e. **EGSB (Explanted Granular Sludge Bed reactor) AnMBR**.

These anaerobic bioreactors can be designed into the three following configurations:

(a) **Side-stream AnMBR**: Here, the membrane is placed separately outside bioreactor tank.
(b) **Internal submerging AnMBR**: Where the membrane is placed inside the main bioreactor tank.
(c) **External submerged AnMBR**: Here, the membrane remains submerged, but not in the bioreactor, but rather in a separate tank.

3.2 How Does Membrane Bioreactor Work?

The use of membrane bioreactor (MBR) for waste treatment has gained popularity over the years. The working principle of MBR is a combination of activated sludge process and membrane separation process [43]. At first, the organic pollutants are degraded with the help of flocculating microbes, after which the wastewater is pumped through the membrane module. Due to the integration of the biological treatment process with membrane filtration, the quality of the product water obtained is higher than that obtained by conventional treatment [41].

3.2.1 How Filtration Proceeds?

Membrane filtration provides us with selective separation and procurement of advanced level of particulate removal [24]. Membranes in MBR are used to achieve a solid–liquid phase separation based on the relative size of the component/colloids and the membrane pore [49]. The pore size of the membrane ranges from 0.1 to 1000 nm which allows high-quality effluent to be obtained without the need for sedimentation. Depending on the pore size of the membrane, the separation process can be called microfiltration (100–1000 nm), ultrafiltration (5–100 nm), nanofiltration (1–5 nm) and reverse osmosis (0.1–1 nm). The process of membrane separation involves passage of the feed water over the membrane surface. The product water which diffuses through the membrane is called permeate and the rejected constituents are known as the concentrate or retentate [49, 56]. In side-stream MBR membrane separation is carried out by pressure-driven filtration where wastewater is pumped through the membrane module and then returned to the bioreactor, whereas submerged MBR vacuum-driven membranes immersed in an aerated bioreactor carry out the process of membrane separation. The sieving effect of the membrane causes particulate or colloid of size smaller than that of the membrane pore being retained, bringing it in contact with the degrading bacteria present in the MBR and ensuring complete degradation of the pollutant [23, 49].

3.2.2 Membrane Integrity

MBR has emerged as an advanced wastewater treatment technology. However, during the course of operation, there are chances of membrane integrity being comprised due to fouling or degradation of membrane fibre. The major consequence of membrane integrity being hampered is a decrease in the permeate flux. It can be defined as the volume of water flowing through per unit membrane area per unit time normalized to standard temperature. The unit of permeate flux is $\mathrm{Lm}^{-2}\ \mathrm{h}^{-1}$, it is denoted by J and is given by

$$J = \frac{Permeate\,flow\,rate}{Area\ of\ the\,membrane}$$

Permeate flux is related to trans-membrane pressure (TMP or ΔP) which can be described as driving force pushing water through the membrane. During the membrane process, a decrease in the permeate flux or increase in TMP is termed fouling [49, 63]. Fouling occurs by different mechanisms which are as follows:

1. Standard blocking due to the constriction of pore opening as a result of particle deposition around the site of pore entry.
2. Intermediate blocking due to superimposition and obstruction of pores by particles.
3. Complete blocking due to plugging of pores by particles.
4. Cake layer formation due to the deposition of particles larger than the size of the membrane pore on the surface of the membrane.

Extracellular Polymeric Substance (EPS) is considered to be one of the major foulants responsible for fouling. It is a polymeric material which provides a hydrated gel matrix in which microorganisms are embedded. The pumping of water causes turbulence which disturbs the activated sludge floc. This results in breakdown of the floc causing generation of colloidal particles, whereas the interior of the floc EPS is released. Moreover, EPS contributes to nearly 90% of the cake resistance [12, 41]. Membrane fouling can be categorized into reversible, irreversible and irrecoverable fouling. Reversible fouling is a result of preferential adsorption of bio-solids on the membrane surface which can be removed by physical cleaning. The procedure is simple and short and lasts for less than 2 min. It involves stopping the flow of permeate and scouring of the membrane with air bubbles. Irreversible fouling is caused by the formation of cake layer on the membrane or clogging of pore by suspended solids. Chemical cleaning is used to correct irreversible fouling as it is more effective in removing strongly adsorbed deposits. It is carried out by soaking the membrane in sodium hypochlorite and sodium hydroxide for removal of organic deposits or acidic solutions for removal of inorganic or lime deposits. Chemical cleaning is performed on weekly basis and requires 30–60 min to complete. After years of operation, irrecoverable fouling builds up on the membrane making it unsuitable for use so it is replaced with a new membrane [24, 41, 49].

The various polymeric and hydrophobic materials used for making the membrane include polyamides, polysulphone, charged polysulphone and other polymeric materials such as polyacrylonitrile (PAN), polyvinylidenedifluoride (PVDF), polyethylsulphone (PES), polyethylene (PE) and polypropylene (PP). The hydrophobic interactions between the membrane and the fouling constituents may lead to precipitation of inorganic matter on the membrane, formation of bio-films on the membrane, adsorption of colloidal matter and continuous deposition of particles on the membrane surface [24, 49]. All the above-mentioned consequences of the hydrophobic interactions decrease the permeate flux. In order to achieve hydrophilic surface, the membranes are modified by grafting, chemical oxidation, plasma treatment or organic chemical reaction. The introduction of shear stress in MBR is necessary to prevent membrane fouling but its generation requires energy. In side-stream MBR, this is achieved by pumping, whereas submerged MBR aeration is employed for this purpose. As aeration is more effective in suppressing membrane fouling, the demand of submerged configuration dominates the market [49]. Fouling can also be neglected if we operate below the adequate initially chosen permeate flux or TMP [41].

Factors contributing to degradation of the membrane fibre or broken fibre include faulty installation, vigorous backwashing causing stress and strain and damage done by sharp objects. Economically, viable and reliable integrity tests are performed which can be classified as direct and indirect methods. Direct methods include pressure decay test, diffusive air flow, vacuum hold test, binary gas integrity test, bubble point test, acoustic sensor test and liquid–liquid poroisometry test. These can be directly applied to the membrane to locate the position of leakage. Indirect method evaluates the change in the performance of the membrane. It depends on the effluent water quality which indirectly estimates the membrane integrity. Particle counting, microbial challenge tests, turbidity monitoring, nano-scale probe challenge tests, surrogate challenge tests and magnetic particle challenge tests are indirect methods which give an early warning of leakage [63].

3.3 Biological Performance of MBR

The performance of the biological process of MBR depends on permeability, filtration resistance, hydraulic retention time, mixed liquor suspended solids and sludge retention time denoted by K and calculated as flux per unit of transmembrane pressure (TMP or ΔP). The unit of K is Lm^{-2} h^{-1} bar^{-1} [49].

Fouling gives rise to filtration resistance (R) which is a critical factor in limiting the overall performance of the membrane [61]. R is given by

$$R = \frac{\Delta P}{\eta J}$$

where η is the permeate viscosity and its unit is kg m^{-1} s^{-2}. Although several authors introduced the concept of total resistance, denoted by $R_{t,}$ which is the sum of three components that is membrane resistance (R_m), cake resistance (R_c) and fouling resistance (R_f) [12, 49].

$$R_t = R_m + R_c + R_f$$

Hydraulic retention time (HRT) is a measure of the duration in hours for which the feed remains in an MBR before being processed. It is given by the formula

$$\text{HRT} = \frac{\text{Volume of the reactor}}{\text{Permeate flow}}$$

It has been observed that the higher value of HRT leads to improved biological performance of the MBR. Although HRT has an indirect effect on fouling. It has been observed that the higher value of HRT is correlated with the decreased rate of membrane fouling [12, 21].

Mixed liquor suspended solids (MLSS) can be defined as the concentration of the suspended solids in the mixed liquor and its unit is grams/l. MLSS is an important operational parameter for working of MBR as it has a direct impact on the viscosity of the liquor. If the viscosity of the suspension increases then high cross-flow velocity is needed to generate turbulence which can scour away the solids from the membrane. On the contrary, if velocity and turbulence are not enough then the deposition of fouling layer on the membrane will be faster [39].

The time duration for which activated sludge remains in the MBR or the age of the sludge is known as the sludge retention time (SRT). An increase in SRT causes an apparent increase in MLSS accompanied by a decrease in EPS, thus MBR should be operated at short SRT. Although continuing operation with short SRT makes it difficult to achieve high-quality effluent and sufficient substrate removal. However, contradictory reports exist suggesting that SRT has no direct effect on membrane fouling [12, 21]. The removal of organic pollutants, inorganic pollutants, pharmaceutical compounds and nutrients from agricultural, industrial and medical wastewater depends on all the above-mentioned parameters [2].

The agricultural wastewater has high concentration of nitrites and phosphates due to the excessive use of fertilizers and pesticides. This results in eutrophication of water bodies which eventually leads to algal bloom. For the removal of nitrates from wastewater, biological nitrification is considered to be affordable. The nitrite is converted to nitrate after which anoxic denitrification is used to remove the nitrogen from wastewater by reducing nitrate to nitrogen gas. The nitrifying ability of the activated sludge is enhanced by using long SRT as it prevents the nitrifying bacteria from being washed [42, 49]. The biological removal of the phosphates forms the wastewater requires the use of phosphate-accumulating microorganisms (PAOs) [67]. Moreover, phosphorus elimination is facilitated in aerated MBR and in membranes with pore size more than 0.5 μm which results in the physical retention of PAOs in the MBR [49]. The various micro-pollutants found in wastewater include antibiotics (erythromycin, loxacin and sulfamethaxazole), analgesics (primidone, ibuprofen and lorazepam) hormones, pharmaceutical compounds (beta-blockers), surfactants and personal care products. The efficient strategies for removal of micro-pollutant include membrane separation, biodegradation and biotransformation (conversion to compound other than the parent compound). MBR has a removal efficiency of 70–80% for beta-blockers. Salicyclic acid and propylparaben are personal care products that can be completely removed by using MBR [23]. The contamination of water with faecal matter is indicated by the presence of *Escherichia coli* and other enteric viruses. Membrane filtration is not effective in removing phage and spores although reverse osmosis can efficiently remove viruses from wastewater [49]. All of this indicates that MBR has a clear advantage over the conventional activated sludge process [23].

3.4 Application of MBR

MBR technique was first introduced in 1969, for the treatment of sewage from manufacture plant [4]. Historically, CAS (Conventional Activated Sludge Process) was used for the wastewater treating purpose, but due to prominent advantages, this technique was substituted by MBR [62]. From then till now, multiple modifications and transformations had been made to enhance the efficacy of this technique. Installations of ultra-filtration membrane [49], utilization of hollow fibre membrane [64] and many more parameters have been altered to generate a good quality effluent. Apart from focusing only on the betterment of MBR, its commercialization after 2008 led to a better aquatic environment. During the last few decades, MBR technology has come up with a variety of applications in different fields, from biofuel production to antibiotics from food to manufacturing of biofertilizers, from wastewater management to amino acid production and what not [9, 47, 50]. Considering above mentioned facts we can depict that MBR-dependent technologies have a broad future aspect with a visible success rate. In this chapter, we will mainly focus on the application of MBR in the treatment of wastewater.

So far, multiple implementations of MBR have been documented but the most explored application is the management of municipal, domestic and industrial wastewater. Reclamation of water by the process of MBR is highly recommended by modern science as it can conveniently reduce the demand for local and industrial water supply. The overall strategies are emphasized below.

3.4.1 Industrial Wastewater Management

Successful application of MBR against high-strength wastewater of industries had been made for several times. Wastewaters produced by the industries are of different grades based on the level of impurities and limitation of nutrients. High-strength wastewater may have different organic and inorganic compounds, grease, oil and many other insoluble, corrosive compounds and harmful substances [35, 49]. These conditions lead to low settlement of biomass and thus the job of treating that water is quite tough. On the other hand, industrial water demand is quite high which is almost around one million gallons a day but, this quantity may vary based on the type of industry. To fulfil this huge requirement, recycle and reuse, wastewater is the only way and for that MBR dependency is necessary. Reuse of processed water in industries will lower the industrial water demand and make potable water more available for environment and local supply.

Utilization of MBR technique to treat industrial waste management includes multiple advantages over any other techniques as it can withstand high temperature and pressure, biomass settling is not mandatory, limited space is required, stable pH level can be maintained throughout the process and so on. But for proper functioning of Membrane Bioreactor multiple parameters should be taken into consideration like MLSS (Mix Liquor Suspended Solid), TMP (Transmembrane Pressure), HRT (Hydraulic Retention Time), F/M (Food to Microorganisms), SRT (Solid Retention Time), flux quantity and many more [46].

Food Industrial Wastewater Treatment

High-strength wastewater is produced by food industries and is filled with biodegradable organic components [15]. Cicek [15] had also reported that almost all industries treat the polluted water primarily before sending them to wastewater management plants. The major pollutants that are present in the wastewater are COD (Chemical oxygen demand), BOD (Biological oxygen demand), oil, grease, fat and many nutrients. Successful trails of wastewater treatment produced from food industries were made by Katayon et al. [33], Acharya et al. [1]. Their experimental outcomes were so evident that they made MBR technique more popular on a practical usage basis. Apart from this, Damayanti et al. [20] had come up with another alternative idea to increase MBR efflux. According to their study, addition of a fouling reducer like PAC (powdered Activated Carbon) can effectively increase the efficiency of MBR in the removal of organic soluble waste products.

Textile Wastewater Management

Wastewater produced by textile industries is full of toxic substances, and biodegradability is also very low [52], which is a matter to be concerned with. Commonly textile industries use membrane technology, chemical precipitation and biological treatment to process the wastewater [65]. Multiple successful trails were made by Hai et al. [25], Badani et al. [8] and several other scientists from time to time to purify wastewater from textile industries.

Pharma and Refinery Wastewater Management

Industries like pharma and refinery also require huge water sources for manufacturing their products and to reduce unnecessary wastage reuse is the only alternative. Vireo et al. (2008) reported that addition of phenol can affect biodegradation of phenolic wastewater. The reclamation technique involves two main steps, in the initial phase, steam treatment was done in absence of phenolic wastewater and removal of COD was approximately 67%. This phase was followed by the addition of phenolic wastewater at a ratio of 1:6 and this time removal of COD was 61% and removal of phenol was 98%. Surprisingly, when the ratio was changed to 1:240, phenol and COD removal were 99.3% and 58%, respectively [57]. In 2011, Katsou et al. had successfully treated heavy metals from wastewater by some modifications of MBR.

3.4.2 Domestic and Municipal Wastewater Treatment

Demonstration of full-scale membrane bioreactor for domestic wastewater (DWW) management was first done in England, having a capacity of almost 1.9 megalitres of wastewater a day (MLD) and since then multiple changes were made to increase the performance of MBR and by now the capacity of MBR tank has reached up to 100 MLD [66]. For domestic wastewater (DWW) management, AnMBRs are considered more efficient [36]. New promising modifications like the addition of antifouling membranes, such as ceramic and polytetrafluoroethylene (PTFE) membranes were made with good surface properties, for the betterment of the technique. Moreover, the capacity to remove micro-pollutants and pathogenic organisms from domestic wastewater had made MBRs more competent than any other existing techniques [36].

Municipal wastewater treatment is an ideal utilization of MBR technique. Rosenberger and Kraume [51] had opined that membrane bioreactor could be the best way to treat municipal wastewater with activated sludge. In their experimental study, Zenon pilot membrane bioreactor was used with three distinct compartments for denitrification, aeration and filtration shown in Fig. 6. The success rate attained by using Zenon pilot was quite high with 100% nitrification, 100% removal of suspended particles, 95% reduction of COD and almost 82% denitrification.

The most advanced and largest operating MBR for municipal wastewater treatment is situated in North America with a maximum capacity of 8.5 MGD (Millions

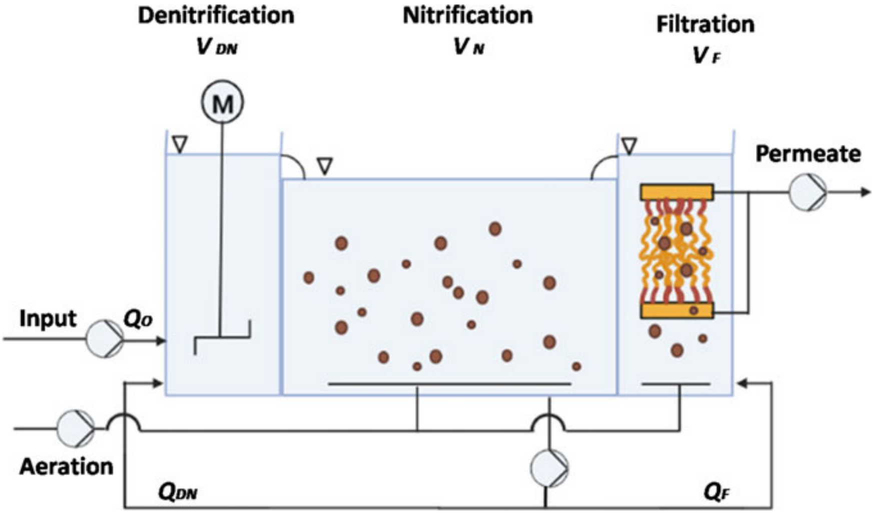

Fig. 6 Schematic representation of Pilot MBR technique for municipal wastewater management

of Gallons per Day). Due to space scarcity, MBR was the only option for treating the wastewater with a sharp increase in its efficiency. Due to the presence of high DO (Dissolved Oxygen) level in the membrane tank, Crawford and Lewis [19] had designed the tank with three distinct zones for recirculation. The overall tank design is depicted in the following Fig. 7.

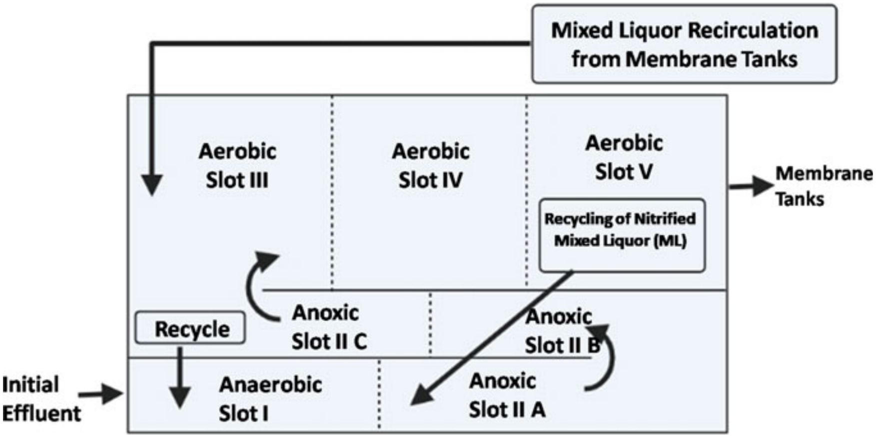

Fig. 7 Blueprint of MBR tank with separate anaerobic, aerobic and anoxic zones

4 Comparison Between MBR and Conventional Sludge System

It is previously considered that there are several positive aspects of MBR. MBR has appeared as an innovative biological treatment strategy in the last few decades [15]. Several advantages make it the best suitable alternative over conventional techniques.

Firstly, most of the suspended matters are retained in the bioreactor and, on the other hand, other soluble compounds present at the bioreactor are discharged as effluent adequately and water is collected in reusable form again. Collected sterile effluent is devoid of bacteria and viruses; this disinfection is done intensively [10]. Although suspended matters are still present in the bioreactor clarifier [7]. In the next step, microbial populations are controlled using solid retention time (SRT) and hydraulic retention time (HRT). Function of a clarifier in MBR is as a selector that not only settle organisms but also enable some slow-growing and sensitive species like nitrifying bacteria to develop and retain in the MBR in SRT [3].

Secondly, these bioreactors have the ability to prevent drainage of exocellular enzymes as well as soluble oxidants and this quality makes them more capable of degrading a number of carbon sources [16]. MBR typically eliminates settling problems and difficulties generally associated with conventional sludge system. So, strength of wastewater is relatively high and simultaneously becomes yield is low [45]. As a result, it reflects a far better system than conventional process. Generally soluble compound with high molecular weight is not easily biodegradable in conventional system. Fluctuation in nutrient concentration takes place and reason behind it is huge biological acclimation. As compared to conventional activated sludge system, MBR is quite costly with around 50% higher operating cost annually. In this regard, conventional activated sludge system cannot produce high-quality effluent but needs lower energy demand and quite cost-effective [27].

5 Advantages and Disadvantages of MBR

Limitations in the process of CAS (Conventional Activated Sludge) have led to the mandatory development of MBR technique. MBR no doubt can reduce the formation of sludge and can lead to mineralization more efficiently as compared to CAS. Compounds with high molecular weight and also soluble, are not really biodegradable in these traditional systems, but MBR utilization has made this happen easily [18]. MBR is also designed to tolerate fluctuations in nutrient concentrations because of huge biological acclimation and degenerated biomass retention [17] theses positive impacts are accompanied with prolonged residence time and oxidation possibility is also improved. Even, in MBR technique, multiple full-scale MBRs were made and implemented with definite modifications from time to time which ultimately led to the advancement of this technique day by day.

Modern MBR technique has several advantages over any other existing techniques to treat wastewater. Activated sludge when combined with membrane separation technique led to an extraordinary result through the process of MBR. This technique drew attention when used for huge biological solid retention and simultaneous hydrolysis is essential to achieve biodegradation of pollutants [13]. The prime advantage of MBR is the formation of good quality effluents which makes the recycle and reuse much smoother for water.

Difficulties related to the settling of suspended matter were also eliminated by implementation of membrane bioreactor technique. MBR can treat high-strength wastewater and low biomass was also obtained which is significantly superior to other existing techniques [45]. Water recycling was made easier and more efficient as compared to orthodox processes [34]. According to Liu and Tay [37], the autolytic mechanism of the biomass under long SRT can actually permit the growth of grazing and predatory communities with considerable trophic-level energy losses.

- Despite its first arrival long back in the 1960s, MBR technology has failed to capture a widespread market at a global platform, the biggest reason of what is considered is the high operational and capital cost [48]. Being a pressure-driven process its dependence on mechanical energy is worth a mention. Apart from that, costs involved in the fabrication process of the membrane material, further modifications of it into special geometrical configurations (FS, HF or MT), membrane fouling strategies are some of the main reasons for the higher cost of the whole programme. Occasional cleaning of the membrane requires a cross-flow of air or water, which again requires a whole lot of energy, though this factor can be reduced in iMBR model, though, this configuration creates shear stress to the microbial flocs, forcing them to disaggregate. Whilst, in sMBR, a higher TMP is required to pass the permeate into a separate tank. The aeration system also required for the bioreactor is essential to a higher cost programme, though this extra need of energy can be avoided in AnMBR (anaerobic MBR), whereas the biogas obtained from the decomposing organic material is itself reused in the aeration process. Studies have shown that the aeration stage requires 50% of the total energy required for MBR [26].
- The most challenging issue for MBR is probably related to membrane fouling. Biofilm formation ultimately results in blockage into membrane surface or may be onto pores of it. In order to control this module must carry out at a high hydrodynamic state. Chemical cleaning of the membrane is of some help, but then, this also led to the corporatization of membrane longevity [6]. Aeration used to control fouling also results in high turbulence, this reduces the microbial floc size and their mass transfer. Air scrubbing or back washing also is subject to the mechanical strength of the membrane [26]. For all those reasons, operational and maintenance costs of MBR technologies are still way higher than widely accepted conventional technologies.
- Solid retention time is MBR is much higher when in compared with CAS. Higher SRT deals negatively with microbial community. This also directly affects the kinetics in case of nitrifying and denitrifying bacteria [22].

- Higher MLSS concentration is required for MBR coupled with the tendency of high foaming is also problematic, which mainly occurs due to the high aeration demand of the bioreactor tank [31].
- Considering all these points, in ground reality, MBR plant is hardly applicable in areas where conventional wastewater treatment is already established, though MBR is promisingly making its way to the global market with the recent development of the membrane technologies.

6 Future Prospect

MBR technology is neither newly introduced nor emerging, but it is an extended purification process. Advancement in re-purification process and membrane technology leads to the extensive use of MBR [38]. A recent study revealed that MBR market shows significant growth, with a projected growth rate of around 17.4%. The main reason behind this is surging demand of waste-water purification worldwide, especially in China. Europe has also experienced an exponential growth. But growth is not up to the mark till now as projected in 2010, the study says. Nowadays, MBR is used in several fields. Besides municipal and industrial use, wastewater reclamation results in production of effluent worthy of drinking and this is the best part of MBR technology. MBR has emerged as a promising approach in food industry, pharmaceuticals and bio-fuel production also. The effluent is used for agricultural purpose recently. The best result is achieved using hydrogen-selective membrane in inorganic membrane reactors. As small plant area is required, MBR is preferred over conventional activated sludge process. Previously, operational and capital cost was a barrier in the industrial application of MBR technology. But in the last few years, this problem is resolved due to an increase in production of membrane and improvement of system, thus cost is reduced [27]. Research is on to mitigate the major drawback of high cost and high energy consumption. Advancement in these two areas will provide a more reliable and economical use of MBR in near future. Moreover, the submerged MBR system has developed increased plant capacity as well as improved effluent quality compared to the conventional process [54]. Considering all these positive approaches of MBR, it can be easily assumed that MBR technology will be economically competitive with conventional system.

7 Conclusion

MBR is a modern technique for wastewater treatment and reuse. It has a wide range of applications including drinking and groundwater abatement, municipal wastewater treatment, industrial wastewater treatment, odour control, solid waste digestion and others. As we know, the wastewater always contains a number of toxic substances that are harmful to the organisms, so it requires to be managed and recycle of that disinfectant water in other fields. There are several conventional techniques of ameliorate the levels of waste to an acceptable phase. MBR acts as an alternative technique due to its high handling capacities of organic loadings and the fluctuations in flow as well as in strength. Therefore, it is more useful than conventional technology because it produces a very eminent quality effluent. Due to its huge advantages, it is used widely in industries. Besides its numerous advantages, the main drawback was the cost of it. Now several manufacturers of MBR are available in the market and the number of MBR installation is growing gradually.

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Chapter 7
Removal of Toxic Emerging Pollutants Using Membrane Technologies

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1 Introduction

With the ever-increasing population and simultaneous rise in the demand and supply chain, an underestimated and unprecedented burden is laid on environmental health. Environmental pollution has been a major concern for decades especially since the second chemical revolution after World War II. Various pollutants and contaminants are constantly added into the natural environment due to anthropogenic activities, however, in the past few years, some new and rare chemicals are being found in

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different ecosystems particularly in the aquatic ecosystems. These contaminating substances are arising from the application of advanced technology and newfound scientific knowledge on new kinds of product development and product enhancement. This in turn depends on the lifestyle we chose and the kind of highly advanced products we use in our daily life and expect to be developed in the future. For instance, skin care and personal care products industry has been growing extravagantly involving the use of a wide range of chemicals that were not used earlier or in the recent past. Similarly, the food industry has been employing numerous varieties of food additives and preservatives for the processing, packaging, and preservation of food. The growth in the pharmaceutical and agricultural industry is beyond fancy with the application of nanomedicines, nanopesticides, and nanofertilisers. In today's time, the pharmaceutical industry is considered to be the biggest source of new kinds of environmental pollutants [118]. And to add to all these, the production of urban industrial chemicals such as paints, resins, disinfectants, antioxidants, antifouling agents, flame retardants, detergents, surfactants, etc. have also been on an up rise. Such chemical substances which were discovered a long time back but have recently found application in various fields and hence are being found as contaminants in different natural environments can be regarded as Emerging Pollutants (EPs).

The characteristics and effects of EPs on man and the environment are not quite clear and therefore are being studied for better understanding. For the last couple of decades, thousands of research works and articles have been published on the growing concern for the EPs. And it has been found that with each passing decade different EPs are added to the watch list by the United Nations Environment Program (UNEP). Presently it includes materials like antibiotics, steroids, nanomaterials, industrial chemicals, microplastics, etc. [27]. Already over 600 million people do not have proper access to a basic level of drinking water [107]. If such EPs are not prevented from reaching the water sources, they have the potential to have an adverse effect on health and the environment and people will further live on water scarcity. So, they need to be monitored, to get the statistics of the intensification of that constituent in the environment. There are several sources of origin of those EPs shown in Fig. 1.

There are several procedures for the removal of EPs from the water like adsorption, ozonation, coagulation, precipitation, filtration, etc. Of them, membrane technology plays the foremost role. Application in membrane technology became known in the mid-nineteenth century, since then various research has been done to improve its efficiency and large-scale application. In membrane technology, there are different methods like Microfiltration [88]. Ultrafiltration [81], Nanofiltration [18], Reverse Osmosis [15], Forward Osmosis [34], Hybrid Processes [94], etc., which are widely used in water purification. A membrane works mainly by obstructing the undesirable particles from purified water. Some of these methods are widely used as they are not only efficient but also economical. With the advancement in the field of science, technology, and nanotechnology, continuous efforts are being given in assembling various materials for the synthesis of novel membranes for attaining higher efficiency in permeate flux rate. Great emphasis is being given to obtaining membranes with special antifouling properties and membranes which could be easily cleaned for

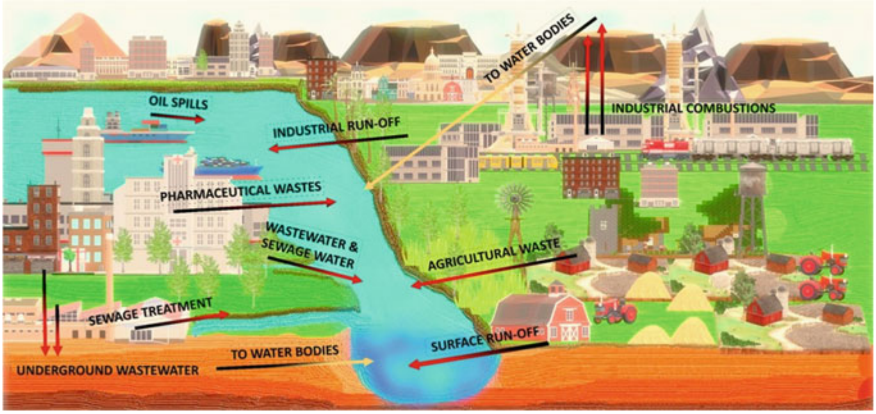


Fig. 1 Sources of water pollution

multiple uses. Even in the case of membrane fouling, effective cleaning methods must be used for the reuse of the membrane.

2 Emerging Pollutants

Emerging Pollutants (EPs) or Emerging Contaminants can be defined as an indefinite group of substances including synthetic, organic, and inorganic compounds that are not regulated under national or international legislations and do not have any set standards or restrictions for emission. These are compounds that have gone unnoticed in the past and are only recently being detected in different concentrations in the environment and are now being identified as a potential threat to the environment and humans. Even with the absence of any current regulations for EPs, it has raised a great deal of global concern due to their associated potential impact and hazards it can impose on ecosystems in near future [16]. On 20 Feb 2020, the United Nations Environment Program (UNEP) organized an event and webinar on “Emerging Pollutants in Wastewater: An increasing threat” to discuss the issue of EPs and waste waters and to focus on case studies, projects as well as specific pollutants that constitute a threat to the environment and livelihoods.

EPs can be regarded as more dangerous because most of them have remained undetected in the environment only until highly advanced and sensitive analytical and detection tools were developed and applied. The World has already suffered from the past activities of human civilization, and studies have shown that every decade a new set of EPs are added to the existing harmful pollutants. Hence, an immediate and effective strategy is required for the detection and identification of such EPs along with regulation policies and restrictions on their emission and discharge. Application of smart technologies for the prevention of EPs at source or modern hybrid remediation scheme at natural ecosystems where they eventually end up is the need of the hour.

2.1 Occurrences and Classification

There are multiple major sources that cause water pollution. The main emerging cases include includes wastes from industrial, agricultural, and pharmaceutical sectors along with some domestic pollutant sources (Table 1).

Table 1 Various sources, categories, and examples of emerging pollutants

Sources	Category	Compounds
Industrial	Nanoparticles	Titanium dioxide, limestone
	Heavy metals	Arsenic, chromium, cadmium, mercury, lead, nickel, thallium
	Food additives	Sucralose, triacetin
	Flame retardants and impurities	Tetrabromobisphenol A, polybrominated diphenyl ethers, polybromonated biphenyls, tris(2 chloroethyl) phosphate, polybromonated dibenzo-*p*-dioxins, hexabromocyclododecanes, polybromonated dibenzofurans
	Water (disinfection)	Chloroacetaldehyde, 2,2,2-trichloroacetamide
	Antifouling compounds	Organotins, cybutryne
	Anticorrosive	1H-benzotriazole
	Perfluorinated compounds	Perfluoroctanoic acid, Perfluoroctane sulfonates
	Detergents	2-[2-(4-Nonylphenoxy)ethoxy]ethanol, 2-[2-(4-octylphenoxy)ethoxy]ethanol
	Wood preservatives	2,4-Dinitrophenol
	Gasoline additives	Dialkyl ethers, tert-butyl methyl ether
Pharmaceutical	Steroids and hormones	Estradiol, diethylstilbestrol, estriol, estrone
	Psychiatric drugs	Bromazepam, lorazepam, carbamazepine
	β-Blockers	Propranolol, bisoprolol, metoprolol, timolo
	Fragrances	Polycyclic, nitro, and macrocyclic musks
	Veterinary and human antibiotics	Azithromycin, ampicillin, doxycycline, trimethoprim, erythromycin, lincomycin, amoxicillin
	Anti-inflammatory drugs and analgetics	Acetaminophen, codeine, aspirin, dipyrone metabolites, ibuprofen, diclofenac
	Drugs of abuse	Cocaine, morphine

(continued)

Table 1 (continued)

Sources	Category	Compounds
	Lipid regulators	Amlodipine, clofibric acid, enalapril, fenofibric acid, simvastatin, cilazapril, atorvastatin
	Sun-screen agents, insect repellents	3-(4-methylbenzylidene)camphor, *N,N*diethyl-3-methyl-benz-amide, benzophenone
Agricultural	Herbicides	Methylchlorophenoxypropionic acid
	Insecticides	Usnic acid, 2-methylanthraquinone, isopropyl-o-cresol
	Pesticides	Thiocarbamates, organophosphorus pesticides, 2-aminobenzimidazole
Lifestyle products	Food additives	Terpineol, phenylethyl alcohol, 1,8-cineol, triacetin
	Artificial sweeteners	Alitame, dihydrochalcone aspartame, neotame, neohesperidin
	Stimulants	Caffeine, nicotine

2.1.1 Industrial and Heavy Inorganic Wastes

The leaching of volatile organic compounds (VOC) and pesticides, heavy metals, etc. into the environment has been known for a long time. But the presence of synthetic organic substances, nanomaterials, endocrine disruptors coming from various industries into natural water bodies is a newfound concern [86]. These EPs from various industrial units can be briefly classified as follows with a few examples:

- Perfluoro alkyl compounds—Perfluorooctane sulfonic acid and its derivatives (PFOS).
- Volatile Organic Compounds (VOCs)—Styrene, Benzene, dichloromethane, xylene, toluene, etc.
- Flame retardants—polychlorinated alkanes, 3,3′,5,5′-tetrabromobisphenol A (TBBPA).
- Corrosion inhibitors—benzothiazol-2-sulfonic acid, 1,2,3-Benzotriazole.
- Antioxidants—2,6-Di-tert-butylphenol, Diphenylamines (DPAs).
- Plasticizers—Bisphenol A, phthalate compounds such as di-2-ethylhexyl phthalate (DEHP)
- Surfactants—Alkylphenol ethoxylate surfactants, octylphenol, nonylphenols.
- Antifouling compounds—acetylcholine esterase (AChE), N-acyl homoserine lactone (AHL), iragrol, tributylin oxide (TBTO).
- Antioxidants—2,6-Di-tert-butylphenol.

There are innumerable compounds that are used directly or as intermediates in chemical industries and manufacturing units for plasticizers, antioxidants, surfactants, detergents, food additives, personal care products, pharmaceuticals, etc. The major issue with these emerging pollutants is that most of them act as endocrine disruptors [60, 63]. The most common compounds that meddle with the functioning of the endocrine system are Bisphenol A (BPA), PFCs, Polybrominated Diphenyl Ether (PBDE), Triclosan, nonylphenol, galaxolide, tonalide, ibuprofen, diclofenac, etc. [63, 92]. Antifouling paint particles (APP) from marine coatings, boatyards, etc. are reported to cause mortality in microinvertebrates and marine sediment dwellers [104]. APP arise from the recreational boat industry and are readily added to the environment. Antifouling dust and pluming particles generated during sanding enter the marine ecosystem with waste washdown and runoff. In fact, the airborne dust of APP does not remain confined to the marine site but travels long distances and can be found in soils and rooftops of houses of the surrounding regions [105]. In addition to these compounds various by-products, such as disintegrated chemicals are generated by the metal industry and are discarded as waste sludge which is often untreated and discharged into water bodies causing various complications to flora and fauna in that area [80]. Various dyes, resins, and solvents used in industries are drained in water bodies resulting in bioaccumulation and biomagnification eventually ending up in the human food chain [38, 80]. Different heavy metals like As, Hg, Cr, Cd, Pb, Ni, Fe, Mn, Zn, and Co are added to the surface water bodies, lakes, and rivers from various sources like metal-based pesticides, fertilizers, antifouling compounds, mining, and manufacturing waste discharge. Natural weathering of rocks due to extreme climatic conditions is a non-anthropogenic activity that also adds heavy metals to the environment. However, the majority of the sources are anthropogenic and require rigorous regulations and monitoring of metal emissions [121]. For instance, chromium is used widely in paints, textiles, and leather industries, and wastewater runoffs from these plants contain large concentrations of Cr^{3+} and Cr^{6+} form which are needed to be removed and recycled [114].

2.1.2 Pesticides and Agricultural Wastes

With the ever-increasing demand for higher agricultural yields, attempts are being made to reduce the application of plant protection products (PPP) and nutrition. Hence the agricultural researchers are switching toward the development of nano-agro chemicals which are often called nanopesticides and nano fertilizers [44, 60, 80, 114]. Such emerging nano-agrochemicals have a potential impact on the environment as it has direct application on the environment [44]. The different types of materials used for nano-agro chemicals can be carbon-based such as Carbon Nano tubes (CNT), metals, and metal oxides such Ag nanoparticles, ZnO, TiO_2, CuO, metalloids such as silica and alumina used as insecticides, non-metals such as sulfur. Moreover, liposomes, lipids organic polymers, oil–water emulsions, etc. are also applied in different formulations in the form of the solid particle or non-solid structures. These EPs from the agricultural sector received delayed attention as compared to other EPs applied in food processing and packaging which are more directly inclusive in the food chain [44]. Although the motive behind using pesticides and fertilizers is to yield better crops and vegetation yet it causes various complications to human health either directly or indirectly. In human pesticides and fertilizer, contamination is mainly caused due to dermal contact and ingestion. Pesticide contamination in water can cause human health issues like immunosuppression, hormone disruption, reduced intelligence, Alzheimer's disease, cancer, birth defects, etc. Additionally, the surface runoffs from agriculture containing fertilizers and PPP promotes water pollution as well [100].

2.1.3 Pharmaceutical Wastes

Pharmaceuticals and personal care products (PPCPs) have been recognized as emerging pollutants as they are constantly added to the environment [45] in the form of complex organic and bioinorganic products which are difficult to breakdown [29]. Although in the past decade there have been numerous reports on the presence of PPCPs in surface water as well as ground water bodies [45], these compounds still remain poorly characterized and unregulated or are still under the process for regulation and legal framework [45]. It would be appropriate to say that the fate of PPCPs has not yet gained much-required attention by policy makers and regulators, but in some countries, this scenario is gradually changing. For instance, European Union has long back added anti-inflammatory drugs to the List of Priority Substances [20]. PPCPs may comprise illicit drugs, over-the-counter drugs, nutritional or health supplements, diagnostic agents, etc. in either whole unused form or as expired products. It can also be widely present as metabolized and partially metabolized forms excreted by the human and animal body. These eliminated compounds from the body with faces and urine which are not possible to treat in the water treatment plant of the municipal bodies. These wastes along with water (called black water) [39, 61] get to the mainstream and thus contributes to water pollution on a large scale. Personal care products like soaps, shampoos, fragrances, cosmetics, etc. are discharged via showering, bathing, and cleaning (Fig. 2).

Acetaminophen has been identified in surface waters and wastewater as well as in drinking water. It has been reported that 58–68% of acetaminophen is released from the human body after therapeutic application and can lead to liver failure and death when used in excess [61]. Therefore, cost-effective and efficient methods are

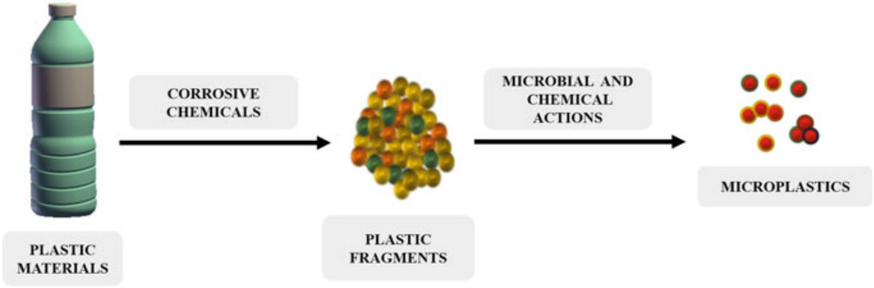


Fig. 2 Formation of microplastics by the action of microbes and chemicals

needed to remove Pb^{2+} ions and acetaminophen from water and different industrial effluents [106].

Organic acids such as acesulfame-K, saccharin, and cyclamate which are the key ingredient of sugar-free products, and calories-free sweeteners are eliminated from the gut largely through urine, without undergoing metabolism ending up in water bodies [90].

2.1.4 Lifestyle Products and Food Stuffs as Emerging Pollutants (EPs)

This category of emerging pollutants comprising a wide range of synthetic organic compounds arise from the lifestyle choices made by people. The major representatives of this class of EPs are stimulants and artificial food additives and preservatives.

Stimulants are referred to as psychoactive drugs which are commonly used for temporary enhancements of the mental and or physical functioning of the body, such as wakefulness, alertness, endurance, productivity, heart and pulse rate, blood pressure levels, and a reduced necessity for food and sleep. Many stimulants are capable of enlightening mood and relieving stress and anxiety, and some can even prompt feelings of ecstasy. Stimulants are used for clinical and therapeutic purposes and their effects are based on a number of pharmacological mechanisms including noradrenaline and dopamine activity, nicotine acetylcholine receptor agonism, adenosine antagonism, etc. such psychoactive drugs are often prescribed by doctors and medical professionals under various mental health conditions. However, the changing lifestyle and ultra-urban way of living have encouraged a large population across the globe to include stimulants in their daily life. The most common stimulants used by people without professional consultations are caffeine and nicotine [26].

- **Caffeine**—Caffeine is a compound that belongs to the xanthine class of chemicals and is naturally present in coffee, tea, and soft drinks and minor amounts in chocolates or cocoa. It is also used in pharmaceutical formulations in the form of tablets. The majority of the ingested caffeine gets converted into secondary metabolites, however, a small fraction ranging between 0.5 and 10% remains unaltered and ends up in waterways through excretion in urine. The fate and final concentration levels of caffeine in WWTP effluent and eventually natural water bodies depend on the consumption of caffeine, which in turn dependents on population size and its consumption habit. Studies have shown that in the United States, per person daily consumption of caffeine typically ranges from 140 to 210 mg d^{-1}, whereas that in Europe accounts for 37–319 mg d^{-1} of caffeine on a daily basis apart from sewer systems, caffeine can also enter waterways through Household or domestic plumbing when caffeine-containing products such as coffee, beverages other caffeinated food products are discarded. Reports have shown that caffeine is now found in different ecosystems such as groundwater of Europe and mountain lakes and aquifers of the United States with concentrations typically ranging in ng L^{-1} [19, 24]. However, elevated levels of caffeine have been reported from metropolitan areas of Chicago and concentrations went as high as 505 ng L^{-1} in aquifers and 4500 ng L^{-1} in the groundwaters of the United Kingdom. Although as of now caffeine does not present any harmful effects on humans or animals, its effect on aquatic organisms needs to be explored. Studies in the recent past have suggested that exposure to caffeine may aggravate the adverse effects of other environmental impacts on corals, thereby making them more prone to bleaching [85].

- **Nicotine**—Nicotine is an alkaloid found in plants of the family *Solanaceae. It is a potent* stimulant drug and is naturally present in the leaves of *Nicotiana tabacum*, approximately ranging from 0.6 to 3.0% of the dry weight of tobacco leaves. Nicotine is toxic in nature and more than 0.5 g of oral intake of nicotine is sufficient to kill an adult. In the past Nicotine was used as an antiherbivore and insecticide, however, that is prohibited now. The most common lifestyle product containing nicotine is a cigarette that contains up to 20 mg of nicotine [16]. The leftovers of smoked cigarettes, cigarette butts, filters, etc. are disposed of directly in the environment in public areas, streets, etc. These plastic litter and remnants of smoked cigarettes are carried with runoff to drains, and sewage channels ending up in, lakes, rivers, oceans, and sea beaches [75]. Though Cigarette litters are composed of cellulose acetate which is apparently a biodegradable polymer, it has been seen that when discarded in the environment, it resists biodegradation and can remain intact for as long as 18 months [52]. Other substances mostly nicotine and ethylphenol that seep out of cigarette butts have shown acute toxicity in freshwater microbes [71]. Different concentrations of nicotine ranging from 144 to 8070 ng L^{-1} have been reported in the groundwaters of the United Kingdom [98]. Nicotine was one of the top five toxic chemicals reportedly released from tobacco-based product manufacturing facilities in 2008 and was designated as toxic release inventory chemicals by EPA [75, 76]. Cigarette ash is altogether a different kind of hazardous pollutant and may be described as particulate matter. It contains several heavy metals such as As, Cr, Pd, Cd, and Nickel. It has potential phytotoxic and genotoxic properties [67].
- **Food additives** belong to a huge class of various substances that are added to the food intentionally for three basic reasons as described by USFDA:
  - to preserve or enhance safety and freshness
  - to increase or maintain nutritional value
  - to enrich taste and texture.

Food additives can include vitamins and provitamins, minerals and trace elements, stabilizers, antioxidants, acidulants, coloring agents, color stabilizers, gelling agents, anti-caking agents, acidity regulators, emulsifiers, artificial sweeteners, chewing gum bases, and many more. The list can go on and on, and hence it has drawn the attention of many researchers and is now being considered as an emerging contaminant. There are many food additives that contain toxicological substances and endocrine disruptors. Triethyl citrate is one such compound that is used as a foam stabilizer and as pharmaceutical coatings [54]. Other food additives having adverse effects are phenyl–ethyl alcohol, terpineol, triacetin, 1,8-cineole (eucalyptol), etc. Artificial sweeteners such as aspartame, neotame, alitame, and neohesperidin dihydrochalcone get largely transformed into major metabolites and are excreted through urine and found in aquatic environments [23]. Authorization for food additives is obtained only after rigorous toxicological testing results show no harmful effects, however, there are internationally set standards for regulating the testing. WHO has laid some guidelines that are widely accepted. These guidelines include testing of the additives for acute, subchronic, and chronic toxicity, along with carcinogenicity, teratogenicity, mutagenicity, and biochemical activity [16].

2.1.5 Microplastic Pollution

One of the immediate causes of emerging pollutants is microplastic pollution. Richard C Thompson in his article titled "Lost at Sea: Where Is All the Plastic?", coined the term microplastic [103]. He described its presence to the world that plastics that are non-biodegradable in nature could be broken down into smaller fragments by physical or chemical means. These fragments are generally less than 5 mm in diameter. When these microplastic fragments mix into larger water bodies they cause water pollution on a large scale.

2.1.6 Sewage Wastes

Sewage waste contains various chemicals, pharmaceutical products, and other unwanted waste materials which get run off to the water source. A study by Kumar A and his team shows that when various microorganisms present in water bodies comes in contact with antibiotic-mixed water they become antibiotic resistant. As a result of this, the effectiveness of the drugs toward targeted organisms and pathogens decreases. Another group of researchers in 2006 reported the increasing trend of ARGs in the environment and its adverse effect on human life. Sewage and drainage lines provide a major source for this problem. Sewage from households, and hospitals contain medicinal excrete which includes primary and secondary metabolites of different medicinal drugs and antibiotics. These contaminants over a time can lead to the development of resistance toward different antibiotics in pathogens (Fig. 3).

2.2 Significance

As discussed above the effect of the emerging pollutant are not fully understood about their nature and their effect on the ecosystem. Although there is much evidence about their harmful nature. Industrial shreds of evidence are that there are a large group of chemical species that will or may cause life hazards in long run. They mainly reach water sources via industrial wastewater which then gets eliminated in water bodies. The same thing applies in the case of pharmaceutical wastes where

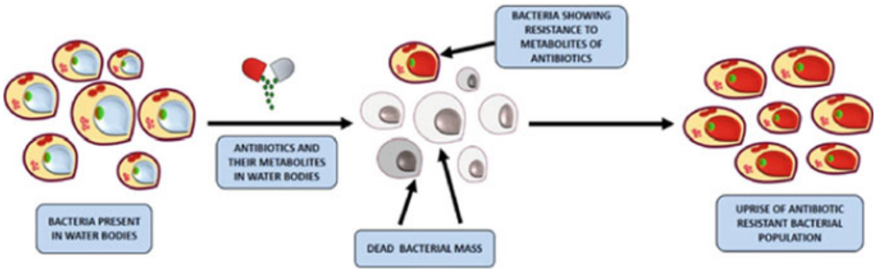


Fig. 3 Formation of antibiotic-resistant bacteria

various mixed chemicals and biomaterials are poured into water bodies without proper treatment. In the case of agricultural wastes, they generally mix with water sources via surface runoffs. Here the various chemical agents which are added to the soil and sprayed on plants to enhance the fertility of the soil and yield higher productivity gets mixed with the water bodies. In the case of microplastic pollution the plastic materials which are considered as non-biodegradable in nature, on actions of chemical agents get broken down into smaller fragments as a result of which they get into the bodies of various aquatic species and ultimately comes in contact with humans. These microplastics pose an extreme form of threat to the ecosystem. Last but not the least the sewage system of a particular area contains various harmful emerging pollutants. This contains harmful wastes of households and the entire town. If not treated properly these contaminants which may contain various emerging pollutants get mixed directly with the water bodies. Not only this but these pollutants also reach water sources by contamination with underground water sources.

2.3 *Guidelines for Disposal of EPs*

Although EPs are often specifically described as substances that are not commonly monitored or regulated or are under the process of setting regulatory standards, yet several organizations across the globe have recognized the need to address this issue of rising EPs especially those present in water bodies.

UNESCO has recognized EPs as a serious threat to human wellbeing their livelihoods and environmental health [32]. It has also been established that good global water quality is essential for sustainable development post-2015. UNESCO has undertaken a project under "UNESCO-IHP International Initiative on Water Quality (IIWQ)" to ensure improved water quality, wastewater management, safe reuse of wastewater, and enhanced water and food security.

This UNESCO Project on "Emerging Pollutants in Wastewater Reuse in Developing Countries" implemented under IIWQ is sponsored by the Swedish International Development Cooperation Agency (Sida) under the Program Cooperation Agreement between UNESCO and Sweden for 2014–2017. It aims at addressing the urgent demand to strengthen the scientific, technical, and policy managing capacity including all UNESCO Member states so as to overcome the global environmental risk posed by the emerging pollutants in water and wastewater. They describe the EPs as "synthetic or naturally-occurring chemical or any microorganism that is not commonly monitored or regulated in the environment with potentially known or suspected adverse ecological and human health effects". However, sufficient knowledge on potential human health hazards and the risk to the ecosystem caused due to the emerging pollutants is lacking. Most EPs arising from various sources are continuously released into the water at very low concentrations, but they can potentially cause chronic toxicity and endocrine disruption in humans as well as aquatic wildlife including the development of pathogen resistance in the bacterial population. Hence, through the above project, UNESCO highlights the need to adopt new appropriate techniques and policies to monitor emerging pollutants and to prevent and control their disposal of water resources.

Another International Project that has given priority recognition to emerging pollutants is "The network of reference laboratories, research centers, and related organizations for monitoring emerging environmental substances in Europe (NORMAN)". It was established in 2005 and is funded by the European Commission in order to encourage the construction of a permanent network between research centers and reference laboratories in alliance with other parties involved such as industries, standardization bodies, and non-governmental organizations.

NORMAN has prepared a list of the chemicals that are considered emerging substances and EPs. The substances are selected on the basis of current citations in the scientific literature, by NORMAN Prioritization Working Group.

Other institutes such as WHO/FAO—Food and Agriculture Organization of the United Nations, USGS, USEPA Australasian society for ecotoxicology (SETAC-AU), Joint FAO/WHO expert committee on food additives (JECFA) have time to time given ample attention to EPs with special concern owing to their potential threat to the ecosystem and mankind. Therefore, recommendations and legislation at different levels are available based on the tested potential risks of the emerging contaminants.

The EPA in the United States has categorized three levels of EPA-set regulatory so as to bound the concentrations of certain pollutants in the water provided by the public water systems. Under the Safe Drinking Water Act (SDWA) EPA has set National Primary Drinking Water Regulations (NPDWRs) which comprises a set of mandatory standards to limit the concentration of certain contaminants in drinking water defined as "maximum contaminant levels" (MCLs). The primary standards are meant to limit the contaminant levels of substances such as microbes, disinfectants, inorganic and organic chemicals, including radionuclides.

Next comes The National Secondary Drinking Water Regulations (NSDWRs) which are applied to contaminants that are not considered to pose a direct risk to human health. This level of regulatory recommendations represents the non-mandatory water quality standards and is defined as "secondary maximum contaminant levels" (SMCLs). The contaminants falling in this category include a small group of 15 substances that do not cause health hazards to humans, however, they have an impact on the taste color, and odor of the water and can cause undesirable alterations tooth or skin discoloration sand can have aesthetic and economic repercussions owing to their corrosive and staining nature.

The third level of recommendations encompasses those contaminants which are currently not monitored as such nor do have any set regulatory standard but have been detected in public water systems and hence are enlisted in the contaminant candidate list (CCL).

In addition to the above recommendations, the European Food Safety Authority (EFSA) and JECFA have established toxicological guideline values for some EPs classes which are shown below in Table 2.

Table 2 Toxicological guideline data as per EFSA and JECFA [26]

Contaminant/compound	Type	Value	Year citation
Metals			
Mercury	PTWI	4 μg kg^{-1} (bw $week^{-1}$)	2011 [56]
	TWI	4 μg kg^{-1} (bw $week^{-1}$)	2012 [51]
Methylmercury	PTWI	1.6 μg kg^{-1} (bw $week^{-1}$)	2003 [55]
	TWI	1.3 μg kg^{-1} (bw $week^{-1}$)	2012 [56]
Lead	BMDL01	0.50 μg kg^{-1} (bw day^{-1})	2011 [26]
Cadmium	PTMI	25 μg kg^{-1} (bw $month^{-1}$)	2011 [26]
	TWI	2.5 μg kg^{-1} (bw $week^{-1}$)	2009 [82]
Arsenic	BMDL0.5	2–7 μg kg^{-1} (bw d^{-1})	2011 [55]
	BMDL10	0.3–8 μg kg^{-1} (bw d^{-1})	2009 [36]
Pharmaceuticals and personal care products			
Benzylpenicillin	ADI	<30 μg kg^{-1} bw	1990 [26]
Oxytetracycline	ADI	0–30 μg kg^{-1} bw	2002 [26]
Emamectin	ADI	0–0.5 μg kg^{-1} bw	2013 [26]
Derquantel	ADI	0–0.3 μg kg^{-1} bw	2012 [26]
Flumequine	ADI	0–30 μg kg^{-1} bw	2007 [26]
Carazolol	ADI	0–0.1 μg kg^{-1} bw	1995 [26]
Dexamethasone	ADI	0–2 μg kg^{-1} bw	2009 [26]
Tilmicosin	ADI	0–40 μg kg^{-1} bw	1998 [26]
Triclabendazole	ADI	0–3 μg kg^{-1} bw	1993 [26]
Tylosin	ADI	0–30 μg kg^{-1} bw	2009 [26]
Avilamycin	ADI	0–2 μg kg^{-1} bw	2009 [26]
Endocrine disruptors			

(continued)

Table 2 (continued)

Contaminant/compound	Type	Value	Year citation
Bisphenol A (BPA)	TDI	4 μg kg^{-1} bw	2015 [26]
E2	ADI	0–0.05 μg kg^{-1} bw	2000 [26]
Testosterone	ADI	0–2 μg kg^{-1} bw	2000 [26]
Progesterone	ADI	0–30 μg kg^{-1} bw	2000 [26]
Melengestrol acetate	ADI	0–0.03 μg kg^{-1} bw	2001 [26]
PFOS	TDI	150 ng kg^{-1} (bw d^{-1})	2008 [26]
PFOA	TDI	1500 ng kg^{-1} (bw d^{-1})	2008 [26]
Polycyclic aromatic hydrocarbons			
Benzo[*a*]pyrene	BMDL10	0.10–0.23 mg kg^{-1} (bw d^{-1})	2006 [26]
	BMDL10	0.07–0.20 mg kg^{-1} (bw d^{-1})	2008 [26]
Chrysene	BMDL10	0.17–0.45 mg kg^{-1} (bw d^{-1})	2008 [26]
PAH$^{(c)}$	BMDL10	0.34–0.93 mg kg^{-1} (bw d^{-1})	2008 [26]
PAH$^{(d)}$	BMDL10	0.49–1.35 mg kg^{-1} (bw d^{-1})	2008 [26]
Brominated flame retardants			
Pentabromodiphenyl ether	LD^{50}	2640–6200 mg kg^{-1} bw	2012 [26]
Polybrominated biphenyls	LD^{50}	64–150 mg kg^{-1} bw	2010 [26]
Hexabromocyclododecane	NOEL	10 mg kg^{-1} bw	2011 [26]
Tetrabromobisphenol A	BMDL10	16 mg kg^{-1} bw	2011 [26]

3 Conventional Technologies for the Removal of EPs

Various types of physical, chemical, and biological processes can be combined in the conventional water treatment process to remove contaminants from water. Solvent extraction, oxidation, carbon adsorption, ion exchange, evaporations are some conventional technologies that are used for the removal of organic matters, metals, etc. Various types of factors determine which technique is applicable for the treatment of wastewater [31] (Fig. 4).

3.1 *Adsorption Technique*

Adsorption is a surface phenomenon where the particles from a fluid are attached to the upper layer of material. This technique is used for water treatment, in which the contaminants get adsorbed on the surface. There are two types of adsorption, i.e., physisorption and chemisorption. If the interaction between the material surface and the adsorbed particles has physical nature then it is called physisorption. In this type of adsorption, the interaction is Van der Waals force. And if the interaction between the surface and the adsorbed particle has chemical nature like chemical bonding then

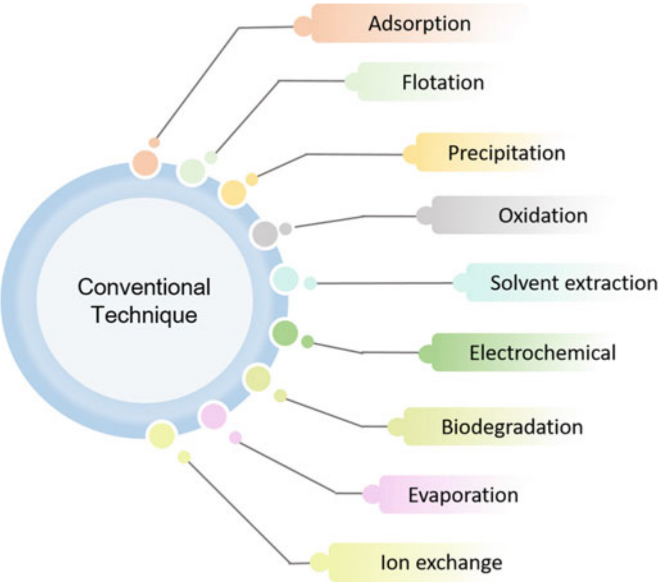


Fig. 4 Different types of conventional techniques

this is called chemisorption. The pollutants removal mechanism can be physisorption or chemisorption depending on the surface and contaminating particle nature [46].

In the water treatment process activated carbon (AC) is wildly used. Activated carbon has a higher surface area which can adsorb a significant amount of pollutants on its surface. It can adsorb heavy metals by physisorption technique. Surface modification of AC is required depending upon the chemistry of the pollutants. Acidic, basic, microwave, biological modification is done to adsorb more efficiently and increase the quality of the treated water. Powdered activated carbon (PAC) and granular activated carbon (GAC) are used for this purpose. In Fig. 5, the adsorption mechanism has been where adsorbents are get adsorbed on the adsorbent surface.

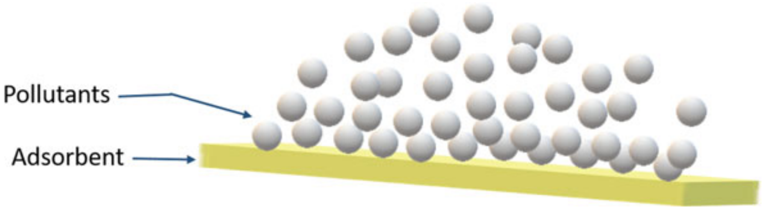


Fig. 5 Pollutant particles adhere to the adsorbent surface

Zeolites are three-dimensional crystalline materials of aluminum silicate. It has a microporous structure. Zeolites are wildly used in water purification processes. It has much space in its structure and can undertake metals through the ion exchange process. Sodium, calcium, potassium, and other charged ions occupy the spaces and they can be replaced by heavy metals. Zeolite can be used as a substitute for activated carbon. Fly ash is a waste material from the thermal power plant. It is a fine gray colored powder consisting of glassy particles. Fly ash contains silica (SiO_2), Alumina (Al_2O_3), iron oxide (Fe_2O_3), and carbon. Cr (VI), Cu (II) can be removed by fly ash. Many types of organic dyes and phenol can also be removed efficiently from wastewater.

Chitin is one type of biopolymer which is present in the exoskeletons of crabs and other marine species. Chitin is one of the world's second largest biopolymer next to cellulose. Chitosan is made from chitin by deacetylation. Chitosan has much greater adsorption capability than chitosan Many cationic and anionic dyes can be removed by chitosan. Many nanocomposite materials are made with chitosan which shows a significant amount of removal of dyes from industrial wastewater [66]. The structure of chitosan is shown below.

3.2 Flotation Technique

Flotation is one type of separation process which can be used in water treatment. In this process, gas bubbles are introduced into the wastewater. These gas bubbles attach themselves to the solid contaminating particles and form bubble-solid agglomeration. The apparent density of these bubble-solid agglomerates is less than the water which causes the agglomerations to float to the surface. Flotation is wildly used in mineral technology in which is used for extracting metals from various ores but now it can be also used in wastewater treatment. Various microplastics, antibiotics, bacteria, fungi, and yeasts can be removed by this technique. Oily wastewater can also be treated by this technique [62]. There are different types of methods to produce gas bubbles. Depending upon this, flotation can be divided into different types such as electro flotation, dispersed air flotation, and dissolved air flotation. In the picture the air bubble generator is producing air bubbles, bubble-pollutant agglomerations are forming and accumulating at the upper surface of the aqueous solution (Fig. 6).

3.3 Precipitation

The precipitation technique which is also known as reagent coagulation is a conventional technique for wastewater treatment. In this technique, the pollutants precipitate

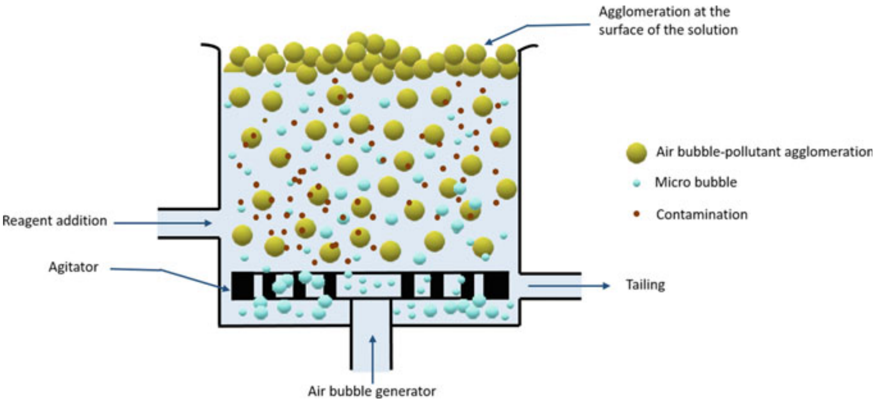


Fig. 6 Flotation technique

from the polluted wastewater and by separating this we can get impurities-free water. The precipitate is formed by changing the PH, coprecipitation using a precipitating agent or elecroxidising potential. Precipitation techniques can be divided into two types such as chemical precipitation and coprecipitation. Chemical precipitation is wildly used in the removal of ionic metals from wastewater. An external precipitating agent is added and this process proceeds through three stages, those are nucleation, crystal growth, and flocculation. In the case of the nucleation stage, a new phase such as a crystal formation occurs from a liquid or vapor phase via the self-assembly process. Two types of nucleation occur, homogeneous and heterogeneous nucleation. In the homogeneous nucleation process, no foreign substances are required but in the case of heterogeneous nucleation, a foreign substance is required to initiate the nucleation. In the crystal growth stage, the addition of new atoms, ions, or polymer occurs to the nucleation sites and the particle size increases as the growth go on. And ultimately in the final stage, the contaminating particles separate out from the solution and form sediment below the water-containing vessel. In the case of the coprecipitation process a soluble component precipitate along with a macro-component by forming a mixed crystal.

3.4 Oxidation Technique

In this technique, the contaminations are oxidized by various oxidants such as gaseous oxygen (O_2), chlorine (Cl_2), ozone (O_3), chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), and in the case of advanced oxidation processes (AOPs) reactive oxygen species (ROS) like hydroxyl radicals (.OH) are used as oxidants. The hydroxyl radicals react with the pollutants initiating the oxidation process and this reaction goes on until all the pollutants are oxidized and transformed into harmless compounds. AOPs are widely used to eliminate the organic contaminants from wastewater by oxidation reaction. There are various reagent systems in AOPs such as photochemical degradation process (UV/O_3, UV/H_2O_2), photocatalysis (TiO_2/UV, photo-Fenton reactives), and chemical oxidation process (O_3, O_3/H_2O_2, H_2O_2/Fe^{2+}) and they all produce·OH radicals.

$$\text{AOPs} \rightarrow \cdot\text{OH} \xrightarrow{\text{Pollutants}} CO_2 + H_2O + \text{inorganic ions}$$

3.5 Solvent Extraction

The main purpose of the solvent extraction process is to separate the wastewater into a water effluent that contains a lower concentration of contaminants and a stream that contains pollutants. This technique is wildly used in the separation of metals from aqueous solution, aromatic compounds from water, and dehydration of acetic acid. Phenols, cresols, or other phenolic acids can be eliminated from this process [58].

3.6 Electrochemical Technique

Electrochemical processes are an important technique for the last two decades for wastewater treatment. This technique is wildly used in metal extraction from wastewater. The electrochemical mechanism for metal extraction is simple. The metal present in the solution gets deposited on the cathode and this process is called cathodic deposition.

$$M^{n+} + ne^- \rightarrow M$$

In this technique, there are various technologies such as electrodeposition, electrocoagulation, electrofloculation, electrooxidation, etc. [68]. Phenolic compounds can be destroyed by the electrochemical anodic oxidation process [70]. In the electrochemical oxidation process, the oxidation of pollutants present in wastewater occurs at anodes through the generation of active oxygen. This is called anodic oxidation process. A toxic, non-biocompatible pollutant can be transformed into a biocompatible organic compound by this process. Electrocoagulation very effective process to eliminate pollutants from water. In this technique, the current is passed through the water, and it destabilizes the emulsified, suspended, or dissolved contaminants. Electric current works as an electromotive force that causes the chemical reaction. In the electroflocculation technique metal ions such as Fe and Al are electrolytically added at the anode and gas bubbles such as H_2 are formed at the cathode. The gas bubbles capture the contaminating particles and most of them float to the surface of the solution. In the electrodeposition technique, various contaminants such as metal ions can be electrochemically deposited on the cathode surface and the electrolyte can be free from that type of metal ions.

3.7 Biodegradation

Biodegradation is one kind of sustainable way to clean contaminated water. Microorganism, bacteria, yeasts, fungi, and green plants are used for this technique. Various organic pollutants, pharmaceutical substances, and polyaromatic hydrocarbons can be degraded by this process. Various processes such as the microfiltration technique can be integrated with biodegradation to increase the removal efficiency of pollutants from water [65]. Two types of biodegradation processes are used, i.e., aerobic degradation process and anaerobic degradation process. In the case of aerobic degradation process the degradation occurs in presence of oxygen and in the case of anaerobic, it occurs in absence of oxygen. Partial degradation can also occur in which the organic pollutants transform into lower toxicity compounds.

3.8 Evaporation

In this technique, the wastewater is heated, and the water is evaporated leaving contaminates in the solution. The vaporized water is condensed to get the pure form of water. This process can be done in a wastewater evaporator. The volume of the contaminated water decreases and the solute concentration is increased in the wastewater. This is an effective technique for removing contaminants and liquid waste. Salts, metals, and hazardous heavy materials can be removed by this technique. This technique consists of two phenomena as a thermodynamic phenomenon and a mass transfer phenomenon. In thermodynamic phenomenon, heat energy is applied to the contaminated solution, and water is converted to water vapor. In the mass transfer phenomenon, of evaporation, the small droplets are carried off by blowers and they are condensed to get a pure form of water.

3.9 Ion Exchange Process

Toxic metals can be removed by this technique. In this water treatment process, one or more contaminants are removed by exchange with less harmful substances with the same charge. That means ions in a solution are replaced by other ions which have the same polarity. Hard water can be treated by this technique in which calcium and magnesium are replaced by non-hardness ions such as sodium. Ion exchange resins are wildly used in this process in which there are ion exchange sites where functional groups of cations or anions are attached. The functional groups attract

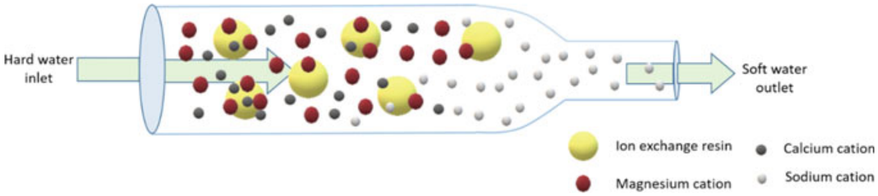


Fig. 7 Mechanism of the ion exchange process

the contaminating ions and the exchange process occurs. In a paper by Rengaraj et al. depicted the removal of chromium by ion exchange resin [89]. Mercury is also removed by ion exchange resin [91]. In Fig. 7, it is depicted how sodium cations are exchanged with contaminating magnesium and calcium cations in ion exchange resins (Table 3).

4 Membrane-Based Technologies for the Removal of Emerging Pollutants

The polymeric membrane which is also known as an organic membrane is basically a selective barrier that separates two phases from each other and it regulates the selective transport of substances between two components [57]. The concept of membranes is from the eighteenth century and after that, a lot of modifications and improvements are taken place to make them suitable for different applications [77]. The main principle of most membrane separation techniques is the selective filtration of effluents through the pores of the membranes [9]. There are various membrane processes such as equilibrium processes, non-equilibrium processes, pressure-driven processes, and non-pressure-driven processes. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are pressure-driven non-equilibrium processes. Electrodialysis is an example of a non-pressure electrically driven process. Besides that, there is some equilibrium process such as membrane distillation and forward osmosis [77].

4.1 Microfiltration

Microfiltration (MF) membranes are capable of removing micrometer-sized colloidal particles from wastewater [109]. This filtration is a pressure-driven technique (up to 500 kPa or 5 bar) that is practiced commercially [120]. This is the least restrictive filtration technique. MF membranes have pore diameters in the range of 0.1–5 µm. Micrometer-sized particles such as suspended particles, major pathogens, large bacteria, proteins, and yeast cells can be separated from polluted water by the MF technique [108]. The wide range of pore size of MF enables to find applications

Table 3 Advantages and disadvantages of conventional techniques

Conventional technologies	Advantages	Disadvantages
Adsorption	This technique has a good ability to separate a wide range of contaminants from wastewater. Activated carbon is wildly used and it is the most important adsorbent in the water treatment process The removal method of the pollutants is easy to design. It works in a wide pH range There is a large variety of available commercial products for this purpose Adsorbents can be made with waste material. So, the wastes can be recycled for these adsorbent purposes It is not a time-consuming process and it follows fast kinetics. So, a large amount of wastewater can be treated in a short time This process does not produce any type of toxic by-products	This process requires high investment and the cost of the materials are high. Especially the cost of commercial activated carbon (CAC) and commercial activated alumina (CAA) are high This process will be inefficient if an inappropriate adsorbent is chosen for a particular contaminate It is a non-destructive and nonselective method Adsorbents require regeneration but the regeneration is expensive and it causes a loss of material
Flotation	Small particles can be removed efficiently by this technique This process is metal selective and various ions can be removed Dissolved toxic organic chemicals are removed by flotation	Energy cost is higher in this process It has a high maintenance cost Energy consumption is also high in this

(continued)

Table 3 (continued)

Conventional technologies	Advantages	Disadvantages
Precipitation	This technique is technologically simple and simple equipment is required for this process A number of substances can be removed by these techniques which cannot be eliminated by other conventional methods Selective precipitation can be done by applying a suitable precipitating agent The precipitation technique is very economical so it can be used for general purposes This technique can efficiently remove metals from industrial wastewater	The precipitate should be immediately separated out after the precipitation Chemical consumption is high in this process It is incapable of removing contaminants at a lower concentration It has high sludge production and also has handling and disposal problems
Oxidation	Some micropollutants are hard to remove from wastewater because of their size in the micrometer range. So, they can be efficiently removed by an advanced oxidation process This process is very simple and efficient $^{\cdot}$OH has some of the fastest reaction rates among the oxidants as a result it has much lower retention times than other techniques It does not produce new hazardous substances after oxidation Color and odor can be removed by oxidation by ozone as an oxidizing agent Viruses and bacteria are eliminated by oxidation No sludge is produced in this process	This technique has higher operation and maintenance costs The chemistry of this process is complex. So, the dosage of the oxidants should be maintained carefully unless a desirable amount of treatment cannot be done Unreacted H_2O_2 should be removed unless it can cause a negative effect on human health In the case of ozone as an oxidant, O_3 has a short half-life This process releases volatile compounds and aromatic amines
Solvent extraction	This process is very simple and the monitoring is also easy It has large selectivity Low operating cost This process is mainly used in large-scale operations	This technique cannot be done in a low dosage of pollutants It has a high investment cost Potential toxic solvents are used in this technique Loss of compounds occurs and this process is not efficient Emulsion formation occurs in this process

(continued)

Table 3 (continued)

Conventional technologies	Advantages	Disadvantages
Electrochemical techniques	A wide range of inorganic and organic pollutants can be removed by an electrochemical process These processes are easy to operate and flexible if the water stream fluctuates An efficient technique for the removal of precious metals from an aqueous solution The electrocoagulation process is better than the conventional coagulation process because of the higher removal efficiency of organic matter from water Various oils, greases, metals, and colors can be removed by electrocoagulation and electroflocculation techniques	These processes require additional chemicals such as coagulants, and flocculants The cost of equipment is high High cost of maintenance Sludge formation occurs so sludge treatment is required
Biodegradation	This process is safe and economical This process is simple, and it is well accepted by people Various emerging pollutants can be removed efficiently and in a cost-effective way from industrial wastewater White rot fungi have high biodegradability by producing various enzymes for this purpose It can efficiently remove various organic pollutants, ammonium ions, and iron	This is a slow process It cannot remove some pollutants more specifically some dyes Entire decolorization cannot be possible

(continued)

Table 3 (continued)

Conventional technologies	Advantages	Disadvantages
Evaporation	These techniques are versatile and various types of evaporators are used for evaporation purposes A wide range of contaminants can be removed by this method This technique is an efficient technique	Some pollutants can come along with the vaporized water droplets A cleaning circuit is required for this process This process requires a high investment cost
Ion exchange	Various types of wastewater can be treated efficiently by this process This process is technologically simple and it is capable to produce high-quality treated water Most metals can be reused after their removal from water This process is very effective in the treatment of water hardness By selecting a particular resin this process can be selective which will eliminate particular ions from water Valuable metals can be extracted from water	The ion exchange process requires a high operational cost This process is sensitive to pH change This process is not effective for all types of pollutants The saturation of the reactors is very rapid

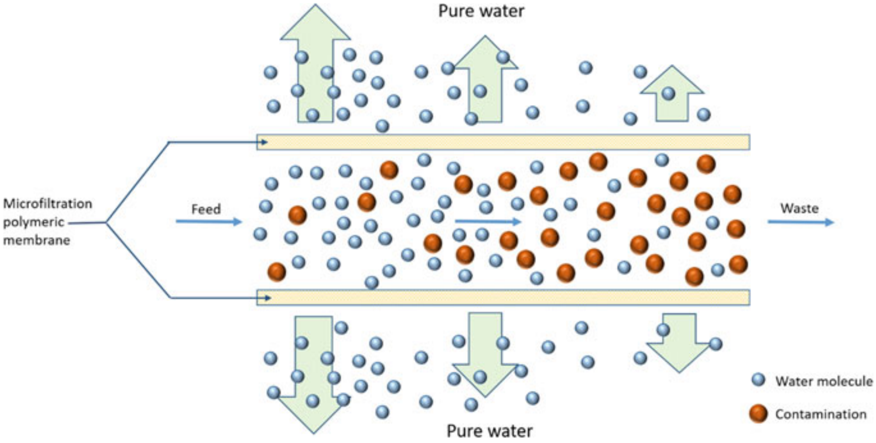


Fig. 8 Mechanism of microfiltration

across many areas like pharmaceuticals [95], food [1], wastewater treatment [73], and desalination [84]. In the figure (Fig. 8) pure water is permeating through the microfiltration membranes and pollutants retain inside.

Porous materials are used to build microfiltration membranes. Various MF membranes were studied to establish the effectiveness of the material for water treatment. Membranes for the MF technique are prepared from different materials which are based on organic (polymer) or inorganic material (ceramic, metals, glasses). In the year 1997 ceramic MF membrane was produced for treating wastewater. Alpha-alumina ceramic membranes modified with polyacrylonitrile were used to microfilter water containing a high level of oil [35]. Zhong et al. succeed to produce a new generation of MF membrane which was composed of zirconia (ZrO_2). Contaminated water containing a high maximum concentration of oil was passed through MF membranes at an applied pressure of 1.1 bar and it was seen that the membrane was able to remove almost all the oil efficiently [120]. According to the studies of numerous researchers, it has been shown that inorganic membranes, specifically ceramic membranes are more effective in case of removal of pollutants from water [14]. Inorganic membranes are used instead of polymeric membranes because inorganic membranes have an excellent chemical or thermal resistance. The pore size of these membranes can be easily controlled, as a result, the pore size distribution is very narrow. Sintering, sol–gel process, and anodic oxidation techniques are generally used to prepare ceramic membranes.

Synthetic polymeric membranes are of two kinds, i.e., hydrophobic and hydrophilic. Some polymers which are used for producing polymeric membranes are listed below. Ceramic membranes are mainly made of Alumina (Al_2O_3) or Zirconia (ZrO_2). Titania (TiO_2) is also used to make ceramic membranes. Other materials

Table 4 Different materials used for making microfiltration membranes

Hydrophobic polymeric membranes	Poly(tetrafluoroethylene) (PTFE, teflon) Poly(propylene) (PP) Polystyrene (PS) Poly(vinylidene fluoride) (PVDF)
Hydrophilic polymeric membranes	Polycarbonate Cellulose esters Polysulfone Polyamide
Ceramic membranes	Zirconia (ZrO_2) Alumina (Al_2O_3) Glass (SiO_2)
Metals	Palladium Tungsten Silver

such as glass (SiO_2) and various metals (palladium, tungsten, silver) are used to make MF membranes. Organic and inorganic materials which are used to produce MF membranes are listed in Table 4.

4.2 Ultrafiltration

Ultrafiltration is a membrane filtration technique that lies between hyperfiltration and microfiltration. In this technique forces like pressure or concentration gradient ultimately lead to the separation through a semi-permeable UF membrane. UF membrane has a pore size of approximately 0.002–0.1 μm. UF membranes are able to partially remove bacteria as well as some viruses. But it cannot provide a full barrier to viruses. Recently complexation-ultrafiltration technique is becoming an emerging technique for the removal of heavy metals [Cu(II), Ni(II), and Cr(III)] from wastewater. Carboxy methyl cellulose polymer is used for producing complex with the cationic forms of heavy metals. These complexes have to be larger in size than the UF membrane pores [14]. Antibiotics can contaminate drinking water. So, removal of these micropollutants from water is required to avoid serious health risks. Mohammad Shakak et al. synthesized a nanocomposite ultrafiltration membrane (Polysulfone/Polyvinylpyrrrolidine/SiO_2) that can efficiently remove amoxicillin from aqueous media [97]. Micellar-enhanced ultrafiltration (MEUF) as the surfactant-based technique can be an effective process to remove metal ions from water. In this process, the surfactant is added to the contaminated water solution, and it forms micelles above the critical micelle concentration (CMC). The metal ions get absorbed on the surface of the micelles by electrostatic attraction. When the solution passes through the UF membrane the metal ion-containing micelles are rejected [11]. Ultrafiltration membranes are prepared from various types of polymeric materials.

Polysulfone, polyether sulfone, poly vinylidene fluoride, polyacrylonitrile, cellulose acetate, and polyimide are used for this purpose. Inorganic materials such as alumina (Al_2O_3) or zirconia (ZrO_2) are also used to produce UF membranes. A thin-film composite UF membrane grafted MCM-41 was prepared by Yixiang Bao et al. which can be used to remove heavy pollutants from water [13]. Nowadays carbon membrane is competing with polymeric membranes. Carbon membranes are one type of porous inorganic membrane [53]. For the purpose of separation of chromium (VI), a modified carbon membrane was prepared by G. Pugazhenthi et al. In this work, the modified UF carbon membrane was prepared by gas-phase nitration using NO_X (NO and NO_2) at higher temperatures and gradually aminated in the second step using hydrazine hydrate at 60 °C [87]. For perchlorate removal from water, surfactant modified UF membrane was prepared which can efficiently remove the contaminate from water [115].

4.3 Nanofiltration

In this filtration method, the pores of the membrane are in the nanometre range. Usually, nanofiltration membranes have a pore size from 1 to 10 nm range which is smaller than the pore size of the microfiltration and ultrafiltration membrane. The water permeability of NF membrane is greater compared to the RO membrane. So, this process can be done at lower pressure that ensures low energy consumption during the filtration process. Nanofiltration has two types of separation mechanisms, i.e., separation of uncharged contaminates due to size effects and separation of charged species such as ions by electrical repulsion. NF membranes are able to remove divalent ions (95% removal) of the same charge in comparison to monovalent ions (20–80% removal) from an aqueous solution [21]. These membranes have a wide range of applications other than ionic separation, for example, micropollutants such as pesticides, dyes, sugars, insecticides, and herbicides can be removed using this filtration technique. The NF membranes have homogeneous barrier films like RO membranes. It doesn’t contain discrete micropores in contrast to UF membranes [25]. This technique also can be used in the health care, biotechnology, food, and pharmaceutical industries (Fig. 9).

The membrane materials depend on what type of aqueous solution is used for filtration purposes. For hydrophobic feed, the hydrophilic membrane material is used and vice versa. Polyamides, polysulfone, polyvinylidene fluoride, polyimides, polybenzimidazoles, and cellulose are used to produce hydrophobic, hydrophilic, or membranes with properties of both hydrophilic as well as hydrophobic membranes. Instead of the conventional filtration technique, high-performance nanofiltration membrane is required for wastewater treatment in industries. So, it is necessary to develop nanomaterial-based NF membranes of desirable properties. Various types of nanomaterials such as Carbon-based, MOF, zeolite, nano-biopolymers, special nanoparticles such as Spinel ferrite nanocomposite (SFNCs), spinel ferrite nanoparticle (SFNPs), polyhedral oligomeric silsesquioxane (POSS), zwitterionic colloid

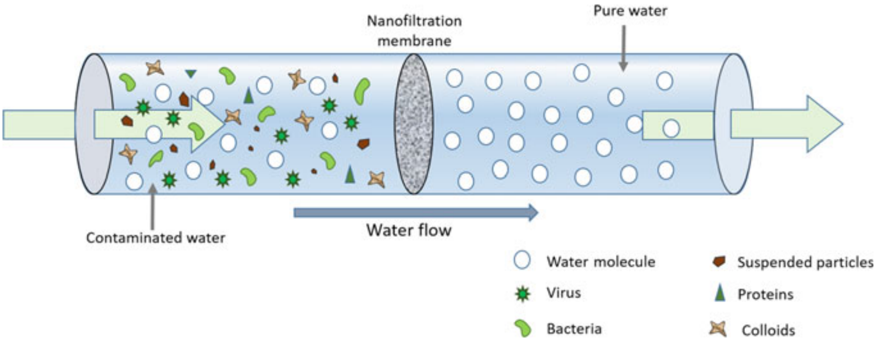


Fig. 9 Water is permeating through the nanofiltration membrane and various pollutants are unable to pass through it

particles (ZCPs), and nickel hydroxide nanosheet are being used for nanofiltration purpose [12]. For the removal of micropollutants in drinking water Jae-Hyuk Kim et al. developed a chemically modified thin-film composite (TFC) polyamide (PA) nanofiltration membrane [59]. To improve the performance of desalination and environmental pollutant removal techniques, novel methods are required. For this purpose, Langming Bai et al. fabricated a TFC membrane with a sandwiched layer and a surface layer. The surface was modified by a polydopamine (PDA) layer [102].

4.4 Reverse Osmosis

Reverse osmosis (RO) is a pressure-driven membrane separation process for the removal of solutes from water or any other solvent. RO membranes can retain 95–99% of dissolved solutes which can be organic or inorganic in nature [111]. In this filtration technique, a partially permeable membrane is used to separate ions, pollutants molecules, and large particles. These contaminants can’t permeate through the RO membrane. In this process, pressure is applied to overcome osmotic pressure which is driven by chemical potential. In the forward osmosis process to equalize the chemical potential in both sides of the membrane, the solvent diffuses from low concentration to high concentration solution. But in this process, the pressure is applied to diffuse pure solvent from the high concentration side to the low concentration side. As a result, the solute or pollutants are retained on the pressurized side of the membrane and the pure solvent is passed to the other side. RO differs from other filtration techniques because in this process the mechanism of the flow of the fluid is by osmosis across a membrane. The pore size of the RO membranes is 0.01 µm or larger than that. The main removal mechanism is based on solubility or diffusivity and this technique depends on pressure, solute concentration, and other conditions. A schematic diagram of RO technique is shown in Fig. 10 where water molecules are

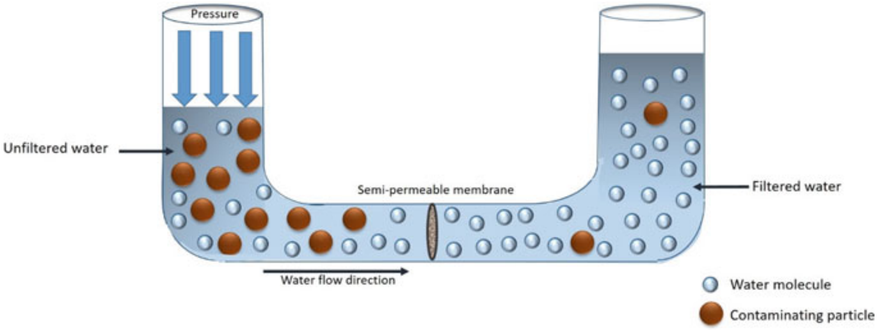


Fig. 10 Reverse osmosis technique

permeating through a semi-permeable membrane to the lower pollutant concentration side in presence of pressure.

RO technique highly purifies water by the rejection of most dissolved salts and organic molecules which contaminates the water significantly. It can also remove large particulates if they are not removed by pre-treatment processes such as MF or UF [110]. Modified RO membranes are used in various processes to remove micropollutants from water or aqueous solutions [15]. Various antibodies are emerging pollutants in seawater, and they can be removed by RO membranes. J. Jaime Sadhwani et al. used spiral-wound polyamide thin-film RO membrane for the removal of Ciprofloxacin which is a synthetic antibody [5]. Phenols are also playing a significant role to contaminate drinking water, aquatic life, and plants, therefore affecting human health. In a study, Mnif et al. showed the removal of organic pollutants like phenol using thin-film composite reverse osmosis membrane [72]. RO membranes can effectively remove 87–98% of radium from drinking water. Uranium and its complexes are heavy, so RO membranes can be used to separate this hazardous material from water. 95–99% uranyl carbonate can be effectively removed by RO membranes.

4.5 Forward Osmosis

Osmosis which is currently referred to as forward osmosis (FO) has many applications in separation processes of wastewater treatment, food processing, and seawater desalination process [28]. So, FO is an osmotic process like reverse osmosis (RO) which uses a semi-permeable membrane to effectively remove dissolved solutes from water or aqueous solvent. The driving force of the FO technique is the osmotic pressure gradient which draws solvent molecules to diffuse from low concentration to high concentration region to minimize the osmotic pressure gradient. In the RO technique, unlike the FO technique, pressure is applied externally to overcome the osmotic pressure, and the solvent drives through the membrane reversibly from the high concentration to low concentration region. So, significantly less energy is

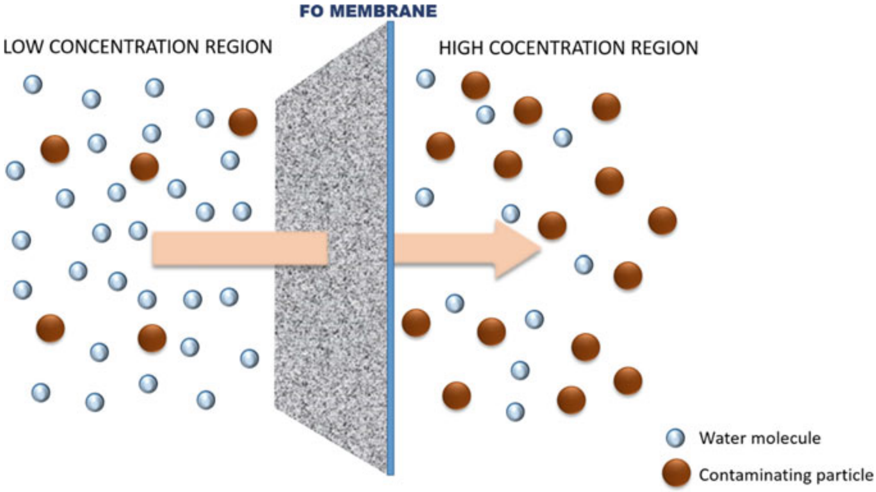


Fig. 11 Forward osmosis membrane

required in the FO technique than the RO technique. The main advantage of the FO technique over the RO technique is that it operates at no hydraulic pressure, it can efficiently reject a high range of contaminates and it has a lower membrane fouling tendency than any other pressure-driven membrane process. A schematic diagram of the FO technique has been shown in Fig. 11.

In general, any dense, non-porous, selectively permeable material can be used as a FO membrane [28]. The first asymmetric cellulose acetate (CA) membranes were developed in the year of 1960s. Thin-film composite materials for FO membranes are developed for water purification purposes. Polysulfone (PSU), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) are used as backbone materials for FO membranes. These polymers are hydrophobic in nature so, the hydrophilicity of the material should be increased to increase the performance. Polysulfone was modified by sulfonated poly(phenylene oxide) (SPPO) to increase the performance of the TFC FO membrane [122]. Wang et al. blended polyethersulfone (PES), sulfonated polyethersulfone (SPES), and montmorillonite (MMT) to synthesize FO membrane which showed improved performance [108]. To increase the porosity and hydrophilicity Emadzadeh et al. introduced TiO2 nanoparticles into the substrate material [37].

4.6 Hybrid Processes

A hybrid membrane process is the integration of one or more membrane-based processes to increase the performance of the separation technique. Conventional membrane techniques which are designed to treat water may have many limitations related to water's osmotic pressure, viscosity, temperature, and high concentration of contaminates. So, to overcome these limitations and increase the efficiency, "membrane-based hybrid" can be used. Hybrid processes combine either a membrane process with the conventional process or a membrane process with another membrane process [40]. The main motto of this technique is to increase the purity, productivity, and yield of the product. These hybrid systems can also reduce environmental pollutions and operating costs. As discussed above, membrane hybrid processes can be divided into two categories such as

(I) Membrane process with a conventional separation process (MCH)
(II) Membrane process with another membrane process (MMH).

4.6.1 Membrane-Conventional Hybrid (MCH) Process

In this process, a conventional separation process is modified by using a membrane process to increase the performance of the conventional technique and the productivity of the process. Microfiltration-adsorption-flocculation is one kind of MF included MCH process. The floating medium flocculation (FMF) and powdered activated carbon (PAC) adsorption process were combined with the microfiltration process to increase the removal efficiency [47]. The ultrafiltration (UF) included MCH process UF membrane technique was combined with the fermentation process to increase the productivity and make the whole process more stable. Reverse osmosis-evaporator hybrid process is one kind of reverse osmosis included the MCH process. In the membrane distillation-fermentation hybrid process, the conventional fermentation technique is combined with the membrane distillation process to increase the efficiency of the technique. There are other types of MCH processes like membrane bioreactor (MBR) included MCH process which is a combination of membrane bioreactor and fermentation process.

4.6.2 Membrane-Membrane Hybrid Process

Conventional processes which are used in water treatment have many disadvantages that affect the performance and efficiencies [8]. To increase the removal efficiency of pollutants from water, these conventional techniques are replaced by a membrane-based hybrid process. These hybrid processes recently came into the picture so, many kinds of research are going on these highly potential techniques. The productivity also increased in comparison to the conventional techniques. These techniques are environment friendly, energy saver, and operating cost reducer.

Microfiltration-Ultrafiltration Technique

UF and UF techniques are wildly used for the water treatment process. But these techniques have many limitations like low efficiency, poor removal of contaminates, fouling, etc. To overcome these disadvantages microfiltration technique is combined with the ultrafiltration technique [8]. Many industries combine them into an activated sludge process which is known as membrane bioreactor (MBR). In this technique, the membrane is submerged inside a bioreactor. Pure water permeates through the membrane and all contaminants are retained in the reactor [64]. This technique reduces the amount of membrane fouling and lowers the energy consumption. A hybrid MF-UF membrane was fabricated by Masoudnia et al. for the treatment of oily wastewater. The crossflow MF membrane was fabricated by polyvinylidene fluoride and the UF membrane was fabricated by polyethersulfone (PES). The separation performance was much higher than MF and UF processes separately [69]. Multilayer slow sand filter (MSSF), microfilter (MF), and ultra-filter (UF) hybrid membrane was designed to purify greywater [10].

Microfiltration—Reverse Osmosis Technique

In this technique, the microfiltration process is combined with the reverse osmosis technique. Conventional processes are unable to remove some specific pollutants and the performance is also low. So, for these limitations, the MF-RO hybrid process is required. Dairy wastewater contains several solids, oils, fats, organic matter, and nutrients as contaminations. MF plus UF technique can effectively remove the pollutants from wastewater. It can reduce 100% turbidity, 100% color, and 84% total organic carbon [22]. Emerging environmental pollutants and several pesticides can be effectively removed by the MF-RO technique [93].

Ultrafiltration-Nanofiltration-Reverse Osmosis—Membrane Distillation

The combination of these four processes can increase the quality of the treated water. Studies showed that the quality of the water is much better than other hybrid processes when this hybrid technique is used. Several organic compounds can be removed by this technique.

5 Membrane Materials Used in Membrane Technology for the Treatment of Emerging Pollutants

The use of polymer membranes for water treatment was known long ago. These membranes have various suitable properties which made them applicable for use in different membrane technology techniques as mentioned in Sect. 4 (Fig. 12).

The selection of a material is a crucial part that determines the property of the membrane. Even the slightest change in the preparation and synthesis of the membrane or in the selection of material can lead to drastic alteration of the effectiveness of the membranes. Then came to play polymeric composite material which lead to the formation of higher efficient membranes for the removal and capturing of other emerging pollutants. There are materials that combine with polymeric materials which can lead to higher efficient capturing of the pollutants in the wastewater. Besides becoming an efficient material for capturing and extraction purposes there are materials that are also cost-effective and economically more favorable to prepare in the lab and on an industrial scale. These types of membranes are called mixed membranes' materials (MMMs). There are different types of material that are ideal candidates for use as a filler in membrane designing.

Then come into play, the polymeric composite material which leads to the formation of higher efficient membranes for the removal and capturing of other emerging pollutants. There are materials that combine with polymeric materials which can lead to higher efficient capturing of the pollutants in the wastewater. Besides becoming an efficient material for capturing and extraction purposes there are materials that are also cost-effective and economically more favorable to prepare in the lab and on an industrial scale. These types of membranes are called mixed membranes' materials (MMMs). There are different types of material that are ideal candidates for use as a filler in membrane designing. Here some of the different kinds of material are described which not has huge application not only in water treatment as membrane material but also has various other applications (Fig. 13).

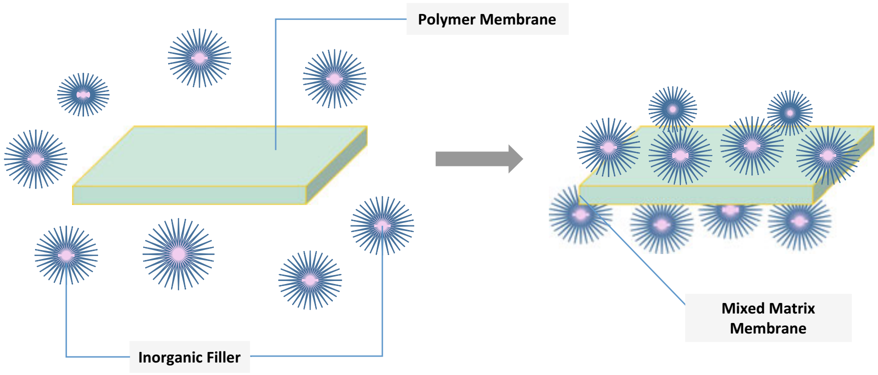


Fig. 12 Preparation of mixed matrix membrane with the application of various materials

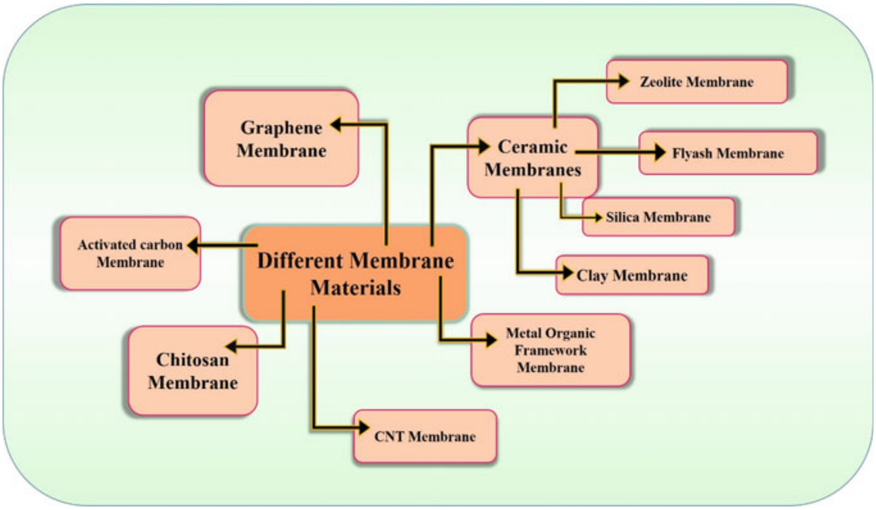


Fig. 13 Showing different materials used in fillers for designing different membranes for wastewater treatment

5.1 Graphene Membrane

Graphene is a novel nanostructural material prepared from graphite flakes or from waste materials or from recycled products. Graphene sheets can be used as a sandwich structure for capturing the pollutants in them by their different binding sites. It has a negatively charged surface layer which is due to the presence of oxygen-bearing functional groups and has a large surface area. Besides the carboxy, epoxy and hydroxyl groups provide proper binding sites for various EPs. Alone use of graphene is quite limited in use for water treatment, so it is generally mixed with polymeric substances during the preparation of composite membrane material for water treatment. There have been research works on the preparation of magnetic-based graphene membrane for easy extraction of the composite material after it has been used in water for the capture of EPs. In a past study a polyethersulfone nanofiltration membrane was prepared by magnetic graphene oxide for efficient dye and metal ion removal [3]. It has been known that graphene membrane acts as a good adsorbent for easy adsorption of various cationic dyes and anionic dyes [117] which have been dumped into wastewater by various units mainly from industrial units. Han et al. prepared an ultrathin nanofiltration membrane which showed high retention of organic dyes [48]. Graphene membranes have also been used for the treatment of wastewater of emerging heavy metal pollutants. Yaseen et al. prepared an rGO composite with incorporated CuO and AgO nanoparticles in polyvinyl acetate MMM which is able to remove Cr^{6+} ion found in paint industrial wastewater [114]. Other effects like photocatalytic methods for the removal and degradation of organic pollutants have been done [83]. The membrane designed here is based on Graphene oxide with TiO_2, it did show higher pollutants removal ability in darkness and better photocatalytic activity on UV–Vis irradiation.

5.2 *Ceramic-Polymer Composite Membrane*

Ceramic materials are widely used for their various properties and application in various sectors. One drawback of ceramic materials can be said that it has a high manufacturing cost which limits their application. A different type of material has been synthesized by combining ceramic materials and polymeric membranes and finally making a ceramic polymeric composite membrane which is cost-effective as only a small amount of ceramic material is required for this and it is equally efficient in caring out the objectives necessary in the case of ceramic material.

In a recent study on ceramic polymer composite material, it has been found that polysulfone membranes when blended with TiO_2 and GO to prepare thin-film nanocomposites are able to efficiently remove nitrotoluene derivatives present in wastewater originating from petrochemical industries [43]. It has also been reported that TiO_2 when embedded into polymeric polyether sulfone also shows antifouling properties of membranes for efficient performance in wastewater treatment [99].

5.3 *Fly Ash Membrane*

Fly ash has been long known as an adsorbent material for wastewater treatment. It has a very high adsorption capacity, so it is an ideal choice for researchers for using it in composite materials for designing water treatment systems. One of the major components of fly ash is silica which is used in the wide-scale preparation of different materials which can be used for water treatment purposes. In a recent study it is shown that not only just in case of wastewater treatment purposes but fly-ash derived membranes can also be used in case of oil–water emulsion treatment [17]. Another report shows that fly ash could be used to enhance the production of microfiltration membrane to treat industrial wastewater [123]. Other works like composite nanofiber membrane with CO_2-activated sugarcane bagasse fly ash membrane were also prepared for efficient removal of organic pollutants [7].

5.4 *Silica Membrane*

As discussed in the above section silica is a very effective material having wide use for application in water treatment. Fernandes et al. mentioned that the use of silica as a filler in membrane technology acts as an effective pore-forming agent and does not affect the contact angle of water in a slight amount [41]. Akther et al. used a polyamide-based thin-film composite made with an ultra-thin layer of silica upon it which shows an enhanced antifouling property of that composite. This composite has enhanced performance in forward osmosis. The membrane also shows long-term use in repetition [4].

5.5 *Zeolite Membrane*

Zeolites have been widely used for water purification and treatment for a long period of time. Zeolite itself is costly, so presently zeolites-MMMs are being used for purification purposes. Hazmo et al. developed a new class of membranes for ultrafiltration by incorporating zeolites and CNTs together which show a high solute rejection rate. This was prepared using zeolitic imidazolate framework-8 and multi-walled carbon nanotubes [50]. Zeolite membrane also shows various anti-biofouling properties which makes it ideal for use in membrane technology. Dong et al. [33] prepared polysulfone ultrafiltration membranes that had embedded alumina and Linda type L zeolite nanoparticles which show anti-biofouling properties. Besides anti-biofouling properties, it also has good chemical and temperature resistance.

5.6 *Clay Assisted Membrane*

While speaking of the ceramic material one must mention about multipurpose use of clay in different sectors of research. Due to its abundance and easy availability, it is extremely cost-effective in practical application. At present Saja et al. [78] prepared a low-cost bentonite/perlite membrane for ultrafiltration. The ultrafiltration membrane showed results in the elimination of Direct Red 80 and Rhodamine B. The efficiency of the individual organic dye removal capacities was found to be 97 and 80%, respectively. Hamid et al. also reported the use of clay on polysulfone membrane for the removal of metal (copper) from an aqueous solution. This study reported that the membrane developed by mixing zeolite showed the highest removal of Cu (II) at low pressure and also confirms the reusability of the membranes for more than once (3–5 cycles) [2]. Hatimi et al. designed an inorganic membrane based on clay and pyrrhotite ash which showed promising results in the removal of organic fats and oil from industrial wastewater and the method is completely eco-friendly [49].

5.7 *Metal–Organic Framework*

Metal–organic framework materials are described as complex macromolecular materials. They are mainly formed of metal ions coordinated with organic ligands. They are porous materials and are capable of binding and capturing different types of pollutants in between them. Mecoprop is a common herbicide known as Methylchlorophenoxypropionic acid is used widely in different households and is a major emerging pollutant. Various MOFs have been used for removing it from water sources. Fu et al. [42] fabricated a MOF/polymer composite that can remove this pollutant from the water source. A chitosan/UiO-66 monolith composite was prepared which achieved an adsorption capacity of 34.33 mg g^{-1} by the Langmuir model. Yang et al. [112] prepared a nanofiltration MOF membrane that shows excellent dye removal capability. MOF has also been used to enhance membrane antifouling properties of cellulose acetate ultrafiltration membranes by making composite with Graphene oxide [112]. Various food additives have proven themselves as EPs Zhao et al. [119] made a fiber-based MOF composite for the removal of amaranth red and vanillic aldehyde from the water by membrane filtration. Their result showed a decrease in the concentration of the pollutants from 10 to 0.1 mg L^{-1}.

5.8 Carbon Nanotube Membranes

There have been cases of the use of carbon nanotube with different membranes for use in membrane technology for water purification. Alpatova et al. [6] prepared multi-walled carbon nanotubes used with polyvinylidene fluoride impregnated with Fe_2O_3 particles for catalytic degradation of organic dyes. CNT is showing promising results in the field of removing micro and nanoscale pollutants. CNT is also now being used in the desalination process Chen et al. [30] for the treatment of salty and brackish water as it is showing its results in salt and micropollutant elimination. Chen and his group obtained 3–20 times higher freshwater flux rate in desalination than the existing polymeric membranes. One of the major use of CNT is its use in oil–water separation. CNT membranes have proved themselves toward fast and efficient oil–water separation [96]. Yang et al. [113] showed improved antifouling and antimicrobial properties of membranes by the use of functional CNT.

5.9 Activated Carbon Membrane

Activated carbon is one such material possessing higher adsorption capacity than most other materials. There have been different use of this material like removal of dyes, pesticides, metals, etc. different works on steroid hormone micropollutant removal from water by activated carbon have been done [101, 116]. In the work on hormone (mainly estradiol), Tagliavini designed a polymer-based activated carbon membrane for ultrafiltration. And estradiol is one such natural hormonal substance that has been included in the watch list of priority substances in 2015 for the risk factors from them in water COMMISSION IMPLEMENTING DECISION (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (2015).

5.10 Chitosan Membrane

When speaking in the case of biopolymer chitosan plays a major role here. Chitosan is a linear polysaccharide prepared by deacetylation of chitin. Chitosan has a wide application not only in the field of water treatment but also in water desalination techniques. Padaki et al. [79] prepared a Nanofiltration membrane for desalination by polypropylene supported chitosan which shows excellent water flux rejection in an acidic medium. In the case of removal of agro-based waste materials Moustafa et al. prepared chitosan functionalized silver nanoparticle polymeric membrane. The membrane showed promising results in the removal of imidacloprid from contaminated water by a pressure-free design. For sole use of chitosan in this application, removal of Imidacloprid was found to be 40% but in the case of Chitosan decorated silver nanoparticle polymeric membrane the efficiency of removal of imidacloprid was found to be 85% [74].

5.11 Factors Affecting the Use of These Materials in Membrane Technology for the Removal of Emerging Pollutants

Membrane technology has been long known to us. There had been a large number of research and work on this but one would be flabbergasted to know that only a few of them is used in practical application on large scale. There are multiple factors that restrict their use on large scale. Among these, the most important factor is its effectiveness and reusability. It has been found that several membranes lose their effectiveness after repeated uses as a result of which their efficiency decreases.

One major factor is membrane fouling and ineffective cleaning methods of membranes. This is the dominating factor behind restricting the use of membrane materials. Another major factor is equipment cost and the production cost of materials is a major factor that limits its use in the application. Details about them will be discussed in Sect. 6.

6 Challenges and Future Perspectives of Membrane Technology

Thousands of research works have been published and countless of them are going on presently in various institutes all-round the globe on fabricating various membrane materials for advancement in membrane technology. But one of the major drawbacks of this research structure is that in most cases the parameters maintained during the use of membranes are quite restricted to foreign elements and products. Let's say a material (M) is synthesized in a laboratory for the removal of a particular substance (X). So here only substance (X) is focused on the removal from the medium. Moreover in general a typical medium is taken for this cause where only substance (X) is present then the efficiency of the membrane material (M) is calculated for the removal of substance (X). In most cases, it has been observed that if these membrane materials are pilot tested for large-scale industrial application in the treatment of wastewater and emerging pollutants from other sources they fail. One of the major causes behind this failure is pretesting in ideal conditions. In the lab, the membrane's efficiency has been measured in an ideal situation and in a practical situation, multiple other substances are present in the medium. As a result of the presence of other substances, they interact with the membranes as a result of which the efficiency of treatment of the membranes decreases.

The main reason behind their failure is economic factors, membrane fouling, energy-intensive process, and the presence of multiple other species which prevents efficient separation of pollutants from the water source.

6.1 Economic Factor

Economic factor plays the most dominant factor in the case of every research work. In the case of pilot testing of any material, one must take into consideration the economic factor above all, since if a project is not cost-effective it will not be of any use to society. There have been reports on different membrane materials, which show excellent adsorption capacity but are not cost-effective so they cannot be used for production and application on a large scale. In the past, different membrane materials have been used and were subsequently replaced by newer efficient and cost-effective material which will again be replaced if advanced materials are fabricated in the near future (Fig. 14).

6.2 Membrane Fouling

If we speak of something which comes in the path of the membrane technology and its growth is membrane fouling. Fouling of membranes with the passage of

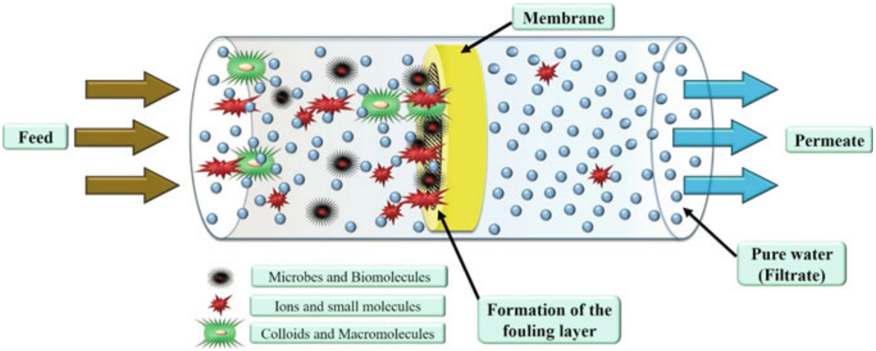


Fig. 14 Overview of membrane fouling in membrane filtration unit

time makes them useless for further use. When one continuously uses a membrane over a long period of time different micro-molecules block the pore and obstruct the flow of water through the pore as a result of which the net flux reduces. This is called membrane fouling. Membrane fouling can be easily defined as the deposition of macromolecules on or inside the membrane pores which ultimately reduces the amount of clean water flow through the membrane. When polluted wastewater passes through a water purifying membrane different particles get stuck in the flow in between the membrane pores. There are different methods through which fouling occurs (Fig. 15).

6.2.1 Pore Blocking

This occurs when micro-molecules or substances get trapped inside the pore of the membrane resulting in complete or partial blockage of that pore in the membrane. When multiple pores get clogged due to different particles the membrane loses its capability of purifying the wastewater and ultimately the efficiency of the membrane material decreases. This can either result from narrowing of the pores or complete blockage of the pores by foreign particles. From the graph, it could be seen that the performance of the membrane decreases with time (Fig. 16).

6.2.2 Adsorption

During the filtration process there are different types of contaminants present in water. Of them, some foulants tend to get adsorbed on the surface of the membrane and in pores. Abdelrasoul and Doan, 2020 described adsorption as the primary factor which led to the formation of irreversible fouling and restricts further reusability and cleaning of the membrane.

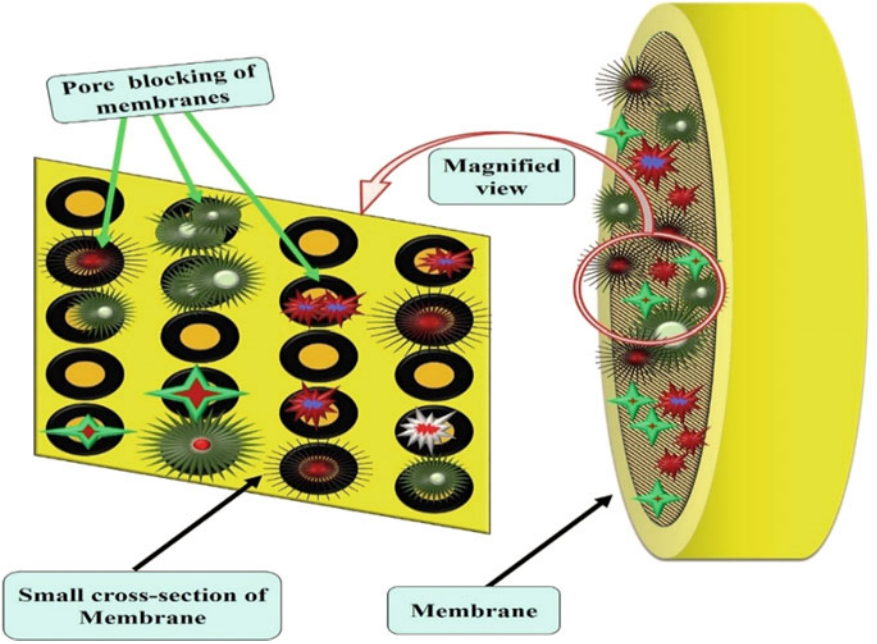
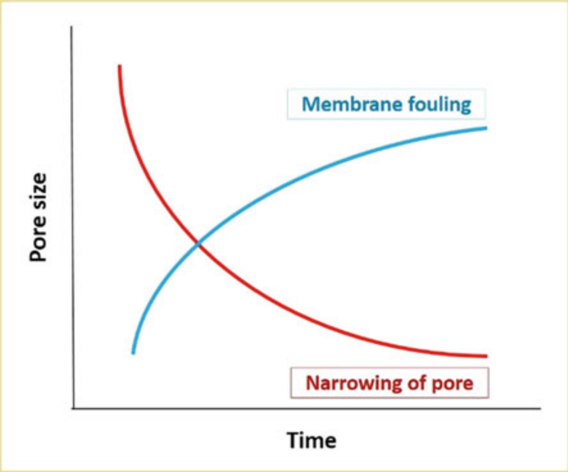


Fig. 15 Magnified view of membrane fouling

Fig. 16 Graph showing decrease in pore size of the membrane with an increase in fouling



6.2.3 Cake Layer

It is the final pore-blocking state where most of the membrane pores get blocked due to the deposition of foulant. Here the foulant covers most of the surface of the membrane which comes in contact with the wastewater. Meng et al., 2007 says that a detailed characterization of the formed cake layer may help find the optimum working range of the membrane (Figs. 17 and 18).

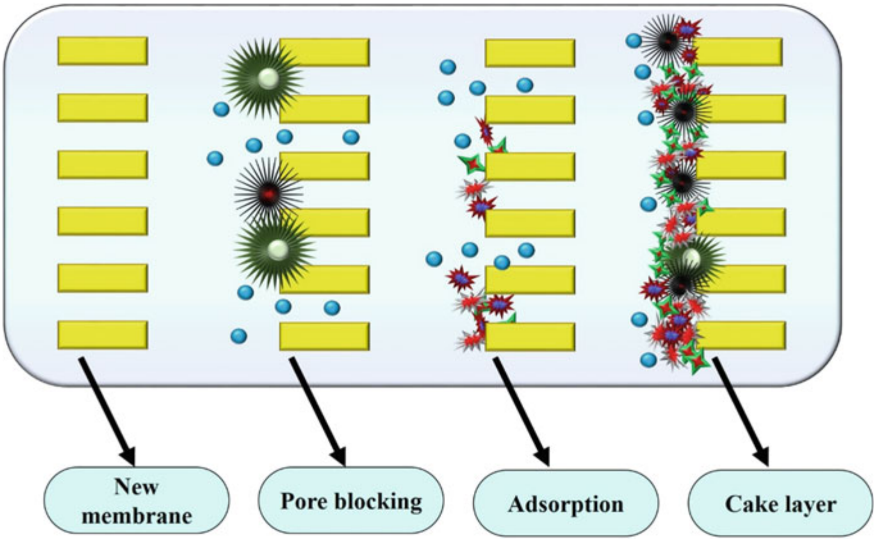
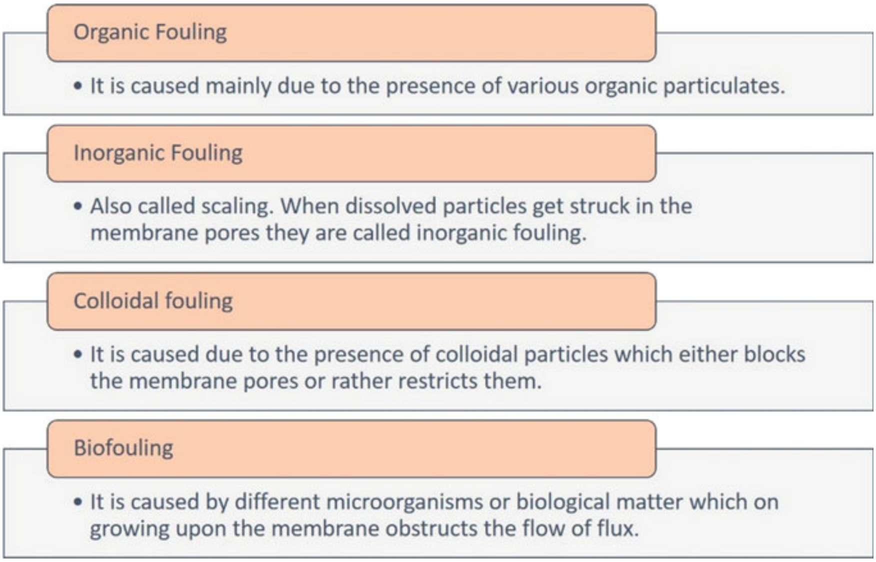


Fig. 17 Various types of membrane fouling



Organic Fouling

- It is caused mainly due to the presence of various organic particulates.

Inorganic Fouling

- Also called scaling. When dissolved particles get struck in the membrane pores they are called inorganic fouling.

Colloidal fouling

- It is caused due to the presence of colloidal particles which either blocks the membrane pores or rather restricts them.

Biofouling

- It is caused by different microorganisms or biological matter which on growing upon the membrane obstructs the flow of flux.

Fig. 18 Different causes of fouling of membranes

6.3 Cleaning of Membranes

With the rapid growth in the field of membrane Technology membrane fouling needs to be avoided. Although we cannot completely remove membrane fouling, with certain cleaning methods, we can minimize fouling to a certain extent and able to reuse the membrane for further treatment of wastewater.

6.3.1 Physical Cleaning of Membranes

As the name suggests physical training is done to remove foulants from the membrane by the use of mechanical forces. There are different kinds of physical cleaning methods like Backwashing, forward and reverse flushing, air flushing, CO_2 back permeation, ultrasound techniques.

Backwashing

In the case of this technique the pressure on the permeate side is higher as a result of which the foulants are cleared from the pores. This pressure is by the use of hydraulic devices which force the foulant particles out of the membrane pores.

Forward and Reverse Flushing

In the case of this technique water or any other solvent is flushed at a high speed from the feed side to clean the membrane surfaces of the foulants.

Air Flushing

In the case of technique air is passed through the feed side as air bubbles. As a result of which the air bubbles cause the cake layer to break down to some extent. This results in the cleaning of the fouling layer.

6.3.2 Chemical Cleaning of Membranes

In most of the cases, these physical treatment methods are used together to yield better results. But even when cleaning is not satisfactory then chemical methods come in handy. There are different acidic, basic, and neutral chemical reagents that can easily remove different fouling layers from the membrane surface without wear and tear of the membrane surface. Different chemical agents such as hydrochloric acid, calcium hypochlorite, nitric acid, and hydrogen peroxide are used for the effective

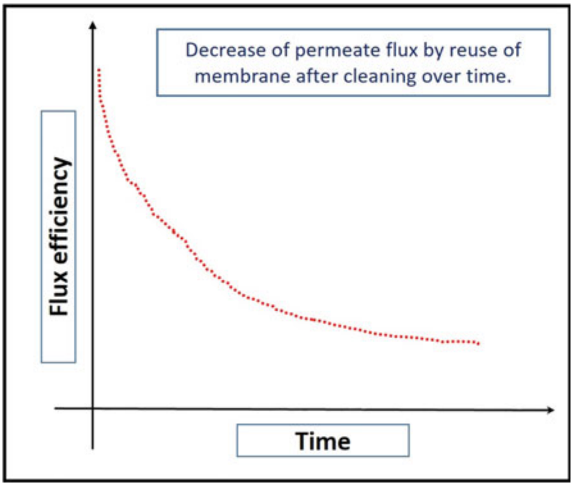


Fig. 19 Graph showing decrease of permeate flux by reuse of membranes after cleaning over time

cleaning of the membranes. Chemical cleaning is mainly handy when physical and mechanical cleaning is not successful. But generally, chemical cleaning is done before mechanical cleaning. After the use of the chemical cleanser where most of the foulants are removed, physical methods are used to clear the pores of membranes with more precision. The effectiveness of the membrane can also be determined by the number of times it could be cleaned of the foulants by the standard cleaning methods. Every membrane has a breaking limit after a certain time they lose their efficiency of production of the permeate flux with repeated cleaning of the membranes (Fig. 19).

6.4 Future Perspectives and Challenges for Membrane Materials

The present perspective of membrane technology is to prepare advanced membranes with higher flux rejection capacity and make a wise decision in the choice of materials for having better efficiency. A better focus must be made on the selectivity of the type of membrane. Different membranes react differently upon passing the contaminated water because of different pore sizes. Each membrane separation method is quite selective toward the size of the contaminants. If in any possibilities the size of the contaminants is smaller than the pore of the material they could easily pass through the membrane pores or could result in clogging of the membrane pores this will result in a decrease in the effectiveness of the membranes and reduced flux rejection rate (Fig. 20).

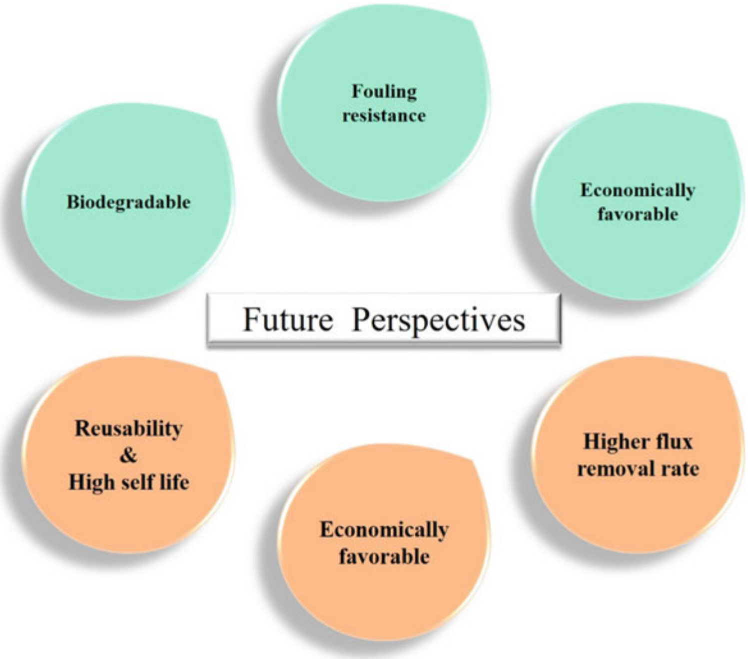


Fig. 20 Future perspective for preparation of advanced membranes

6.5 Alternatives and Scope for Overcoming Existing Challenges

The major problems in the present membrane technology are membrane fouling which limits its use to a large extent. As a result of membrane fouling the chance of reuse of the membranes also decreases. Alternative scopes must be looked upon for designing membranes with better antifouling properties which will provide a longer self-life of the membranes. Advance types of machinery must be designed which more would precisely clean the membranes of the existing fouling. Better research on cleansing agents must be done so it would act in a more material selective nature. So that these cleansing agents would more effectively remove fouling without hampering the membrane material. While talking of futuristic models of membrane technology one must mention the economic factor. The aim must be focused to develop and provide a more economical solution to prepare membranes for water treatment. Sustainable membranes must be developed so that they could be used in industrial up-scaling for a larger batch water treatment. Preference must be given to the membranes which are bio-derived materials and are environment friendly in long run.

7 Conclusion

Over the most recent twenty years constant efforts have been made concerning the recognizable proof of emerging pollutants, their interpretation, characterization, global guideline, assessment of their poisonousness and destiny in the amphibian climate, and their effects on human wellbeing, just as to the identification and evaluation of different treatment advancements for eliminating such toxins (particularly from wastewater). Arising contaminations are classes of substance compounds with various origins and aquatic paths that have expanded their dangers for human wellbeing and the aquatic environment.

This chapter fundamentally audits the principle research points connected with the significance of arising contaminants expulsion for the production of drinking water by attending to progress made in wastewater treatment systems.

There are significant issues that should be additionally examined or to be tended to by researchers and water organizations about the protected and practical stockpile of drinking water from surface sources:

Predictable definitions, rules for characterization, and guidelines of greatest permissible convergences of EPs should be tended to by global and public guideline bodies toward water supplies and drinking water treatment, particularly looking at their dangers for human wellbeing;

Evacuation or debasement of EPs, carried out by advanced water treatment, generally varnishes (as pre-treatment or last treatment) the customary stages for drinking water production from surface sources. Accordingly, membrane processes, advanced oxidation processes, and adsorption on activated carbon or different materials tracked down numerous applications at pilot and full scale, and their choice is predominantly founded on specialized and monetary issues;

Correlations of advanced drinking water treatments choices comparable to the "degradation" of advanced oxidation processes or "phase change" (membrane processes, adsorption) processes are seldom made for drinking water treatment, because of the moderately small amounts of target pollutants within the influent, despite the fact that there are many investigations at research facility scale that help these applications. Nonetheless, these examinations ought to be utilized for increasing investigations that allude to EPs expulsion;

Different appraisal instruments might finish the manageability profile for the determination of innovative novel drinking water treatment choices for emerging pollutants expulsion using membranes since other large numbers of options include extra energy and intricate material utilization. There are just a couple of studies that consider this kind of way toward full-scale establishments. Albeit even membrane technology calls for attention with regards to its power utilization in comparison to other approaches, as possibly being the main effect generator: there are not many examinations that consider the effect of utilizing sustainable power sources. At long last, the analysis tools/devices should be refined to all the more likely cover the related natural effects of eliminating emerging pollutants.

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Chapter 8
Biopolymeric Hydrogels: A New Era in Combating Heavy Metal Pollution in Industrial Wastewater

Aliva Saha, Souravi Bardhan, Shubham Roy, Subhojit Dutta, and Sukhen Das

1 Introduction

In modern society, rapid population escalation is resulting in an exponential increase in urbanization and industrialization. These in turn result in the massive generation of wastewater and water contamination. Among the various industrial discharges, heavy metals have become a major issue nowadays due to their tendency to cause bioaccumulation, biomagnification, organ damage, cell functioning disruption, and mutation on exposure above a threshold level. Chronic toxicity can lead to Parkinson's disease, muscular dystrophy, Alzheimer's disease, cancer, and even death [1]. Presently heavy metal pollution is becoming a serious concern because of the rapid surge in their concentration due to the high discharge of industrial effluents in water from industries without adequate treatment [2]. Most of the heavy metals like mercury, lead, cadmium, arsenic, and chromium have a high toxic effect even in minute quantities imposing serious health issues to humans and other organisms. In a recent report by Central Water Commission (CWC), out of the 442 surface water samples collected, 287 were contaminated by heavy metals like lead, iron, nickel, chromium, cadmium, and copper which were mostly generated from industrial activities present above the safe limit.

Fast and accurate detection of heavy metals in water is extremely important to combat heavy metals-related issues. Hence various instrumental and spectroscopic techniques, such as atomic absorption spectrometry (AAS), chemiluminescence, inductively coupled plasma mass spectroscopy (ICP-MS), electrochemical and amperometric techniques are employed for the detection of heavy metals in aqueous medium. Although these techniques are widely used, most of them require complicated sample pre-treatment, are expensive, and are limited to off-site study. To

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overcome such drawbacks, fluorometric and colorimetric sensors [3] are currently gaining huge popularity due to their high precision, tremendous selectivity and sensitivity, rapid response time, cost-effectiveness, ease in handling, and most importantly on-site performance. Moreover, at present, various techniques like coagulation and precipitation, ion exchange treatment, and membrane filtration have been adopted for heavy metal removal from the aquatic system. Although some techniques can successfully treat heavy metal-laden water, most of them suffer drawbacks like lack of feasibility in real-world application, time-consuming, costly materials, laboriousness, and even can generate secondary pollution. Alternatively, the adsorption technique offers various potential advantages over other methods for the removal of toxic heavy metals. Among all conventional adsorbents reported, hydrogels are considered efficient adsorbents which are even proved to be useful for heavy metal detection.

Hydrogels are basically three-dimensional, hydrophilic, cross-linked, composed of homo-hetero-co-polymers containing functional groups like amine ($-NH_2$), amide (–CONH), carboxylic (–COOH) or sulphonic ($-SO_3H$) groups that can absorb a significant amount of water [4, 5]. Hydrogen bonding, covalent, Van der Waals forces, or physical entanglements result in cross-linkage [6]. Hydrogels exhibit remarkable water holding capacity and can hold water or biological fluids more than 400 times their original weight. This pertains to the chemical cross-linkage of three-dimensional polymeric networks that allows them to swell instead of dissolving in water or fluid [7, 8]. Moreover, their biocompatible nature and a high degree of flexibility make them potential candidates for biological applications without causing toxicity. The characteristics of hydrogels can be regulated by changing the parameters like concentration of monomer, reaction vessel, reaction time, cross-linker and monomer ratio, and degree of cross-linking of the polymer chains and initiator concentration [9–12]. The hydrophilic properties of hydrogel help them form a flexible network of polymer chains which in turn allow metal ions present in the aqueous medium to penetrate into the network and they form stable complexes with the functional groups present in the polymeric chain [13, 14].

According to the structure, physicochemical properties, and application purposes, three classes of hydrogels are commonly applied in wastewater treatment; hydrogel beads, hydrogel films, and hydrogel nano-composites [15]. This chapter focuses on various aspects of hydrogels as an upcoming, potential, next-generation material for the detection and removal of heavy metals from aqueous medium.

2 History of Hydrogels

The term “hydrogel” was initially published in an article by Lee, Kwon, and Park in 1894, but the colloidal gel prepared from inorganic salts was quite different from today’s hydrogels [16]. The first synthetic hydrophilic gel named poly (2-hydroxyethyl methacrylate) (pHEMA) having three-dimensional cross-linked was reported by O. Wichterle and D. Lim in 1960, which was developed for soft contact lens application [17]. The application in contact lenses opened up a new avenue in the biomedical field and various properties of hydrogels like inertness to biological processes, permeability to metabolites, and structural features permitting desired water content made them suitable candidates for various applications. Initially in the 1960s hydrogel was used for permanent contact applications with tissues. In 1968, Daniele et al. [18] developed glyceryl methacrylate (GMA) hydrogel as a vitreous implant in rabbit eyes. Antibacterial properties of hydrogels were also explored during the initial period, such as superabsorbent, thermally stable chitosan-g-poly (AMPS-co-AA-co-AM)/ground basalt hydrogel composite was synthesized by Said et al. [19] under microwave irradiation which successfully inhibited the growth of *Escherichia coli* and *Staphylococcus aureus*. These cross-linking-based hydrogels exhibiting high swelling properties which were favorable for various mechanical applications are regarded as the "first generation hydrogel" [14]. Hydrogels gained more popularity in the decade of 70s [20] and scientists focussed more on their response to various stimuli, such as pH, temperature, or concentration variation of specific molecules in solution. This property was further explored for various applications, such as controlled drug delivery, material polymerization, or reverse-osmosis related applications [21, 22] and such hydrogels are considered as "second-generation hydrogel" [14]. In the recent past, hydrogels are modified for diversified applications in various fields such as pharmaceutics [23, 24], biomedical [25], biotechnology [26], tissue engineering [27], soil management and agriculture [28, 29], sensor [30], electronics [31], mechanical [32] and optical [33] fields. Recently, hydrogels are gaining research interest for their practical application in water and wastewater treatment due to their ability to swell, porous surface, hydrophilic structure, modifiable, biocompatible nature, and superior absorptive performance for removal of various contaminants [34]. Moreover, the recent trend shows that hydrogels can be a great alternative for various conventional adsorbents used for the removal of organic (such as dyes, pesticides) and inorganic (toxic heavy metals like chromium and arsenic) in terms of effectiveness and adsorption capacity [35] (Fig. 1).

The hydrogels can be classified into numerous categories based on their physical structure, chemical properties, mechanical strength, types of crosslinkers used, origin and polymeric composition, electrical charges, etc. A detailed classification has been illustrated in Fig. 2.

Earlier, natural polymers were considered to be safer and better than synthetic ones in terms of biocompatibility, although nowadays synthetic and hybrid polymers are gaining immense importance. Yet, the presence of certain synthetic crosslinkers and initiators exhibits some toxicity concerns as purely synthetic hydrogels [9]. Hence, the biocompatibility issue attracted widespread attention for the use of biopolymers which are produced or derived from natural sources like exoskeletons of arthropods, silkworm cocoon, plants, skin, and hair (Fig. 3) and are recognized as eco-friendly, potentially sustainable, biocompatible, exhibits low or almost no toxicity and practically abundant in nature [38]. The composition of the biopolymers is mainly consisted of polysaccharides (such as starch, cellulose, chitin, chitosan, alginate), polypeptides (such as collagen, keratin, gelatine, silk), and polynucleotides (DNA, RNA) [39]. Such biopolymers when structurally modified with various natural or synthetic

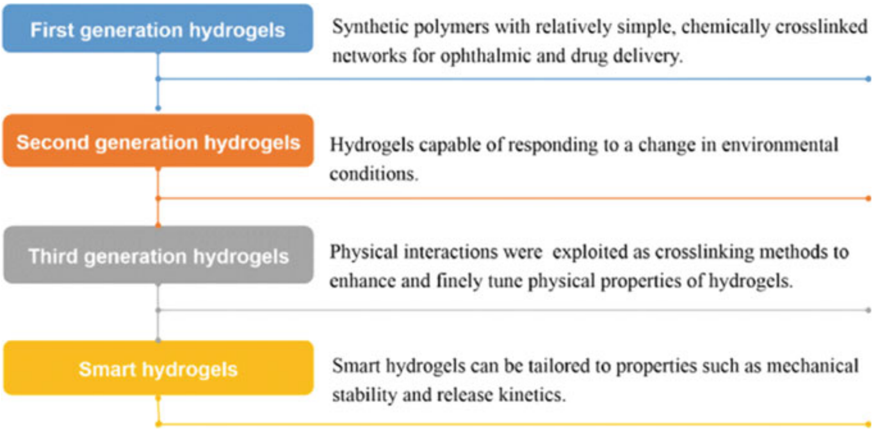

Fig. 1 Schematic representation of various generations of hydrogels. Reproduced from [36]

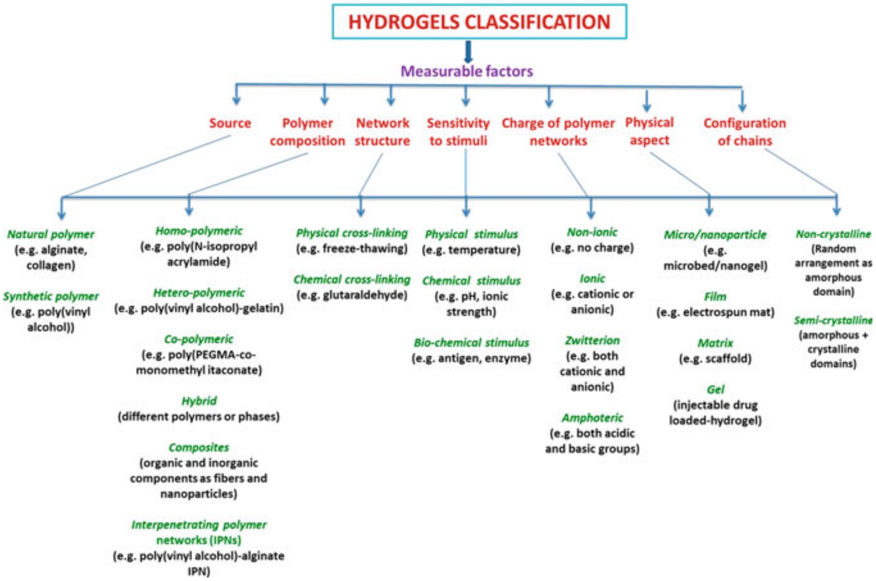

Fig. 2 Classification of hydrogels. Reproduced from [37]

nanoparticles such as carbon nanomaterials, mineral nanostructures, or metal and metal oxides to enhance the flexibility and mechanical properties, morphological features, optical response, stability toward harsh environment, antimicrobial nature, swelling behavior and adsorption capacity [40–42]. For example, in a recent study, fluoride removal from fertilizer industry effluent has been demonstrated using carbon nanotubes (CNT) stabilized chitin sponge [43]. CNT is well known for its massive

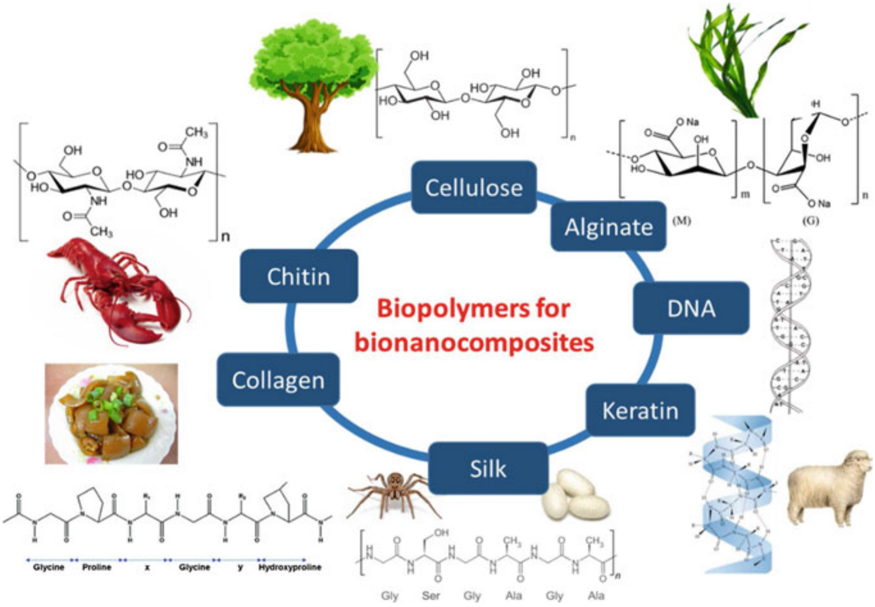

Fig. 3 Various sources of biopolymers. Reproduced from [38] Copyright 2018, with permission from Elsevier

surface area, mechanical strength, thermal and chemical stability, yet it suffers drawback like difficulty in removal from the medium after use. Hence incorporation of CNT into chitin matrix through cross-linkage overcomes the limitation and further improves adsorbing capability, regeneration potential post-application, and stability in industrial conditions. Similarly in the past decade, chitosan, a biocompatible N-deacetylated derivative of chitin has gained immense popularity for its high adsorption capacity and high potential for removal of heavy metals like Cd^{2+}, Cr^{3+}, Hg^{2+}, and Pb^{2+} from wastewater [44]. Moreover, various researches are conducted worldwide by modifying chitosan structure using thiourea, glycine, istatin, or diacetylmonoxime which introduces more functional groups for enhancing adsorption performance and removal of a diverse variety of contaminants [45, 46]. Heavy metals like Hg^{2+}, Zn^{2+}, and Cd^{2+} were selectively and efficiently chelated out from aqueous media using phenylthiourea functionalized chitosan [47], which can be later regenerated according to need.

3 Heavy Metal Removal from Water Using Hydrogels

3.1 *Removal of Mercury Ions*

Selective removal of mercury from wastewater using biopolymeric hydrogel, especially from chitosan precursor is gaining the limelight. In a recent study, it was found that amino, amide, and C=N functional groups containing nitrogen atoms, present in chitosan-poly (vinyl alcohol) hydrogel adsorbent with a three-dimensional network structure, possess remarkable adsorption capacity and selectivity for Hg^{2+} ions. The lone pair of electrons possessed by the nitrogen atom of these functional groups are donated to the metal ions and hence metal complex is formed. The amino group shows high adsorption capacity where the amide group shows excellent adsorption selectivity for Hg^{2+}. A tendency of coordination with transition-metal ions is exhibited by the amide groups due to the electron-withdrawing effect by carbonyl groups. As amide and $C\equiv N$ groups are soft basic ligands, they can interact with very soft acid like Hg^{2+} [48–54]. Wang et al. [55] reported that the hydrogel adsorbent has the commendable selection and adsorption capacity (585.90 mg g^{-1}) for Hg^{2+} ions by parallel adsorption experiments and comparative studies shown in Fig. 4.

Wang and his group observed a change in the binding energies of N 1s and C 1s band of C=N groups and also of C1s band of C=O groups before and after Hg^{2+}adsorption. Since the $–NHCOCH_3$ group contains the C=O group, from the observations they concluded that the $–NHCOCH_3$ group was involved in adsorption. Moreover, the C=N group is a softer basic ligand in comparison to $–NH_2$ or –OH groups. FT-IR spectral alterations further confirmed the interaction of C=N groups with Hg^{2+}. Interaction of the hydrogel with the heavy metals can also bring about changes (Fig. 5) that can be detected by the scanning electron microscope (SEM).

Another report by Saber-Samandari and Gazi [56] focuses on the efficient removal of Hg^{2+} using biopolymeric hydrogel formed from chitosan via UV irradiation. The

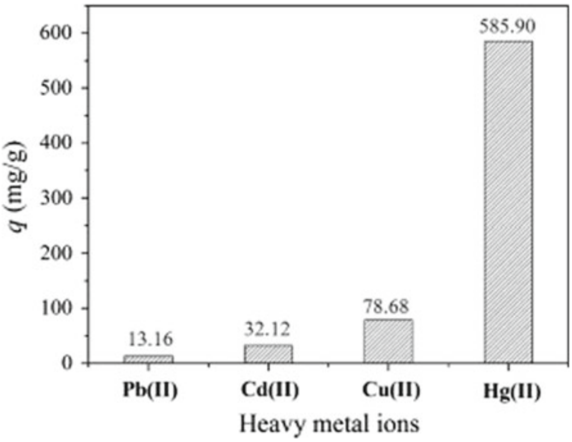

Fig. 4 Comparative study of heavy metal ions adsorption capacities of CTS-PVA hydrogel. Reproduced from [55] Copyright 2013, with permission from Elsevier

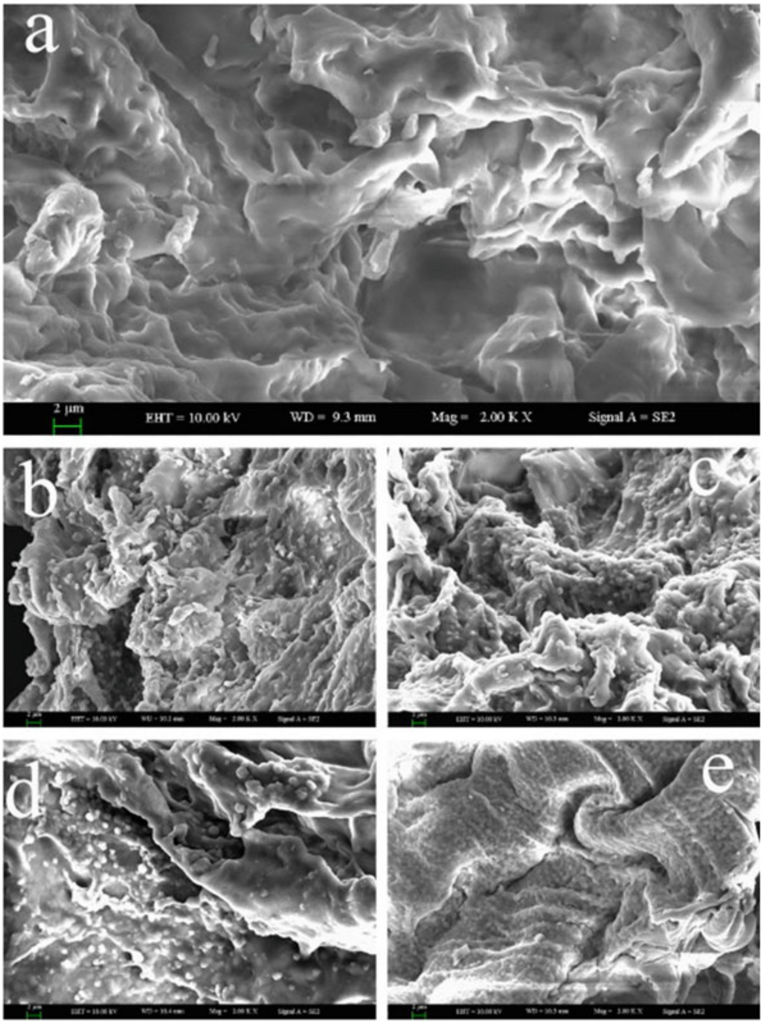

Fig. 5 SEM images of **a** the CTS-PVA hydrogel; **b** the Cu^{2+} loaded CTS-PVA hydrogel; **c** the Cd^{2+} loaded CTS–PVA hydrogel; **d** the Pb^{2+} loaded CTS-PVA hydrogel; **e** the Hg^{2+} loaded CTS-PVA hydrogel. Reproduced from [55] Copyright 2013, with permission from Elsevier

Hg^{2+} adsorption capacity of the hydrogel under non-buffered conditions through the colorimetric technique was nearly 9.98 mmol g^{-1}, which is around 2001.8 mg of Hg^{2+} removal by 1 g of the hydrogel.

Besides chitosan, another biopolymeric hydrogel based on starch can be used for the removal of Hg^{2+} from wastewater. Saberi et al. synthesized a novel starch-based/PEG-AcA hydrogel (St-PEG-AcAH) and AgNPs-starch/PEG-AcA nanocomposite hydrogel (AgNPs-St-PEG-AcANCH) to investigate the antimicrobial activities and its removal capacity of metal ions from contaminated aqueous solutions simultaneously. The Ag nanoparticle doping can impart antibacterial nature along with enhancement of mechanical properties, chemical stability, and adsorption capacity. Such properties of the hydrogel also make it a potential candidate for biomedical purposes. It was noted that the maximum adsorption capacity of Hg^{2+} ions for St-PEG-AcAH achieved was 158.21 mg g^{-1} at pH 7 and for AgNPs-St-PEG-AcANCH the adsorption capacity was 182.53 mg g^{-1} at pH 6 in aqueous solutions [57–59].

Similarly, a study by Hashem and his group [60] shows the removal of Hg^{2+} from an aqueous environment using three types of maize starch-based hydrogels. They possessed different nitrogen and carboxy group. The optimized sample showed the maximum adsorption capacity of 1250 mg g^{-1}. The ion exchange occurred between the anionic carboxy groups present in the hydrogel and the cationic Hg^{2+} ions. This results in the saponification of the poly (AN)-starch composite. Hg^{2+} form chelates with the oxygen- and nitrogen-containing groups present in the starch hydrogel as those groups can donate electrons that were accepted by Hg^{2+}. Another adsorption process was observed where Hg^{2+} present in the bulk solution goes to the surface of the absorbent and diffuses through the boundary layer at the surface of the absorbent. The active sites on the surface of the hydrogel adsorption of Hg^{2+} occurred and the ions diffused into the interior pores (free volume) of the hydrogel.

3.2 Lead Ion Removal

Recent literature shows the removal of Pb^{2+} using hydrophilic alginate biopolymer extracted from *Laminaria digitata* [61]. The alginate-acrylamide hydrogel has been synthesized using free-radical polymerization. This hydrogel serves as a strong absorbent material in water purification as they have high swelling and adsorption capacity of Pb^{2+} ions. The adsorption capacity of the hydrogel was investigated by changing the pH conditions but no significant change was observed. The factors on which the adsorption capacity depend was mainly the osmotic pressure inside the hydrogel, the presence of hydrophilic groups and electrostatic repulsion (–COOH) functional groups. Carboxyl groups are present in the alginate molecule of the hydrogel and for Pb^{2+} adsorption they also act as active sites. Therefore, as the alginate composition increases, swelling capacity also increases which leads to a rise in metal ions adsorption. Hence, they inferred that the SA0.75-AM0.25 (sodium alginate-acrylamide) can be a promising hydrogel for the removal of Pb^{2+} from polluted water.

Qi et al. [62] synthesized a polysaccharide (salecan) based superabsorbent, which was developed to remove lead ions (Pb^{2+}) from water by graft copolymerization of acrylamide and sodium vinyl sulfonate the salecan. The optimal adsorption capacity of Pb^{2+} achieved by the biopolymeric hydrogel absorbent was 172.8 mg g^{-1}. Moreover, the adsorption capacity was found to be directly proportional to the polysaccharide concentration as salecan possessed mesopores which provide larger space for Pb^{2+} adsorption. However, beyond 300 mg L^{-1} Pb^{2+} concentration, removal efficiency drastically decreases due to saturation of the active sites. At lower pH of 1, fewer binding sites were active ($–SO_3^-$) to chelate Pb^{2+} as the active sites are already occupied by those H^+ ions, which are existed in solution at that pH. However, the protonated $–SO_3H$ groups in hydrogel network were ionized, strengthening the chelating capability of hydrogel toward Pb^{2+} and as a result, causing the increase of q_e for Pb^{2+} at pH 7. Hence, the optimum adsorption capacity was achieved at pH 7.

3.3 Cadmium Ion Removal

Hydrogels based on natural biopolymer chitosan, gum arabic, and maltodextrin were used as adsorbents for removing Cd^{2+} from aqueous solutions with and without magnetite nanoparticles by Paulino et al. [63]. After the adsorption of Cd^{2+}, the hydrogels without magnetic properties are often recovered through the use of HCl or HNO_3 like chemicals but here by the application of an external magnetic field, magnetic hydrogels and Cd^{2+} may be recovered. 4.5–5.5 was the best pH range for the removal of Cd^{2+} from water using hydrogels based on chitosan, gum arabic, and maltodextrin. The anionic groups (COO^-–acrylate groups) of hydrogels interact with H^+ ions at pH lower than 6. As a result, the electrostatic repulsion in the polymeric chain of hydrogel decreases. The H^+ ion occupies the active adsorption sites of the hydrogel in this condition. Cd^{2+} adsorption efficiency of the hydrogel also decreases as the effect of it. The removal of Cd^{2+} was influenced due to the formation of hydroxide at pH lower than 6. Hydrogel mainly adsorbs water prior to metal ion adsorption. When greater hydrogel mass is added, larger volume of water is adsorbed and hence metal concentration increases in the remaining solution. When small amount of hydrogel (about 5 mg) was used, significant cadmium removal was observed. Addition of magnetite nanoparticles to the hydrogel is responsible for the decrease of Cd^{2+} removal capacity of the hydrogel. Hydrogel expands due to the electrostatic repulsion among the ionized groups present in the three-dimensional network. This decreases the stability of the hydrogel network and hence the inorganic or organic solutes can enter into the polymer matrix. Different complexes are formed between metal cations present in water and COO^- and NH groups present in a hydrogel network. When magnetite like Fe^{3+} ions was added, covalent bonds were formed in between hydrogel and iron ion. That means degree of cross-linking increases and electrostatic repulsion among polymer segments decrease resulting in

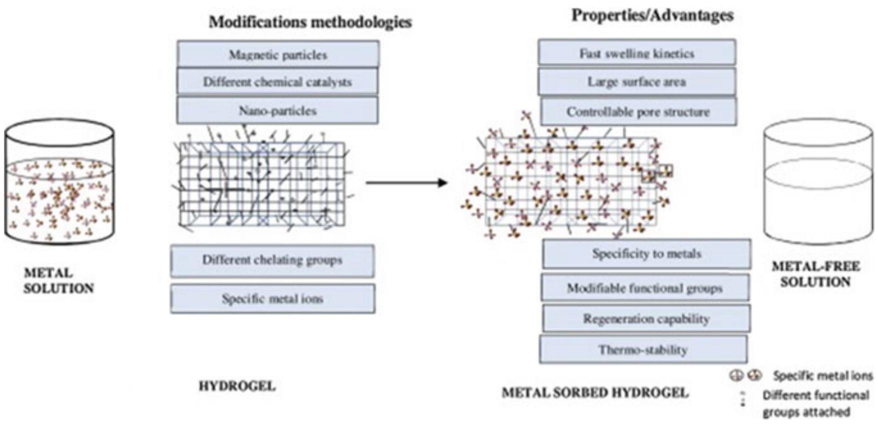

Fig. 6 Pictorial representation of metal adsorption and removal using hydrogel. Reproduced from [65] Copyright 2019, with permission from Elsevier

obstruction in the diffusion of water and metal through the hydrogel. The interaction of cadmium ions with the active sites of the hydrogel network and the diffusion process both are getting affected due to the presence of magnetite nanoparticles. Higher efficiency of Cd^{2+} adsorption was noticed when polysaccharide-based hydrogel with no magnetic properties is used for the treatment of industrial effluents.

Another natural gum-based hydrogel containing silica [64] was used for the adsorption of Cd^{2+} from wastewater. It was synthesized via microwave assisted method in which ammonium persulfate (APS) and N,N′-methylene bis-acrylamide (MBA) has been used as initiator and cross-linker respectively. The factors influencing adsorption capacity of the absorbents xanthan gum-cl-Dimethyl acrylamide hydrogel (XG-cl-DMAA/SiO_2) such as contact time, and initial dye concentration were investigated via a batch adsorption system. The maximum adsorption capacity, q_{max}, of 150.7 mg g^{-1} at room temperature (30 °C) was calculated based on the Langmuir isotherm (Fig. 6).

3.4 *Arsenic Ion Removal*

As already stated above, chitosan is known as the most efficient biopolymer for the adsorption of metal ions and chitosan composites have been extensively used for arsenic removal. Chen et al. [66] used agricultural waste to synthesize chitosan beads for arsenic removal. The maximum adsorption efficiency obtained was 1.83 mg g^{-1} for As^{5+} and 1.94 mg g^{-1} for As^{3+} at pH 5. Chitosan bead could not adsorb efficiently diluted arsenic whether it was As^{3+} or As^{5+}. The predominant species are $HAsO_2$ (neutral molecule) for As^{3+}, and H_2AsO^{-4} and $HAsO_2{}^{-4}$ (anion) for As^{5+} at near-neutral pH. Comparing the charge properties and chemical configurations of arsenic compounds, it could be said that As^{5+} can be easily removed from water than As^{3+}. As^{3+} removal at pH 4–9 and As^{5+} removal at pH higher than 5.6 by chitosan bead may be due to the formation of hydrogen bond or due to the Van der Waals force acting between them. However, at pH lower than 5.6, positively charged chitosan adsorbed easily As^{5+} with a negative charge. At pH 5, almost 80% of the chitosan surface was positively charged. However, the As^{3+} ions were there in the solution as neutral molecule, so it was adsorbed by chitosan bead by forming hydrogen bond or hydrophobic bond. Whereas As^{5+} ion was there in the solution in the form of H_2AsO^{-4} and $HAsO_2{}^{-4}$. Hence charge neutralization was occurred between those negatively charged ions and positively charged chitosan. As a result, precipitation was observed and high amount of As^{5+} ions was collected from the supernatant of the tested solution. On the basis of experimental results, they have inferred that pH 5 was the proper operating condition for the removal of coexisting As^{3+} and As^{5+} from wastewater and the effect of coexisting ions was more for As^{5+} adsorption compared to As^{3+} adsorption.

Chitosan was again used by Su et al. in 2016 [67] for arsenic removal from aqueous solution. They fabricated highly porous nanoscale zero-valent iron/chitosan composite foams (ICCFs) by using freeze-drying method for arsenic removal from wastewater shown in Fig. 7. Excellent mechanical properties along with good adsorption efficiencies were shown by ICCFs. The removal efficiencies were 114.9 mg g^{-1} and 86.87 mg g^{-1} for As^{3+} and As^{5+} respectively. The active sites of ICCFs adsorbed the anionic $H_2AsO_3{}^{-}$ (As^{3+}) and $H_2AsO_4{}^{-}/HAsO_4{}^{2-}$ ions (As^{5+}) by electrostatic attraction of protonated amine group present in chitosan foams and nZVI (Nanoscale zero-valent iron) particles or by chelation. Then the adjacent nZVI partially reduced the adsorbed arsenic ions and Fe^{3+} ions became oxidized. Afterward, the Fe^{3+}-chitosan complex was formed in the ICCFs by forming the attachment with $–O^{-}$ and $–NH_2$ sites of chitosan. As the newly formed Fe^{3+}-Chitosan complex created new active sites for the adsorption of arsenic ions, the removal capacity of nZVI-chitosan composites increased. Moreover, the unreacted As^{5+} and reduced As^{3+} and As^0 were all adsorbed on the ICCFs.

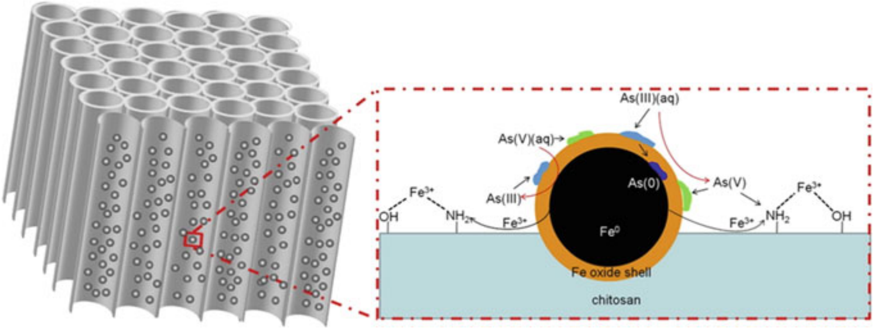

Fig. 7 Schematic representation of mechanistic pathway for arsenic removal by ICCFs. Reproduced from [67] Copyright 2016, with permission from Elsevier

In the alkaline conditions due to the repulsion between the $H_2AsO_3^-$ (As^{3+}) and $H_2AsO_4^-$/$HAsO_4^{2-}$ ions (As^{5+}) and the negatively charged surface of ICCFs, the removal efficiency decreases. The equilibrium removal amount of As^{3+} was almost unchanged from pH 4–7 but a significant decrease was observed beyond pH 7. For As^{5+} removal, with increasing pH value from 4 to 9, the equilibrium removal efficiency decreases drastically from 74.5 to 24.3 mg g^{-1}.

3.5 Removal of Chromium Ions

Cr^{6+} ions were removed from aqueous solutions by adsorption using a chitosan-based hydrogel made by chemical cross-linking of radical chitosan, N,N′-methylene bis-acrylamide, and polyacrylic acid. A recent literature revealed that the optimum adsorption capacity of Cr^{6+} by a chitosan-based hydrogel was 93.03 and 73.14 mg metal per g dry hydrogel from the isotherm models and non-linear Langmuir respectively [68]. After 1440 min, Cr^{6+} adsorption capacities were 40.79, 43.90, and 47.36 mg metal per g dried hydrogel at pH 6.5, 5.5, and 4.5, respectively. The hydrogel has a great number of active sites at first, resulting in high initial adsorption rates. As contact duration rises, the rate of adsorption reduces due to partial saturation of the active sites. As a result, depending on the adsorbate rate transferred from the solution bulk to the adsorbent surface, the adsorption kinetics changes. With a lower pH, the Cr^{6+} adsorption capacity increased. At pH values below 6.0, the NH_2 and –COO groups in the chitosan-based hydrogel protonate, yielding NH^{3+} and –COOH. The intermolecular contact forces between Cr^{6+} ions and active sites decrease as a result of this.

In the pH range 2–6, $HCrO_4$ ions are the primary ionic forms of Cr^{6+}, whereas CrO_4^{-2} ions are the main ionic forms of Cr^{6+} in the pH range higher than 6.4. As a result, the hydrogel absorbed higher $HCrO_4$ ion concentrations at lower pH values. $HCrO_4$ ions are obtained as the primary ionic forms of Cr^{6+} in the pH range 2.0–6.4, whereas CrO_4^{-2} ions are obtained as the main ionic forms of Cr^{6+} in the pH range higher than 6.4. As a result, greater $HCrO_4$ ion concentrations were adsorbed by the hydrogel at lower pH levels, resulting in an increase in removal capacity. Cr^{6+} adsorption effectiveness reduced as pH increased due to a decrease in $HCrO_4$ ion concentrations in aqueous solution and cationic group concentrations in the hydrogel network. Moreover, when pH increased, the adsorption capacities decreased due to the electrostatic force of repulsion among CrO_4^{-2}, $Cr_2O_7^{-2}$, $HCrO_4^-$, and $HCr_2O_7^-$ ions and carboxylate groups (COO^-) in the hydrogel network.

With increasing starting metal concentrations at pH 4.5 and 5.5, the Cr^{6+} removal capabilities and percentages rose until the active sites in the hydrogel network were saturated. Otherwise, as the initial metal concentration increased at pH 6.5, the Cr^{6+} removal capabilities and percentages declined. At higher pH levels, CrO_4^{-2} ion affinity by active sites in the chitosan-based hydrogel is lower than $HCrO_4$ ion affinity, which predominates in more acidic solutions, it can be concluded.

Another biopolymer guar gum obtained from natural resources is used for preparing hydrogel, which can be used for removing hexavalent chromium ion from wastewater [69]. To obtain the hydrogel, polyacrylamide/guar gum graft copolymer (PAamGG) was cross-linked with glutaraldehyde (GA). Adsorption capacity of Cr^{6+} depends on the pH value of the solution and Langmuir and Freundlich sorption isotherms were obeyed by the adsorption data. pH 3 is the optimal condition for the adsorption of Cr^{6+} by the hydrogel. The Langmuir sorption capacity was 588.24 mg g^{-1} and Freundlich constants like K_F and n were found to be 55.03 and 2.835, respectively.

Active functional groups are present in carbohydrate polymers, composed of repeated anhydro glucose units, for metal ion complexation and that's why they are considered appropriate for the removal of heavy metals and dye. The coordination bonds between the metal ion and the functional group present in the polymer are mainly observed. Depending upon the structure of hydrogels and functional groups metal ion sorption is a combination of two processes, that is ion exchange processes and simple adsorption processes. As the grafting increases the functional group introduced in the polyacrylamide graft chain also increases and hence, the density of sorption sites for metal ions is increased, and hence the percentage of Cr^{6+} sorption increases. In addition to the physical adsorption forces, poly-pendent amide groups present in polyacrylamide chains also can form complexes with the metal ions by forming coordination bond. $Cr_2O_7{}^{2-}$, $HCrO_4{}^{-}$ and $CrO_4{}^{2-}$ are the dominant species of Cr^{6+}, at an acidic pH range and under this condition, the sorbent surface became protonated, and hence anionic species of Cr^{6+} were attracted toward it. With the increment of pH, the removal rate of Cr^{6+} was decreased. At low pH, the electrostatic attraction between the Cr^{6+} species and the sorbent surface decreased due to the decrement of the protonation of the sorbent surface. It was observed that with the increment of sorbent concentration, the percent removal of Cr^{6+} was increasing. The percent removal increased from 54 to 93%, as the hydrogel dose increased from 1 to 5 g L^{-1}. This is due to the higher availability of adsorption sites and surface area with the increasing sorbent doses.

Cationic hemicellulose-based hydrogels [70] were prepared to remove chromium from water. Initially, glycidyl methacrylate (GMA) has been applied to O-acetyl galacto glucomannan (GGM) for transesterification to synthesis of novel GGM macromonomers. A good amount of methacrylate groups was present there in GGM macromonomers (GGM-MA). For the synthesis of the hydrogel, [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MeDMA) was used as monomer and selected GGM-MA derivatives were applied one after another as a cross-linker. In successive batches the study of the maximum adsorption capacity was done. S is the amount of Cr^{6+} adsorbed into the hydrogel matrix (mg metal adsorbed per g of hydrogel). After the first batch S value for Cr^{6+} was around 40 mg g^{-1} and for the second batch the value increased to 80 mg g^{-1} in the second batch. The value reaches to the maximum, $S = 127$ mg g^{-1}, after the adsorption of the third batch. At pH 9, anionic species of chromium $CrO_4{}^{2-}$ are predominant and so the highest retention capacity was reached. Due to the presence of $Cr_2O_7{}^{2-}$ ions, the sorption was similar at pH 3 and pH 9. At pH 6, $CrO_4{}^{2-}$ and $HCrO_4{}^{-}$ ions exist in equilibrium and that's why chromium removal was getting lower. The sorption of chromate by the GGM-based hydrogel was high at a wide pH range, this facilitates the application of the hydrogel for wastewater treatment.

4 Conclusion and Future Prospect

In recent years, biopolymers like agar, guar gum, agarose, cellulose, alginate, carrageenan, xanthan, chitosan, dextran, gelatine, pectin, etc. are turned out to be as sustainable alternative for water treatment (Fig. 8) due to their non-toxicity, bio compatibility, flexibility and moreover their biodegradability. The mechanism of heavy metal adsorption by polysaccharide-based hydrogels generally proceeds via electrostatic attractions within oppositely charged pollutants and adsorbents. Nanostructures like nanotubes, nanoparticles are incorporated into biopolymers to enhance the water purification property of biopolymers by their significant features like large surface area, high chemical reactivity, etc.

These processes are limited to the laboratory scale for lower metal concentration and these experiments are not done in variable environmental conditions for commercial practice. Reusability of bio-based hydrogels is a major concern now. Depending upon the pH value of the aqueous solution, the performance of those biopolymeric hydrogels is highly affected. Another challenge is the recovery of the hydrogel after adsorption of metal ions. Different processes are followed like sedimentation, precipitation, centrifugation, and also magnetic particles are incorporated to collect the hydrogel magnetically. When the particle size of the hydrogels is reduced, the adsorption time also decreases due to the increase in surface

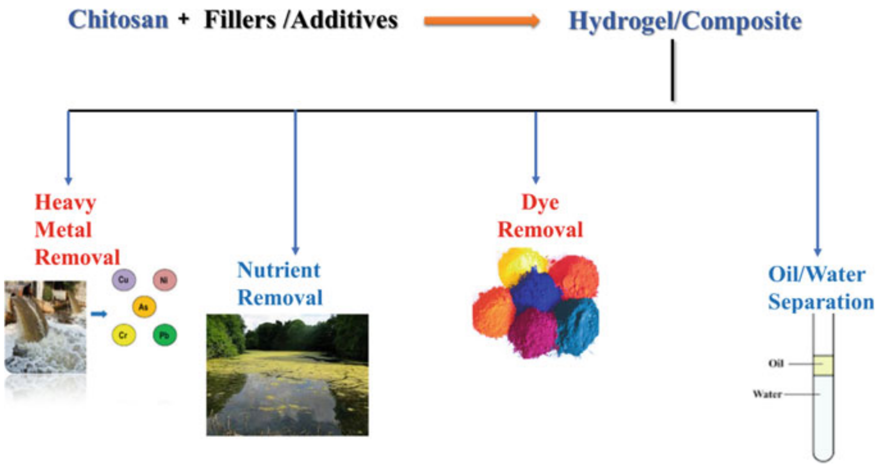

Fig. 8 Illustration of application of biopolymer-based hydrogel for industrial wastewater remediation

area. However, for smaller size hydrogel, recovery after adsorption becomes a major concern. If several metal ions are present in the solution, then competition among them is observed for occupying active sites of hydrogel. Hence selective adsorption is disturbed. As biopolymers have a good complexing and chelating properties due to the presence of repetitive hydroxyl and carboxylic group, to resolve the problem of selectivity, specific functional group must be introduced in the hydrogel so that it can make hydrogen bonds with the target metal only. Regeneration and functionalization of hydrogels are major fields that can be explored more in the future. Several heavy metals having high market value can be extracted from the hydrogel after adsorption and reused in different industries. It can be studied whether the waste product we get after adsorption can express any significant properties or not. If the waste product can be employed for any other purposes, then the procedure will become more cost effective. In this chapter we have discussed the adsorption of several metal ions from water by biopolymeric hydrogels and addressed few parameters like surface charge, pH of the solution, and adsorbate interactions between adsorbent, etc. If we can keep the green hydrogels stable and reusable after several cycles of treatments, then it can be proved as a promising adsorbent for future to provide clean water to our growing population. Although the incorporation of nanoparticles increases the mechanical stability and swelling capacity of the hydrogels, still the durability and mechanical properties of hydrogel are still a matter of concern. Research efforts are required to develop hydrogels having higher selectivity toward a specific heavy metal ion, so that the targeted metal ion can not only be selectively adsorbed but also recovered in a pure form to reuse to minimize secondary pollution.

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Chapter 9
Resource Recovery from Wastewater Using Polymeric Membranes

Arkapriya Nandi, Arindam Rakshit, and Priya Banerjee

1 Introduction

According to the world census, the global population is projected to reach 10 billion by 2050. This increase implicates more resource consumption and waste generation [27]. This pressure is also being exerted on the fresh water resources of this planet. Water crisis is worsening all over the world due to unmonitored exploitation of water resources resulting from unplanned agricultural, industrialization, mining, urbanization as well as unequal distribution of water resources. Presently, almost one-third of the global population is living in water stressed areas. By, 2025, almost two-third of the global population will be faced by water crisis. Hence, in recent research, increased attention is being paid to determination of alternative water resources for meeting this impending water crisis.

In recent studies, researchers are focusing on reclamation and reuse of wastewater for addressing this issue [66]. However, wastewater treatment plants (WWTPs) contribute to air pollution and consume a lot of energy (accounting for almost 5% of global energy yield). Therefore, recent studies are focusing on integrated wastewater treatment processes that ensure simultaneous reduction of cost incurred and energy required as well as recovery of valuable resources from the concerned wastewater stream [44]. Moreover, wastewaters bear rich loads of nutrients which may be recovered as sludge post treatment. Energy is also generated as a byproduct of different treatment processes. Hence, resource recovery ensures reduction of waste footprint as well [66].

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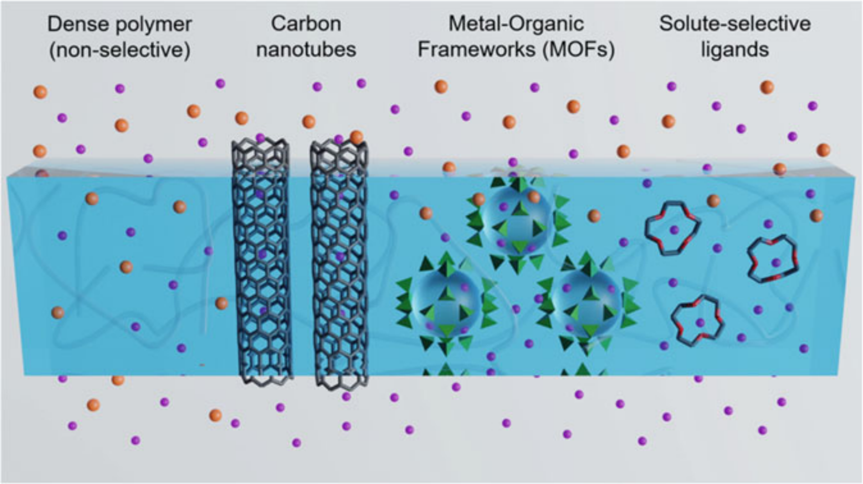

Fig. 1 Structured nanomaterials and polymer ligands capable of efficient, solute-specific separations when applied in conventional, dense, or porous polymeric membranes. Purple and orange spheres represent different solutes, scaled to the dehydrated sizes of Li^+ and Na^+ ions (Reproduced with permission from Sujanani et al. [55] © American Chemical Society)

Polymeric membranes have been widely investigated for recovery of resources like ammonia, dyes, metal ions, methane, organic acids, etc., from wastewater and subsequent reuse of the same in industrial purposes for promoting sustainability [44]. This review compiles recent research on resource recovery from wastewater using polymeric membranes. It also discusses different aspects of synthesis and characterization of different nanomaterials and composites used for preparing polymeric membranes capable of efficient, solute separation from solutions. Few such structured nanomaterials and polymer ligands have been shown in Fig. 1.

2 Significance of Polymeric Membranes

On the basis of composition, membranes may be classified as inorganic and polymeric membranes [2]. Polymeric membranes have been preferred for water treatment and resource recovery owing to their lower manufacturing cost, convenience in handling and tailorable pore size distribution [27]. Polymeric membranes are more convenient in comparison to inorganic membranes as the membrane properties of the former are easily modified by altering monomer molecules and concentration, synthesis procedures, etc. [15]. A polymeric membrane is considered as the best option for resource recovery due to its high efficiency in removing and emulsifying oil and other pollutant particles. Polymeric membrane-based setups require less energy and lower operating temperatures for wastewater treatment. It also requires less materials for construction of the membrane modules [27]. Advances in polymer science facilitates resource recovery from recalcitrant wastewater in turn promoting sustainable environmental development [55].

3 Resources Recovered Using Polymeric Membranes

3.1 Methane

Methane (CH_4), a greenhouse gas, is commonly emitted from WWTPs [20]. Recent studies have reported methane recovery from effluents using hydrophobic membrane contactors (HMCs) [46]. Advantages of this process includes large area to volume ratios for mass transfer, absence of requirement for phase dispersion, convenient operation and reduced energy consumption. McLeod et al. [38] reported the use of vacuum condition and/or a stripping gas as a driving force for mass transfer during methane recovery. According to another study, energy consumed by an upflow-anaerobic sludge blanket reactor (UASB) coupled with HMCs for methane recovery from domestic effluent consumed lower energy than that recovered from the process [48]. In a study by Cookney et al. [11], authors used dense polydimethylsiloxane (PDMS) membranes for effective mass transfer of methane owing to the anti-wetting property demonstrated by the membranes. They also suggested a pretreatment of the effluents subjected to treatment with a more porous membrane for reducing particle clogging and resultant volumetric mass transfer coefficients. According to another recent study, high flow rates of strip gas and low vacuum pressure yielded maximum net energy (0.0495 kWh m^{-3}) and a methane recovery efficiency of 88–90% [47]. In another study, authors reported PDMS coated porous polyvinylidene difluoride (PVDF) membranes which demonstrated a total mass transfer of 70%, enhanced membrane performance and reduced membrane fouling [50, 51]. Authors also suggested that any decline in membrane efficiency (resulting from fouling) may be reversed by physical cleaning using water [48]. HMCs have also been used in membrane biofilm reactors (MBfRs) and anaerobic membrane bioreactors (AnMBR) for methane recovery [20, 57]. Schematic representations of the same have been shown in Fig. 2a and b respectively. Images of different polymeric membranes have been shown in Fig. 2c. In the presence of N_2 gas stripping, PDMS membranes demonstrated a methane recovery efficiency of 98.9% [11]. However, dilution ability of N_2 reduced the economic viability of this process. Nevertheless, gas extraction in vacuum reduced energy consumption of the process by 85%. However, membrane pouring and wetting were two limitations of the same. Substitution of vacuum by organic solvents yielded a net energy production and methane recovery higher than 90% [33].

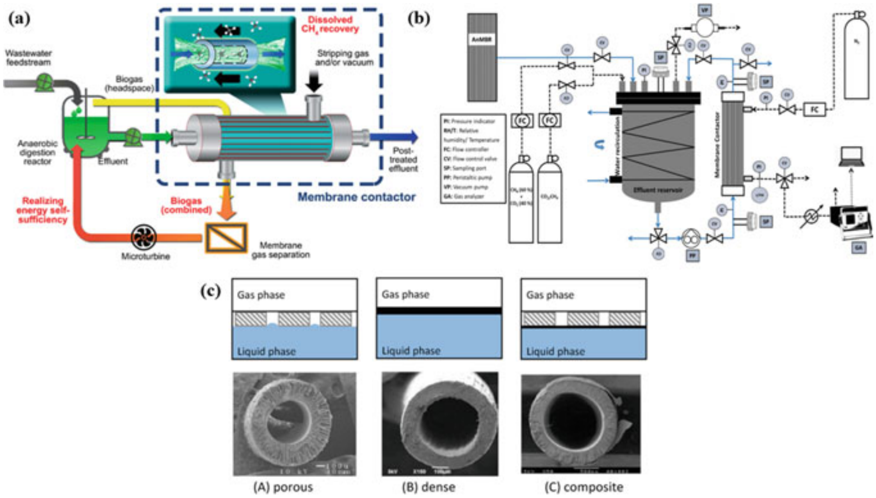

Fig. 2 Methane recovery using hydrophobic membrane contactors (HMCs). **a** HMC coupled with MBfR (Reproduced with permission from Hou et al. [20] © 2019, American Chemical Society); **b** HMC coupled with AnMBR (Reproduced with permission from Sohaib et al. [54]); **c** SEM images of polymeric membranes used as HMCs (Reproduced with permission from Velasco et al. [57])

3.2 Ammonia

Ammonia (NH_3) is another valuable resource recovered from wastewater. However, processes of NH_3 recovery reported so far have been energy intensive and inefficient. In recent studies, HMCs have been widely investigated for NH_3 recovery from wastewater. Reduction of partial pressure by application of vacuum or stripping gas reportedly facilitates diffusion of dissolved NH_3 from liquid to gaseous phase, thereby improving the efficiency of NH_3 recovery [20]. In an HMC, ammonium nitrogen is converted to ammonia at pH 11 [46]. The reaction for the same is given as follows:

$$NH_{4},{}^{+}{}_{(aq)} + OH^{-} \leftrightarrow NH_{3,(g)} + H_{2}O$$

Schematic representation of the same has been shown in Fig. 3. In a recent study, a polytetrafluoroethylene (PTFE) membrane was used for recovering ammonia as a fertilizer [48]. These PTFE membranes demonstrated stability in the presence of concentrated (63% v/v) H_2SO_4 used as a stripping solution in the process of recovery.

NH_3 recovery is economically viable when carried out with any stream of wastewater bearing a minimum of 1000–1500 mg L^{-1} of total ammonia nitrogen [58]. NH_3 recovery may be achieved from these effluents with 70% economic efficiency. Presence of urine or any other source of nitrogen in effluents render them more economically viable for NH_3 recovery [48]. In another study, nitrogen ammonia

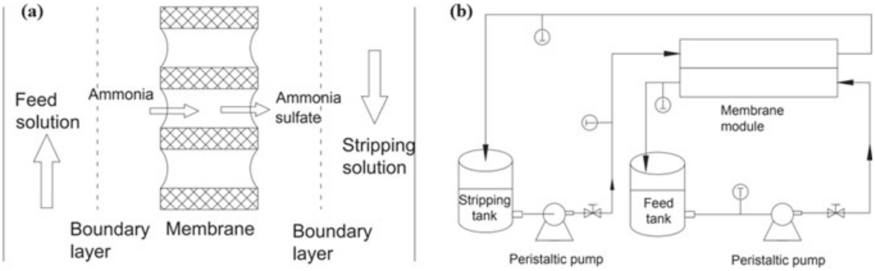

Fig. 3 Ammonia recovery from wastewater using HMC. **a** Schematic representation of NH_3 recovery by HMC; **b** schematic representation of setup (Reproduced with permission from Liu and Wang [35])

was reportedly recovered as a fertilizer using a liquid–liquid hollow fiber propylene HMC [49]. In this study, application of nitric and phosphoric acids as stripping solution resulted in a total nitrogen recovery of 95%. In a recent study, authors reported NH_3 recovery from human urine using hollow fiber polypropylene (PP) membrane contactors [64]. H_3PO_4 was used as a stripping solution in this study. Ammonia recovery efficiency recorded in this study ranged from 88.47 to 90.90%. In a similar study, authors reported a PVDF-based hollow fiber membrane contactor (HFMC) for recovering NH_3 from human urine [12]. The recovered products included liquid ammonium monophosphate/diphosphate, ammonium nitrate and ammonium sulfate of high-quality. PVDF–hexafluoropropylene (PVDF-HFP) membrane reportedly demonstrated higher NH_3 recovery efficiency in comparison to membranes procured commercially [36].

Ammonia recovery is also carried out by integrating membrane separation with electrochemical processes [31]. In this process, OH^- electrochemically liberated from water increases the solution pH, in turn causing the conversion of NH_4^+ to NH_3. This NH_3 is then recovered using membrane separation. Schematic representation of the same has been shown in Fig. 4. Urea hydrolysis reportedly accelerates this process by increasing the concentration of NH_4^+ and therefore facilitates NH_3 recovery in turn [7, 9]. Hou et al. [20] reported the synthesis of a similar integrated, flexible and cost-effective PP based membrane electrode coated with a thin film of hydrophilic nickel. In this study, electrolysis increased solution pH which in turn increased NH_3 conversion as seen in similar studies. NH_3 recovery recorded in this study was 40% higher than reported in other contemporary studies [20].

3.3 *Metal Ions*

Anion exchange membranes (AEMs) coupled with diffusion dialysis (DD) reportedly yield promising results for acid recovery and treatment of industrial acid wastewater

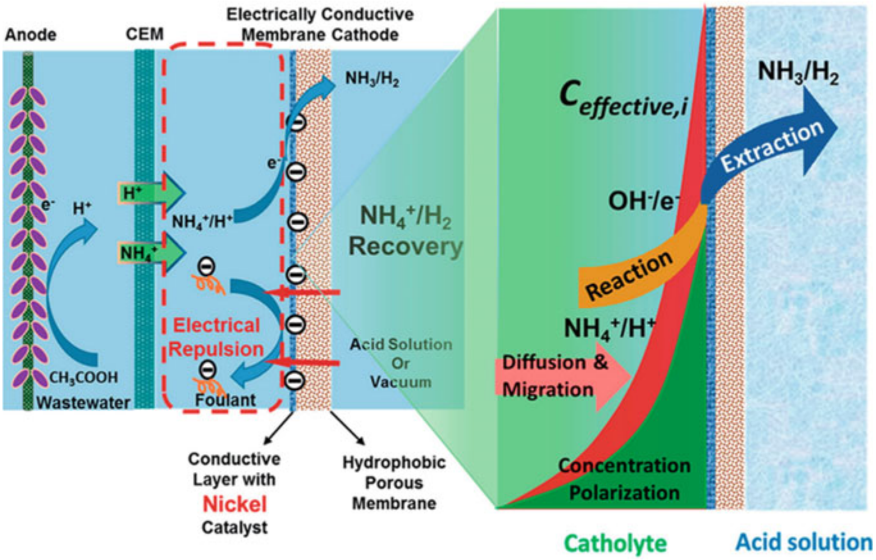

Fig. 4 Integrated hydrophobic membrane and electrode for ammonia recovery (Reproduced with permission from Hou et al. [20] © 2019, American Chemical Society)

[25]. The advantages offered by this process includes low energy requirement, convenient installation, and cost-effective operation. The driving force resulting from the difference in concentration between the dialysate (usually water) and the feed side facilitates the recovery of acids from acid effluents. However, according to another similar study, polymer inclusion membranes (PIMs) reportedly demonstrated better efficiency for metal ion recovery in comparison to [67]. PIMs generally consist of a carrier, usually a molecular or ionic liquid (IL), a base polymer, and a plasticizer [66]. The carrier moiety encapsulated within the polymeric structure selectively binds with the target metal ion. The base polymer provides mechanical strength to the membranes.

Different extractants have been used for synthesis of polymeric membranes for recovery of metal ions. Different classes of extractants used in PIMs for metal recovery have been enlisted in Table 1. Baczyńska et al. [4] reported the use of extractants Cyphos IL 101, 104, and 167 in cellulose triacetate (CTA)-based PIMs and PVDF-supported liquid membrane (SLMs) for recovery of Zn(II), Fe(II), and Fe(III) ions, respectively. Membranes prepared with Cyphos IL 101 and 167 demonstrated an 80% increase in Zn(II) and Fe(III) ion transportation. Cyphos IL 104, having the largest structure, offered lowest mobility for transportation of anions and showed promising results only in case of Fe(II) ion (40%). Selectivity of the extractants were found to increase as Cyphos IL167 > Cyphos IL101 > Cyphos IL 104 in case of Zn(II) recovery using PIMs.

Table 1 Classification of extractants employed for recovery of the target ions (Reproduced with permission from Jha et al. [24])

Extractant type	Example	Metal recovered
Basic	Aliquat 336	Co(II); Cr(VI)
	TOA	Cr(VI); Cu(II); Co(II); Ni(II)
	TIOA	Cu(II); Co(II); Ni(II)
Acidic and chelating	D2EHPA	Cr(IV); Zn(II)
	Cyanex 272	In(III)
	LIX 841	Cu(II)
Neutral and solvating extractant	TBP	Cd(II); Pb(II)
	Cyphos® IL 101	Zn(II); Fe(II); Fe(III)
	Cyphos® IL 104	Zn(II); Fe(II); Fe(III)
Macrocyclic and macromolecular	Calix [4]-crown-6	Zn(II); Cd(II); Pb(II)
	1-Alkylimidazole	Cu(II)
	Proton ionizable lariat ether	Zn(II); Cd(II); Pb(II)

In another study, Kaya et al. [28, 29] reportedly used seven types of plasticizers, including Bis (2-ethylhexyl), Bis (2-ethylhexyl) adipate (DOA), Dioctyl terephthalate (DOPT), 2-Nitrophenyl octylether (2-NPOE), 2-Nitrophenyl pentylether (2-NPPE), Tris (2-butoxyethyl) phosphate (TBEP) and Tris (2-ethylhexyl) phosphate (T2EHP), in combination with CTA–PIMs for recovery of Cr(IV) from plating bath water. Authors had also modified the membranes with reduced graphene oxide (rGO,1 wt%). Of all the different plasticizers used, 2-NPPE yielded maximum Cr(IV) recovery (98%) due to its lowest viscosity and high dielectric constant. Moreover, modified membranes yielded stable rates of Cr(IV) recovery which remained the same even after ten consecutive cycles. Inclusion of rGO increased membrane hydrophobicity and in turn enhanced rates of Cr(IV) recovery. However, 2-NPOE is used widely due to its cost effectiveness [28, 29].

In a similar study, DOPT yielded better results than N-[N,N-di(2-ethylhexyl) aminocarbonylmethyl] glycine (D2EHAG), when added to CTA-based PIMs for recovery of Co(II) and Mn(II) [3]. According to another recent study, SLMs were found to demonstrate better rates of Cu, Cr, and Zn recovery in comparison to chemical precipitation-based processes [48]. Heavy metals recovered in this study using SLMs were also in better usable form. Schematic representation of chromium recovery using PIM has been shown in Fig. 5. Different studies reporting metal recovery using polymeric membranes have been enlisted in Table 2.

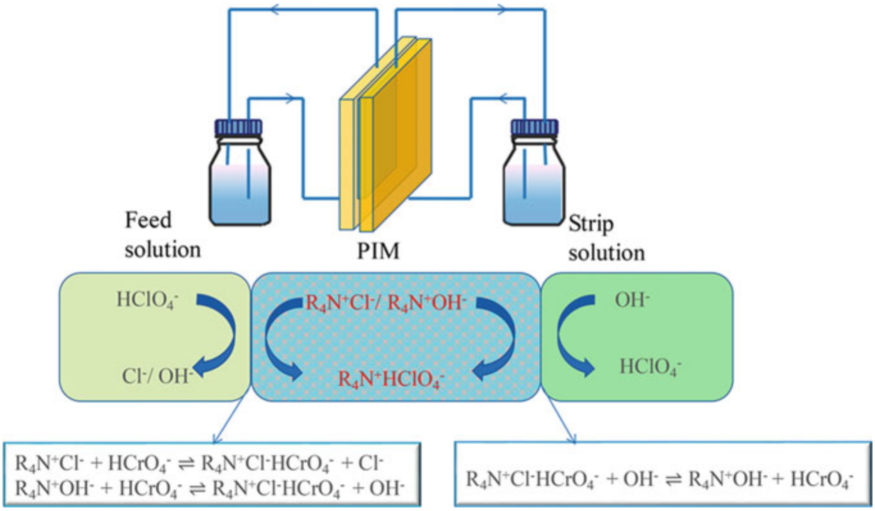

Fig. 5 Schematic representation of Cr(VI) recovery using PIM (Reproduced with permission from Zhao et al. [66] © 2018, American Chemical Society)

3.4 Energy

Rapid growth of urbanization as well as industrialization, is paralleled by a similar increase in the demand for energy. This has facilitated the need for alternative sources of renewable and sustainable energy. Chemical potential and/or salinity gradient of industrial effluents may be utilized for meeting this requirement [66]. A recent study proposed an integrated membrane distillation (MD)-reverse electrodialysis (RED) process for production of power from low-grade heat. In RED, the NH_4HCO_3 present in a thermolytic solution is converted to NH_3, CO_2, and water at 40–60 °C. This temperature is further converted to energy [5]. A huge salinity gradient power exists between fresh water (like surface water or domestic effluents) and saline water (like seawater, industrial effluents, reverse osmosis (RO) concentrates, etc.) [66]. Different types of salts have been investigated to induce high salinity in RED processes. Nevertheless, substantial amount of energy is required for transportation of sea and surface water, control of membrane fouling, etc. However, substitution of natural waters by RO retentates or membrane bioreactor treated domestic effluents may reduce the cost incurred by the process. Schematic representation of power generation from salinity gradient has been shown in Fig. 6.

Bioelectrochemical processes have also received significant attention for energy recovery from effluents [43]. An example of the same, a microbial fuel cell (MFC), offers advantages like direct conversion of substrates to energy in the presence of biotic electro-catalysts, operability at extreme temperatures, solution pH and in the presence of different types of biomass, reduced production of activated sludge and energy saving (as a result of non-requirement of aeration). Organics present in sludge

Table 2 Polymeric membranes for metal ion recovery (Reproduced with permission from Castro-Muñoz et al. [6])

Membrane type	Membrane process	Metal ion recovered	Recovery rate (%)
MMGO filled PES	Nanofiltration	Copper	92
f-MWCNTs filled PVC	Nanofiltration	Zn^{2+}	98
CNFs/TiO_2 filled PAN	–	Pb^{2+}; Cu^{2+}; Cd^{2+}	87; 73; 66
(MEUF) PES	Ultrafiltration	Cd^{2+}	90
(MEUF) cellulose	Ultrafiltration	Arsenic (V)	89
PAH-PSF	Ultrafiltration	Pb^{2+}; Cd^{2+}	91.5; 72.3
s-PES	Ultrafiltration	Fe^{3+}	>90
Composite-CA	Reverse osmosis	Pb^{2+}; Cd^{2+}; Ni^{2+}; Zn^{2+}; Mn^{2+}; Co^{2+}	100
Composite GPC	Ultrafiltration	Pb^{2+}	>95
Goethite filled PAN	Ultrafiltration	Cu^{2+}	49
Composite PEI-zein	Forward Osmosis	Pb^{2+}; Cd^{2+}; Ni^{2+}	99.5
GMA-PAN	Ultrafiltration	Cu^{2+}	98
PBI/PES	Nanofiltration	Mg^{2+}; Cd^{2+}	98; 95
PA	Nanofiltration	Cu^{2+}; Cd^{2+}	98; 99
Sulfonated PVDF	Electrodiyalysis	Co^{2+}; Ni^{2+}	90; 69
CA/PMVEMA	Nanofiltration	Pb^{2+}; Cd^{2+}; Cr^{6+}	85; 72
PES-PE	Nanofiltration	Cu^{2+}; Zn^{2+}; Ni^{2+}	>90
PAN-PEI/PSS	Nanofiltration	Cu^{2+}; Zn^{2+}; Ni^{2+}; Cd^{2+}	98; 96; 96; 95
PVDF/2-Aminobenzothiazole	Ultrafiltration	Cr^{6+}	92
PVDF/PANI	Ultrafiltration	Pb^{2+}; Cd^{2+}	98.5; 97.3

Acronyms Carbon nanofibers (CNFs); Cellulose acetate (CA); Functionalized multi-walled carbon nanotubes (f-MWCNTs); Grafting glycidyl methacrylate (GMA); Graphene oxide-polydopamine-(b-cyclodextrin) (GPC); Micellar enhanced ultrafiltration (MEUF); Modified magnetic graphene oxide (MMGO); Poly(methyl vinyl ether-alt-maleic acid) (PMVEMA); Poly(sodium 4-styrenesulfonate) (PSS); Poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH); Polyacrylonitrile (PAN); Polyamide (PA); Polyaniline (PANI); Polybenzimidazole (PBI); Polyelectrolyte (PE); Polyelectrolyte complex nanofiltration (PECN); Polyethersulfone (PES); Polyethylenimine (PEI); Sulfonated polyethersulfone (s-PES)

generated by any conventional process of wastewater treatment may also be used in MFCs. Effluent treatment and electricity generation in a MFC has been schematically depicted in Fig. 7.

MFCs and MBRs have also successfully generated methane via efficient treatment of effluents [8, 10, 20, 37, 62]. Ion exchange membranes (IEMs) used to separate the electrodes in MFCs allow selective transport of charged solutes while retaining uncharged ones [66]. IEMs are also able to convert dissolved solutes to

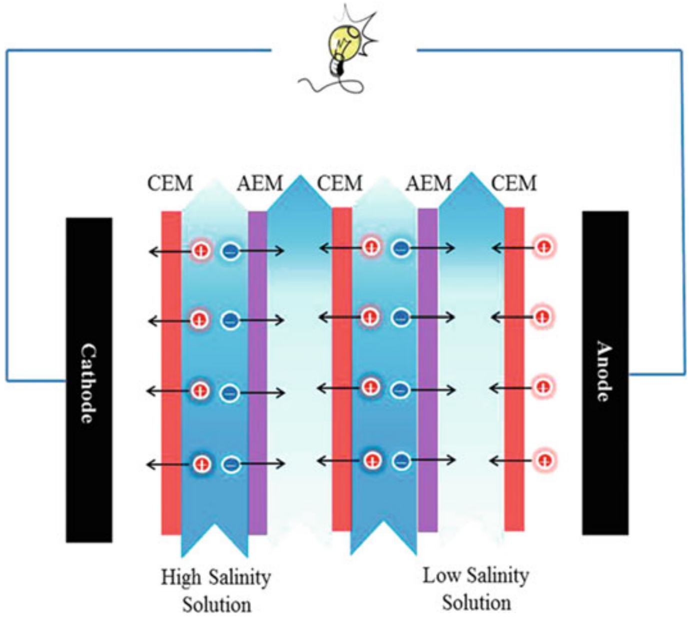

Fig. 6 Schematic diagram of the RED stack for electrical power generation from a salinity gradient (CEM: cation exchange membrane; AEM: anion exchange membrane) (Reproduced with permission from Zhao et al. [66] © 2018, American Chemical Society)

acids, bases, or new salts via bipolar membrane electrodialysis (BMED), electrodialysis metathesis (EDM), RED or other similar processes. MFCs integrated with RED have reportedly yielded more energy than each process applied individually [66]. Biohydrogen and methane may also be yielded using MFCs [43]. Polymer-based IEMs have been widely reported in contemporary literature. Al-Taie et al. [1] have reported the synthesis of IEM from a blend of polyethersulfone, expandable polystyrene, polyvenylidinefluride for application in an MFC. In another recent study, Shabani et al. [52] reported polymer electrolyte membranes synthesized from a composite of graphene oxide (GO) and sulfonated polyetheretherketone (SPEEK) for application in an MFC. These membranes were found to be more efficient than commercially obtained Nafion 11 membranes.

3.5 *Organic Compounds and Dyes*

Nanofiltration (NF)-based processes facilitate recovery of organic solvents. HMCs like emulsion liquid membrane (ELM), and supported liquid membrane (SLM) have also been reported for the same. Hydrophobic membranes are mostly used for the separation of organic solvents from wastewater streams. SLMs used for separation of

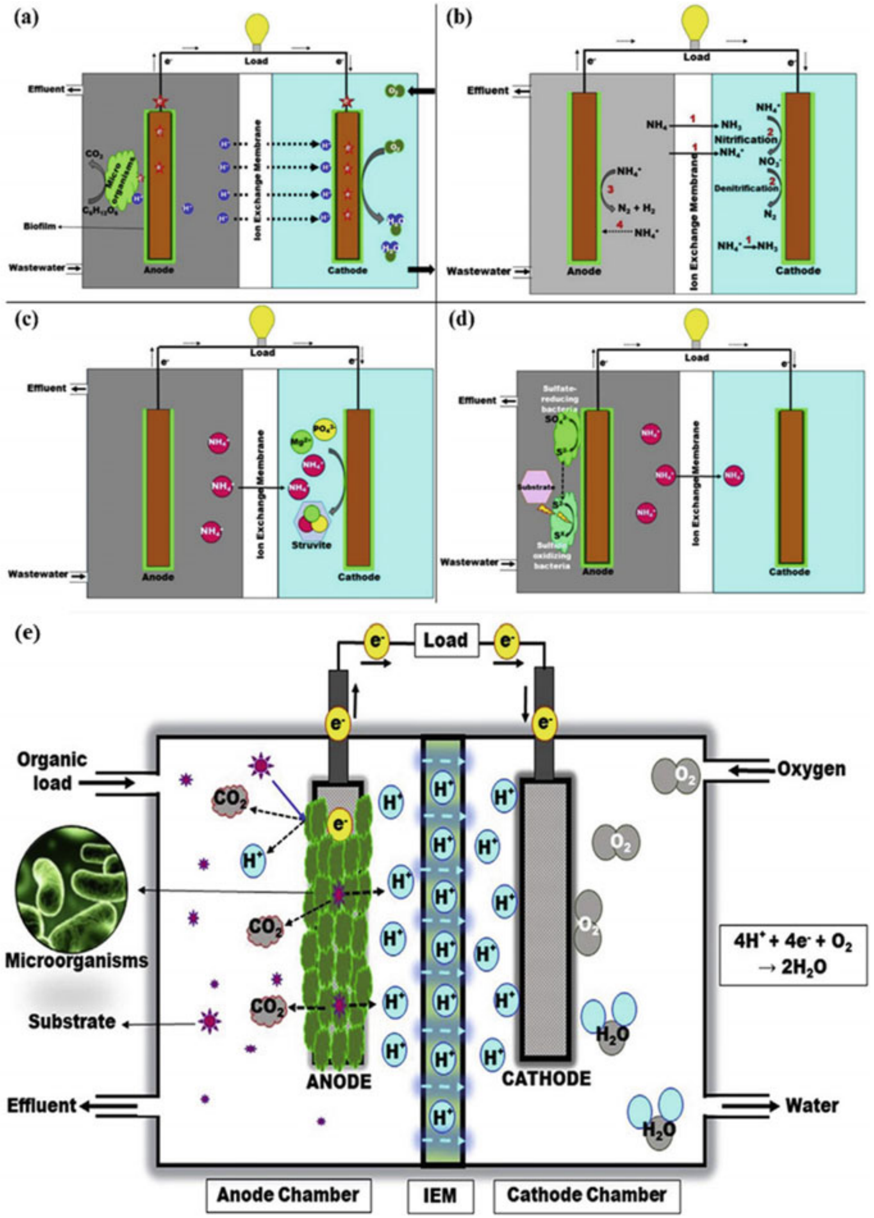

Fig. 7 Schematic representation of a microbial fuel cell (MFC). **a**–**d** COD, nitrogen, phosphate and **d** sulfide removal respectively, **e** working principle (Reproduced with permission from Palanisamy et al. [43])

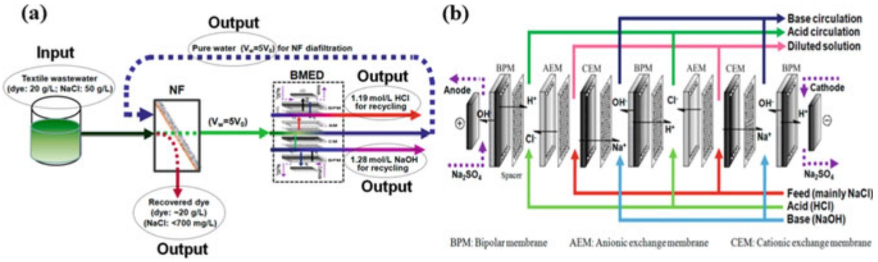

Fig. 8 Schematic representation of salt and dye recovery from effluents using BMED processes. **a** Scheme of resource recovery from textile wastewater by loose NF-BMED hybrid process; **b** BMED stack used for recovery (Reproduced with permission from Guo et al. [16])

reactive dyes usually have three phases including the feed phase, liquid membrane phase and strip phase. Othman et al. [42] reported the recovery of Red 3BS dye (60%) using PP membranes. Jiang et al. [26] reported the simultaneous recovery of dyes and salts from textile wastewater using an integrated UF-diafiltration process. PP membranes used in this study demonstrated 99.84% desalination (removal of Na_2SO_4) and 97.47% recovery of reactive blue from mixtures of the same. In a recent study, authors reported an integrated loose NF-BIMED process which offered enhanced selectivity and a dye recovery potential >99.93% [17]. In another study, authors designed a novel loose NF-based electrodialysis process that yielded dye and salt recovery potentials of 98.9 and 99.4%, respectively. PES NF membranes used in this study showed greater selectivity when PES nanocomposites (with GO, MoS_2) were used for membrane synthesis. Schematic representation of simultaneous dye and salt removal from effluents have been shown in Fig. 8.

4 Limitations of Polymeric Membranes

The main problem of polymer membrane is fouling and membrane wetting. In case of membrane fouling the deposition of different macromolecules, microorganisms, salt in the surface area of the membrane cause the decline in membrane performance during the filtration practice, decline in membrane flux, selectivity change etc. On the basis of the nature of the foulant, membrane fouling can be categorized into 4 groups such as inorganic fouling, colloidal fouling, organic fouling and biofouling, discussed as follows [63].

- **Inorganic fouling**: inorganic fouling means the super saturation of inorganic minerals in the surface area of the polymer membrane. Most of the inorganic minerals such as calcium phosphate $Ca_3(PO4)_2$, calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$) etc. are the cause of inorganic fouling.

- **Colloidal fouling**: Colloidal fouling means the accumulation of organic (proteins and aggregated NOM) and inorganic colloidal (oxides/hydroxides of iron, silica etc.), heavy metal hydroxides material in the pore area of polymer membrane.
- **Organic fouling**: in the case of organic fouling the organic matter proteins and aggregated natural organic matter, humic substance, polysaccharides) get accumulated in the surface of the polymer membrane because of their hydrophobic fraction.
- **Biological fouling**: Biological fouling means the fouling of polymer membrane occurs because of the biological agent such as (bacteria/bacterium). The biological agent strongly adheres in the polymer membrane and generates sessile colonies by utilizing the feed water nutrients.

The sessile bacteria further form the biofilm. As a result, release of extracellular polymer secretion occurs [39] Electrostatic and hydrophobic interaction between the microorganisms and polymer membrane surface cause destruction of the polymer membrane. The rough surface, and non-polar nature of the polymer membrane are more vulnerable to biofouling [59].

Increasing the driving pressure (draw solution at high concentration) augments the permeate flux but this makes the fouling issues more severe [14, 53, 56]. The severity of fouling decreases when the driving pressure is lowered because of the lower concentration of the draw solution [14]. Fouling mostly occurs in polymer membranes from the organic material due to their greater affinity towards the membrane [48]. When fouling occurs due to inorganic agents, the membranes become clogged and enlarged. As a result, the solution seeps into the pores of the membrane. Challenges and opportunities of membrane-based processes have been shown in Fig. 9.

Fouling reduces the hydrophobicity of the membrane which leads to membrane wetting [19, 23, 50, 51]. The performance of the membrane generally relies on the hydrophobicity of the membrane. This hydrophobic nature can be broken down due to membrane wetting [40]. Membrane wetting causes the increase in mass transfer resistance, damage in membrane morphology, and deterioration of the performance process of membrane [48]. This occurs because of the following reasons [48]:

- The organic contents present in water reduces the surface tension of water which in turn causes a reduction of membrane hydrophobicity;
- capillary condensation of the volatile species inside the membrane pores.

In case of MBfRs and MABRs, the biofilm layer is the most essential part for wastewater treatment. Excessive biofilm accumulation also creates a negative impact on the membrane. It decreases the removal fluxes of contaminants and biofouling happens [20]. Membrane fouling also causes the increase in operation cost due to high pressure requirement and decreases the membrane lifetime due to severe physical and chemical cleaning, in that case some strategic steps are very much essential for pressure driven membrane practices [23].

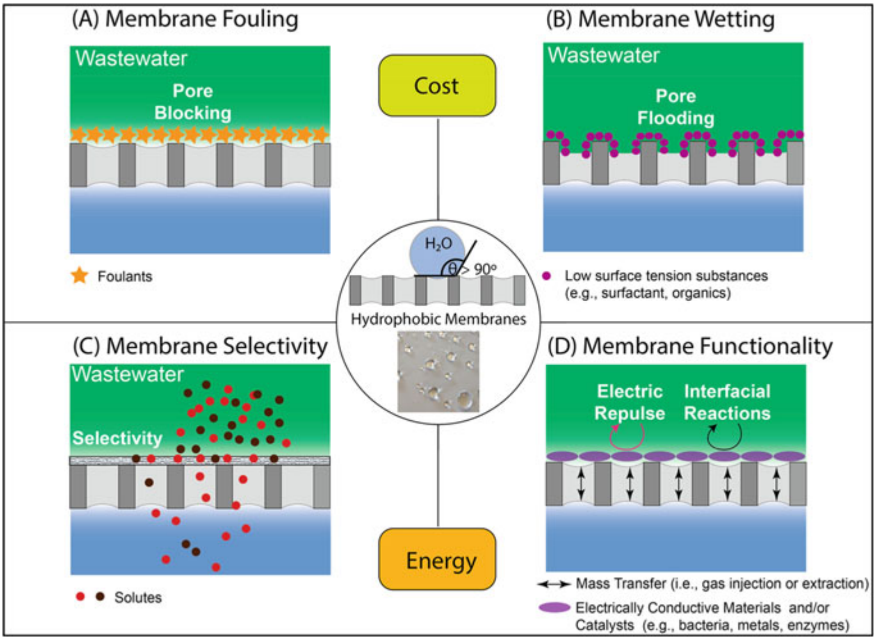

Fig. 9 Challenges and opportunities: **a** membrane fouling, **b** membrane wetting, **c** membrane selectivity, and **d** next-generation membrane (Reproduced with permission from Hou et al. [20] © 2019, American Chemical Society)

5 Strategies for Increasing Membrane Efficiency

With the help of nanomaterial and cleaning practice the severity and probability of membrane fouling and membrane wetting can be reduced. Polymer nanocomposite membrane is a kind of strategy that helps to fouling control, membrane wetting control, and improvement of resource recovery with the help of their special property. Nanomaterial applied in liquid–solid, gas–gas, and liquid–liquid separations or recovery. Nanomaterial can be classified into four groups such as organic material, inorganic material, hybrid material and biomaterial. The nanomaterial can be mixed with the polymer solution prior to the phase inversion method. After the phase inversion it gets shaped into the hollow fiber and flat sheet configuration etc. [63].

Filtration of the membrane can be improved by adding the nanomaterial, and it has the ability to increase the membrane pores which provide better permeability. It also decreases membrane roughness and has an antifouling and antimicrobial property. The optimal concentration of the nanomaterial is helpful to improve membrane filtration practices, but increase in the nanomaterial causes the decrease in membrane working capacity. The optimal concentration depends on the membrane composition and the properties of the nanomaterial [59]. Permeability and selectivity of synthetic membranes is lower but in the case of the biological material the selectivity and permeability is higher. Potassium ion channel present in the biological system shows better potassium (K+) transport (∼108 ions/s) with K+/Na+ selectivity [55]. So this idea has been imposed in synthetic membranes by the following two processes:

- By incorporating Single Digit Nanopores (SDN) from porous metal–organic framework or carbon nanotubes;
- By grafting of solute selective ligand with polymer.

SDNs have a uniform and narrow pore diameter which provide selectivity and permeability. And a solute selective ligand can select the desired solute [55]. For preventing the membrane wetting, ominophilic membrane was used in membrane bioreactors, which throws out both water and oil. This ominophilic membrane surface free energy is very low which prevents the LST initiated wetting. This property of the ominophilic membrane is helpful to recover chemicals from the fermentation broth [20]. Sometimes the hydrophilic chitosan is used to control the membrane wetting because this chitosan reduces the hydrophobic–hydrophobic interaction between the membrane and oil. After that the membrane can be cleaned by using backwashing, chemical and drying practice [34].

5.1 Use of Composite Polymer Membranes

5.1.1 Incorporation of Inorganic Nanomaterials

In case of increasing the efficiency of resource recovery practice on a large scale, the metal organic framework and zeolitic imidazole frameworks play a vital role. They are mainly used in gas and ion–ion separation. According to Zhang et al. a ZIF membrane with 3.4 Angstrom pore window size has the ability to alkali metal ion selectivity [55]. In another study, some metal oxides such as Silver (Ag), Zinc Oxide (ZnO), Copper (Cu), Titania (TiO_2), Zeolite, Iron Oxide (Fe_2O_3), etc., have been helpful to control the fouling and wetting of the membrane [63].

The porous structure of mesoporous silica and zeolite nanomaterial porous structure provide high surface area and porosity to the membrane which helps to increase the permeability of the membrane. The zeolites have a smaller size which provide a better sieving property to the membrane [63]. Mesoporous silica nanoparticles have a non-oriented spore distribution, uniformity and spherical morphology. The hydrophilic nature and high surface area of the mesoporous silica property reduce the severity of fouling. These nanoparticles have mechanical and thermal stability which provide strength to the membrane and also increase the lifespan of the membrane [63]. Razmjou et al. [45] focused on lithium recovery by designing Li + selective membranes. They emphasized on the vital membrane design principle, such as:

- the effect of nanochannel dimensions,
- the effect of nanochannel chemistry,
- the effect of morphology, and
- the effect of driving forces.

5.1.2 Incorporation of Metal Organic Frameworks (MOFs)

MOFs are largely used in metal recovery because of the high porosity, high flux and adsorption efficiency, surface-to-volume ratio, large surface to volume ratio and low cost of the substrate. When the effective pore of a synthesized membrane is large then the function of embedded membrane is metal adsorption [34]. Zr-based MOF-808 incorporated in polyacrylonitrile (PAN) membranes demonstrate Cd^{2+} and Zn^{2+} recovery as high as 225.1 and 287.1 mg/g. This kind of membrane also removes 60−70% of pure Cd^{2+} and Zn^{2+} ions [13]. In case of Cr^{6+} recovery, UiO-66-NH_2/cellulose, UiO-66-NH_2/PAN/chitosan, and ZIF-67/silk nanofiber membranes used demonstrated 99% of Cr^{6+} removal efficiency [32]. Silk nanofibrous membrane with ZIF-8,229 exhibited 92% efficiency to recover As^{5+} [32]. The MOF-808/PAN membrane reportedly adsorbed Hg^{2+}, with a removal efficiency of 34%. UiO-66-$(COOH)_2$/PAN membranes reportedly demonstrated recovery of rare earth heavy metals Tb^{3+} and Eu^{3+} with capacities of 214 and 191 mg/g, respectively [22].

5.1.3 Incorporation of Graphene/Graphene Oxide

Graphene oxide is extremely helpful for preventing fouling and membrane wetting. Graphene oxide layers are intercalated with various oxygen rich functional groups such as carboxyl, hydroxyl etc. group. Hu et al. [21] report that graphene oxide and reduced graphene oxide nanosheet are able to inhibit the metabolic activity of *E. coli* by ~80 and ~70%. The sharp edges of graphene oxide are able to puncture the cell membrane of *E. coli*. Wei et al. reported a layer-by-layer assembly of alternating positively (amine containing graphite oxide) and negatively charged (graphene oxide nanotubes) polyamide or PES membrane which provided efficient antifouling activities [59]. Graphene oxide has a very good antifouling, anti-wetting and antibacterial property. The actual mechanism of bacteria killing of graphene oxide is unknown. However, it is assumed that graphene oxide contains oxygen groups in their surface area which act as Reactive Oxygen Species that are able to break the bacterial cell, inhibit replication, inactivate bacterial enzymes and demonstrate a better antibacterial property [65].

5.1.4 Incorporation of Carbon Nanotubes

Carbon nanotubes (CNTs) have a uniform size and shape so they have an ability of size selective separation and are also helpful for fouling control [55, 59]. Polyamide or polysulfone RO membranes impregnated with multiwall carbon nanotubes (MWCNTs) show lower water contact angle than the primary membrane which facilitates higher hydrophilicity [59]. It has been tested that polyethersulfone membranes grafted with oxygen-containing CNTs have the ability to reduce the fouling of bovine serum albumin and ovalbumin on the membrane surface. Generally, CNTs are not effective in fouling control because of their hydrophobic nature. Functionalization of CNTs with H_2SO_4 and HNO_3 renders the same hydrophilic nature resulting in lower antifouling and higher roughness of membranes. More such negatively charged functional groups are carboxylic, polyethylene glycol groups, etc. [59].

5.2 Methods for Controlling Membrane Wetting

Membrane wetting may be controlled via the following strategies suggested by Xu et al. [61]:

- **Polymer blending**: To increase the hydrophobicity of the membrane the polymer blending technique has been adopted. The fabrication of polymers such as PVDF and PTFE happens.
- **Surface modification**: In that case fine-tuned surface hydrophobicity and roughness adopted by grafting, coating of polymer membrane.
- **Composite membrane**: A dense layer coated over a porous substrate for increased protection
- **Mixed matrix membranes:** the addition of inorganic filler are able to modify the hydrophobicity and roughness of the resultant membranes with the help of their physicochemical properties.

5.3 Methods for Controlling Membrane Fouling

Membrane cleaning is one of the necessary practices. Regular cleaning practice helps to improve the water filtration practice and also increase the longevity of the membrane. Membrane cleaning practice is mainly divided into three groups such as physical cleaning, chemical cleaning and biochemical cleaning but physical and chemical cleaning is the most common practice. Membrane cleaning techniques may be in situ or ex situ. In situ means when the cleaning practice of a membrane module is taken inside of the reactor. Ex Situ means when the membrane cleaning practice is taken outside the reactor [41].

5.3.1 Physical Cleaning

Periodic back flashing is an effective method of fouling control in which pressure is applied in the permeate site of the membrane. Backward movement of the permeate through the membrane causes the deposited material to be lifted on the membrane surface as a result the severity of membrane fouling decreases. This practice does not work in case of irreversible fouling (clogging of the membrane pores with dissolve material and colloidal suspensions [41]. Membrane fibration, particle scouring, is an effective physical cleaning approach of membranes. It requires less energy consumption and reduces the severity of membrane fouling [30]. Forward flushing is an effective physical cleaning approach for a forward osmosis process [14, 60]. Xiao et al. [60] reported the direct FO of synthetic gray water. After 10 filtration cycles, forward flushing was done on both draw and feed solution side for 30 min with clean water. This practice showed 85% membrane flux recovery. Results of this study indicated that osmotic backwash is able to achieve 95% flux recovery [60].

5.3.2 Chemical Cleaning

In chemical cleaning practice chemicals generally break down the bonds between the foulant and the membrane. Understanding the nature of fouling and polymer membrane is very much essential before the cleaning practice. This practice is mainly done as a cleaning in place, in which the chemical solution is present in a retail channel of the membrane and breaks down the bond of the foulant. Cleaning agents can be classified into acids, alkalis, chelating agents, enzymes, surfactants, disinfectants, etc.; in case of acid-based cleaning H_2SO_4, HNO_3, etc. are used for treatment of membranes. Acid cleaning's main aim is to clean inorganic foulants such as metal oxide, precipitated salt, etc., the basic chemical cleaning agent (NaOH, carbonate, phosphate, etc.) used for the removal of organic foulants [41]. According to a study by Henares et al. [18], inorganic and organic fouling of PP membranes used for methane recovery from a UASB effluent was restored by cleaning with 2 wt% NaOH and 10 wt% citric acid for 2 h. In another study, cyanide mass transfer coefficient had increased by 95% on cleaning with water, HCl, NaOH, and EDTA [48].

6 Conclusion

Resource recovery practice helps to promote reuse options and also is able to reduce waste water footprint. By recovering the resources, we are able to mitigate further resource consumption. Membrane fouling and wetting is the main problem of polymer membranes but nowadays using several nanomaterials (graphene, CNTs, etc.,) helps to prevent fouling and membrane wetting. Polymer membrane construction and configuration for resource recovery practice is a major research area. Use of polymer nanocomposites for membrane synthesis reportedly improved the recovery practice. More research needs to be undertaken, for achieving efficient recovery of resources from wastewater. This practice will be able to resolve pollution problems to a great extent and promote resource conservation.

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Chapter 10
Antibacterial and Antifouling Properties of Membranes

Priyankari Bhattacharya and Priya Banerjee

1 Introduction

Biofouling is the process of formation of biofilms at the membrane surface or inside the pore wall of the membrane due to adhesion of extracellular polymeric substances and bacterial cells. They account for about 50–90% of total organic carbon. Presence of dissolved nutrients promotes biofilm adhesion caused due to concentration polarization in the membrane. Absence of convection at the membrane surface causes dissolved and suspended solids to assemble at the surface. This biofilm once formed prevents chemicals or other forces to disrupt the bacterial layer [37]. Biofouling can be detected if:

- differential pressure gets higher
- membrane flux gets lower after
- operating pressure increases at a given flow rate
- scaling occurs at a low operating velocity [34].

Fouling can occur at the membrane surface resulting in external fouling or deposition of particles inside pores of the membrane thereby resulting in internal fouling. Fouling may be due to inorganic particles, organic particles, particulate matter or biomaterials [2]. Flux decline due to fouling increases the operating cost in industrial applications due to the need for membrane cleaning or replacement as well as lower flux with higher time makes the membrane application energy inefficient.

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2 Life Cycle of Biofouling

Of all forms of membrane fouling, biofouling is considered the most complicated [47]. Microorganisms naturally multiply in aqueous media. These organisms coming in contact with the membrane surface adhere to the same [19]. Then these microorganisms extract nutrients from the aqueous medium and begin to reproduce. This rapid growth of microorganisms results in bacterial colonization and subsequent formation of biofilms, when the bacterial colonies are encapsulated by extracellular polymeric substances (EPS) [47]. Biofilm is formed through the following four sequential stages (as shown in Fig. 1):

- At the initial sage, bacteria are reversibly attached to the membrane surfaces. This is more significant if the membrane surface is pre-contaminated by proteins and other macromolecules.
- Secondly, bacterial cells are irreversibly attached to membrane surfaces via bio-adsorption and bio-adhesion.
- Thirdly, biofilms are formed as a result of bacterial reproduction and proliferation.
- Fourthly, and finally, bacteria are redispersed into the aqueous environment.

The biofilm formed as a result of cell adhesion gradually thickens to a layer of EPS having a complex microbial community. This community is stable under adverse physical and chemical conditions and hence difficult to displace [68]. Moreover, once the biofilm attains maturity, the EPS containing glycoproteins, lipoproteins, polysaccharides and other biomacromolecules strongly protect the biofilm from bactericides, making it even more difficult to kill the microorganisms present therein. Therefore, it is extremely essential to control initial cell adhesion to the membrane surface in order to achieve long-term operational stability against biofouling [67].

EPS deposited on the membrane surface limits the permeation of water molecules through the same by causing friction between the permeating water molecules [11, 15, 24]. Besides microorganisms, non-migratory natural organic matter (NOM) and biomolecules (such as protein) may also be deposited on membrane surfaces. These foulants participate in specific inter-foulant or nonspecific interactions with the

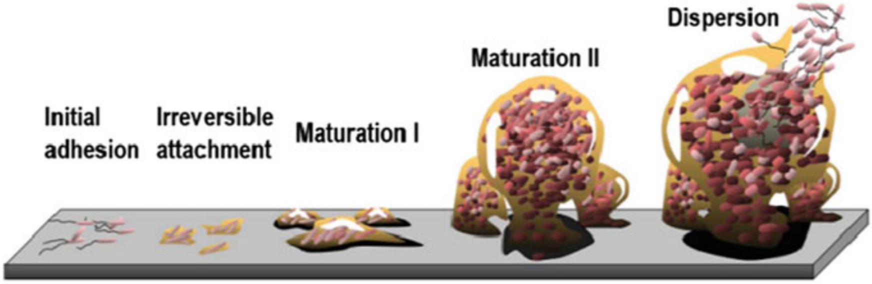

Fig. 1 Biofilm formation and maturation process on membrane surfaces (Reproduced with permission from [68])

membrane surface to form a stable organic layer over the same [47]. Besides EPS, transparent exopolymer particles (TEPs) also play a crucial role in biofilm formation [68]. TEPs are aquatic organic microgels having sizes ranging from 0.4 to 200 μm and above.

3 Properties of Membrane Favouring Biofouling

Membranes have been widely used for water purification and concentration of targeted pollutants from aqueous phases. Application of these membranes include water reclamation, wastewater treatment, desalination and removal of organic matter from aqueous phases [68]. Membrane filtration processes offer several advantages like high separation efficacy, convenient scale-up and operation, small environmental footprint and reduced consumption of energy. On the basis of pore size and operational pressures, membrane filtration maybe classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO).

Membranes prepared from polymers like polydopamine (PDA), polyether sulfone (PES), polysulfone (PS), polyvinylidene fluoride (PVDF), and polypropylene (PP) have been widely investigated for water treatment owing to their cost effectiveness for commercial scale manufacture and favourable chemical and thermal resistance [3, 41, 66]. Despite these advantages, wide-scale application of polymeric membranes is limited by challenges like process optimization, membrane longevity, cleaning and replacement of membranes, etc. [68]. Of all these challenges, fouling (including biofouling, colloidal fouling, inorganic scaling/deposition and organic fouling) is reportedly a major constraint [61].

The properties that enhance membrane biofouling are surface roughness i.e. more the surface is rough more will be the adhesion; charge of membrane surface i.e. neutral charge on the membrane surface attracts negatively charged bacteria to deposit on the surface; and hydrophobicity i.e. more the hydrophobicity of the membrane more is the deposition [43]. A significant irreversible decline in membrane permeability caused by fouling largely reduces membrane efficiency and longevity. Several studies have been undertaken to enhance antifouling properties of membranes in terms of improved hydrophilicity, reduced surface roughness and fine-tuning of membrane surface charges [29, 52, 63]. Nevertheless, surface biofouling still poses an enormous challenge to the wide-scale application of membrane-based processes. Biofouling results in significant decline of productivity and increases energy uptake of the process. Membrane biofouling is strongly governed by membrane surface properties, operational parameters like solution pH, ionic strength and species as well as the microorganism causing the fouling [68].

4 Enhancing Antifouling Behaviour of Membranes

In contemporary studies, researchers have focused on incorporation of biocides into polymer matrix or on membrane surfaces. Several review papers have summarized the antibacterial properties of biocides like metal/metal oxide nanoparticles (NPs), metal organic frameworks (MOFs), polymeric nanostructures, carbonaceous NPs, etc. However, few studies have focused on incorporation of the same in the design of polymeric membranes in order to inactivate bacterial colonization without any pre-treatment of feed solution. Endeavours undertaken to enhance the antifouling potential of polymeric membranes have been discussed as follows.

4.1 Membrane Surface Modification

Enhancing antifouling properties of the membrane by surface modification can be effective way to minimize biofouling. Different processes of membrane surface modification have been shown in Fig. 2. Coating on the membrane surface or grafting polymer on the membrane surface can greatly reduce fouling. Material chosen for such coatings or grafting has repulsive behaviour towards fouling agents like proteins, organics or solids [22, 37]. Incorporation of nanofillers in polymers resulted in overcoming problems related to membrane surface modification i.e., flux profile, fouling, thermal, chemical and mechanical stability and that of rejection [9, 16]. Carbon-based nanomaterials, metal organic frameworks, metal oxide nanoparticles, fumarate alumoxane [32, 54], zirconium dioxide [39], cystein incorporated grapheme oxide [20], etc. are used as fillers in PES membrane for surface modification [33].

Surface coating will also prevent internal fouling if dense non-porous coating is conducted. Another approach will be to modify the surface chemistry of membrane i.e., to reduce surface roughness and modify surface charge [37]. Modifying the nutrient source so as to reduce bacterial deposition may be another way to reduce fouling. Use of disinfecting reagents or surface sterilization of membranes can be also done. Physical methods to prevent biofilm formation include air scrubbing, crossflow filtration or backwashing [45]. Thermal and chemical disinfection methods can be done on membranes having higher thermal and chemical stability like ceramic membranes but are not applicable to standard RO membranes [38]. Use of biocides to prevent fouling can be oxidizing and non-oxidizing. Chlorine is one of the oxidizing agents used as biocide but due to the formation of by-products other biocides like ozone, iodine, iodine, potassium permanganate, chlorine dioxide etc. are used [30, 69]. Incorporation of nanoparticles in polymeric membrane synthesis increases surface hydrophilicity that can be confirmed from contact angle measurements. Moreover, these membranes exhibited higher flux due to a more effective surface area.

Additional benefit arises from incorporation of TiO_2 NPs having photocatalytic activity that excludes bacteria/viruses from system. In another study, authors reported

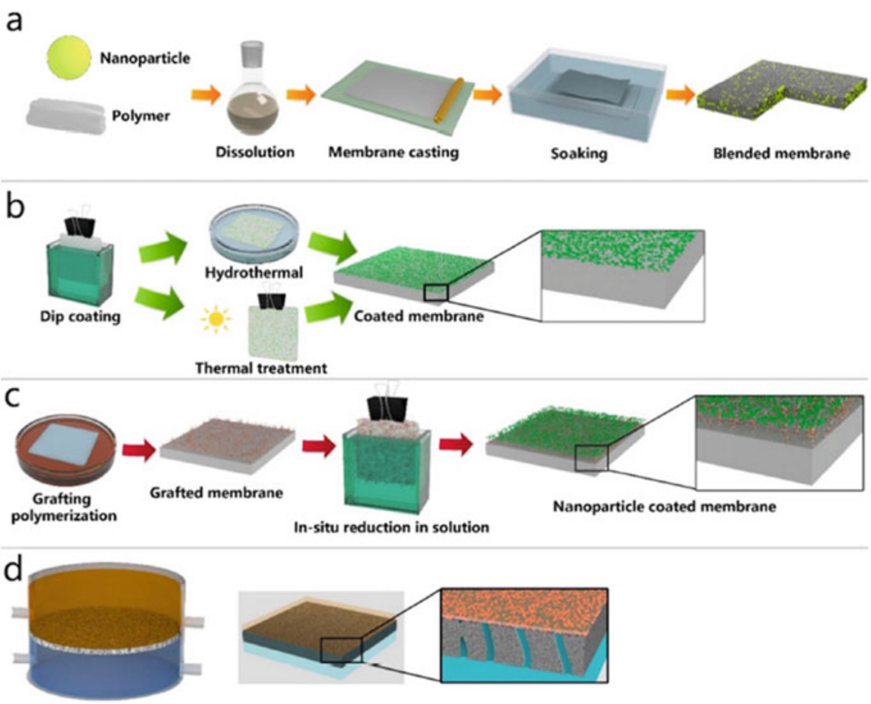

Fig. 2 Different processes of membrane surface modification for enhancement of antibacterial property of the membranes. **a** Blending antibacterial agent within polymer membrane matrix. **b** Membrane surface coating with antibacterial agent. **c** Membrane surface grafting with antibacterial agent. **d** Membrane surface interfacial polymerization with antibacterial agent (Reproduced with permission from Zhu et al. [68])

that when membrane surface charge is positive, it rejected positively charged proteins thereby reducing biofouling. Addition of zwitterionic charged material exhibits more antifouling property than conventional charged membranes. Commercial PES membrane was surface modified by addition of chitosan and alginate and $AgCl/TiO_2$ was incorporated. The membrane exhibited excellent permeability and lesser biofouling and improvement in biofouling resistance [4, 6, 25, 42, 44, 49]. Most foulants carry negatively charge on their surface which can be suppressed by electrostatic repulsion and electrophoresis [40]. This type of charged membrane possesses non-destructive fouling approach as compared to surface modified membranes.

4.2 *Incorporation of Nanomaterials in Membrane Matrix*

Integration of biocides like silver in these electrostatic charged membranes will have additional benefit of bacterial repulsion that will reduce biofilm adherence in the cathode and increase the life span of antifouling properties of the membrane [13]. Coating on membranes with nanoparticles having antimicrobial properties like silver, titanium dioxide, carbon nanotubes etc. can reduce adhesion. Incorporation of nanomaterials (shown in Fig. 3) in the membrane matrix also enhances antifouling activity of the membranes. Nanoparticle addition to change the surface property of the membrane in terms of hydrophilicity and charge is observed. Nanocomposite-based membranes are developed from metal oxide nanoparticles like TiO_2, SiO_2, Al_2O_3, CuO etc. and carbon-based nanoparticles like graphene oxide and carbon nanotubes. Thermal grafting of PEG and Ag for modification of the PES hollow fibre membrane increased hydrophilicity with enhancement of water flux by ~36% [55]. It was observed that TFC membranes fouled rapidly than cellulose acetate membranes due to surface roughness.

Antibacterial properties of silver are used for coating silver oxide nanoparticles on the membranes as well as medical implants or devices. Application of silver oxide coated membranes finds its application in the field of drinking water treatment, milk industry etc. The antibacterial activity of silver depends on temperature and pH.

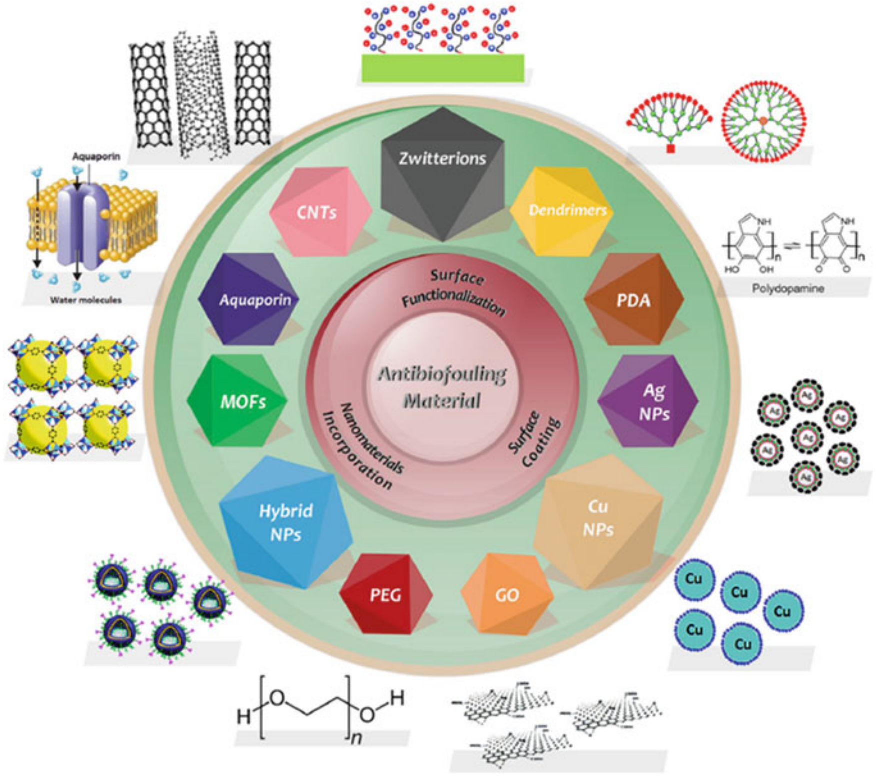

Fig. 3 Different types of materials applied in surface functionalization (Reproduced with permission from Firouzjaei et al. [14])

Silver ions interact with bacterial DNA and protein and disrupts bacterial cell. Silver oxide coated membrane shows antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. Silver oxide nanoparticles synthesized in chemical route had stability problem and aggregated at a high concentration which can be overcome by synthesizing AgO NPs by the green route. Ag by bio route when incorporated in PES to develop nanocomposite membranes had excellent antibacterial efficiency as observed against cultures of *E. coli* and *Pseudomonas aeruginosa* as well as mixed bacterial consortia. Comparative antibacterial activities of various inorganic membranes were studied against *E. coli*, *S. aureus*, and *Bacillus subtilis*. Alumina coated with copper exchanged zeolite showed antibacterial activity both in static and dynamic conditions of operation. Tubular membranes without copper layer resulted in decreased permeation for filtration of bacterial culture whereas copper coated membranes showed less permeation decrease and increased antifouling properties [8, 17]. Impact of metal and metal oxides on bacterial cells have been shown in Fig. 4.

Incorporation of chitosan and silver nanoparticles in montmorillonite resulted in antibacterial activity of the membrane that previously did not exhibit and antibacterial properties against *E. coli* and *S. aureus* [9, 51]. Many research works demonstrated that incorporation of silver and titanium dioxide in the Na-bentonite membrane [21], metal nanoparticles like gold, silver, copper, zinc in the membrane [12] increased antibacterial activity against *E. coli* and *S. aureus*. Green synthesized NiO nanoparticles showed antibacterial activity against *S. aureus*.

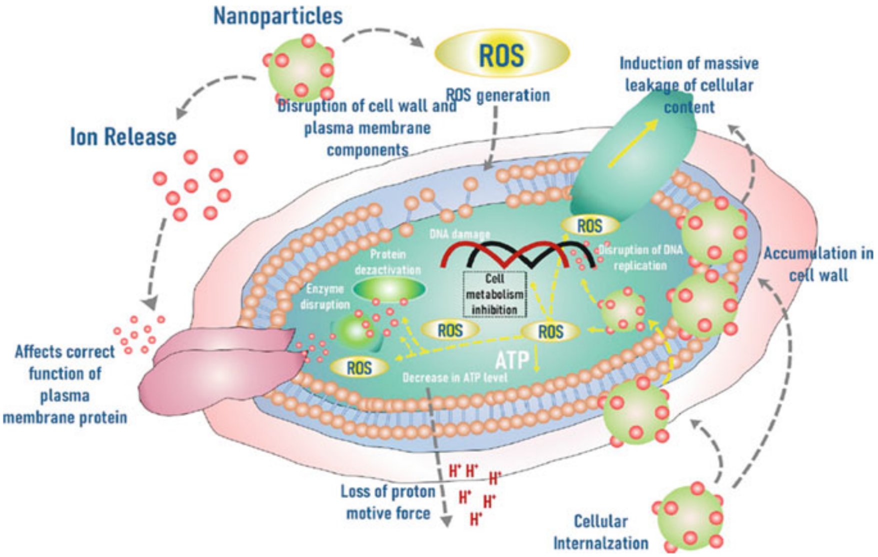

Fig. 4 Antibacterial mechanism of metal and metal oxide containing systems (Reproduced with permission from Firouzjaei et al. [14])

4.3 Inclusion of Enzymes in Membrane Matrix

Several natural compounds reportedly demonstrate anti-inflammatory, antimicrobial, antioxidant, and antiproliferative properties towards various pathogenic bacteria [28]. The strong antimicrobial effect exerted by some components is primarily due to the presence of bioactive agents like acids, aldehydes, aliphatic alcohols, antimicrobial enzymes, isoflavonoids, terpenes and phenolics in those components [5]. Of these bioactive agents, antimicrobial enzymes are widely available in nature where they protect living organisms from bacterial infestation. These enzymes are presently being widely investigated for their potential of directly attacking microorganisms, interference/destruction of biofilms and catalysis of reactions which in turn produce antimicrobial compounds [28]. Some investigations have been inspired by the enzymes present in fruits and vegetables, like allinase (garlic), bromelain (pineapple extract), glucanases and pectinases (pomegranate peel), lysozyme (broccoli and cauliflower), papain (papaya), peroxidase (turnip), etc., their antimicrobial potential and subsequent attachment/incorporation into artificial surfaces [1, 10, 53]. In these host-defense enzymes, polar cationic residues are directed to one side of the molecule, while, hydrophobic residues accumulate at the opposite end [28]. The amphiphilicity arising from such an arrangement facilitates the attachment of the hydrophilic faces of these enzymes with the negatively charged bacterial membranes while the hydrophobic face of the enzyme is inserted in a membrane [28].

Recent studies have investigated different antimicrobial enzymes like anti-quorum sensing, polysaccharide degrading, proteolytic, and oxidative enzymes. Of all such enzymes, α-amylase and lysozyme are reportedly the most efficient polysaccharide degrading antimicrobial enzymes available naturally [36]. α-Amylase and lysozyme target carbohydrates, which are one of the main constituents of EPS and bacterial cell wall [28]. These enzymes reportedly demonstrate broad spectrum antibacterial activity through synergistic effects. According to a recent study, functionalized PES membrane bearing immobilized α-amylase and lysozyme demonstrated efficient antifouling potential. Enzymatic modification of polymeric membranes for enhanced antifouling properties have been shown in Fig. 5a, b.

5 Blended Polymeric Matrices for Enhanced Antibacterial and Antifouling Properties

Surface modifications are carried out by either incorporating antibacterial agents during membrane preparation or introducing antibacterial agents by grafting. Coating on membrane surface by nanoparticles showcasing antibacterial properties is yet another approach of surface modification. This may prevent initial surface attachment of the biofilm. Blending, grafting and coating are some of the methods for surface PES UF membrane that was surface modified by phase inversion technique using silver

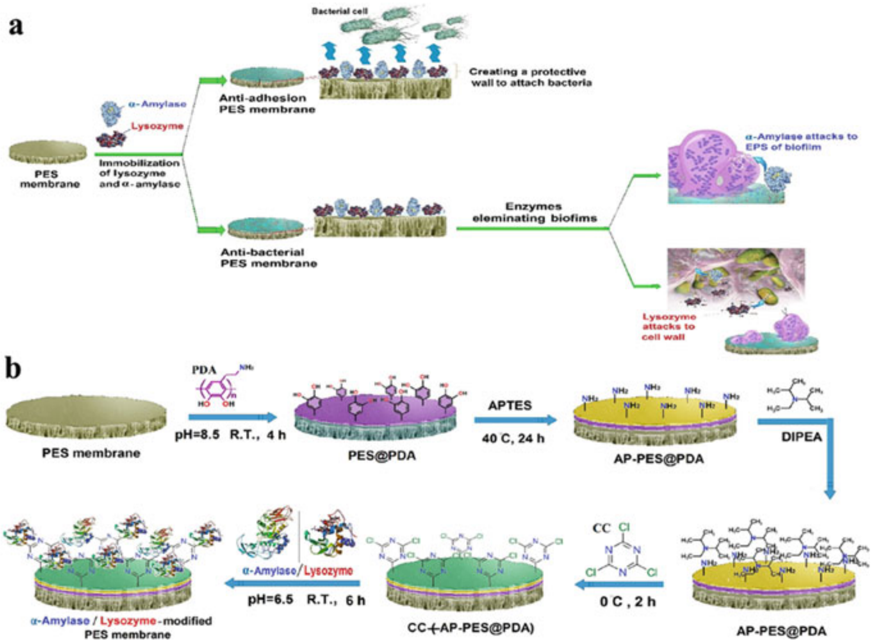

Fig. 5 Enzymatic modification of polymeric membranes. **a** Establishment of anti-adhesion and antibacterial properties on membranes to suppress biofilm formation; **b** schematic representation of covalent immobilization of α-amylase/lysozyme on functionalized PES membrane surface (Reproduced with permission from Mehrabi et al. [28])

loaded sodium zirconium phosphate nanoparticles. These modifications increased thermal stability, permeation, protein rejection and hydrophilicity [64].

The surface of the thin-film composite osmosis membrane was modified by incorporation of zwitterions and silver metal organic frameworks. This membrane exhibited antifouling and antibacterial activity as well as lesser flux decline [50]. Increased water flux of 300% when compared to the unmodified membrane was achieved in terms of water and salt flux for forward osmosis. PES nanofiltration membrane was surface modified by using nickel-bentonite nanoparticle fillers by the phase inversion method and applied for removal of heavy metals. The modification increased hydrophilicity, charge of membrane surface and porosity. Additionally, the membrane showed antifouling activity with effective rejection of heavy metals. Antibacterial activity exhibited by the membrane was higher against *E. coli* and *S. aureus* [9].

In a recent study, the membrane surface was modified by incorporation of silver-carbon nanotube composites via electrochemical deposition. The modification enhanced antibacterial activity and increased flux as compared to the unmodified membrane [13]. Co-polymer was synthesized from hydrophobic poly(butyl methacrylate), hydrophilic poly(ethylene glycol) methyl ether methacrylate and low surface energy poly(hexafluorobutyl methacrylate) by free radical polymerization technique. These copolymers were added to synthesize the polyvinyldiene difloride membrane bearing antifouling properties via the non-solvent induced phase separation method. This membrane showed excellent antifouling properties when used for oil/water emulsion filtration and membrane activity was regained by simple hydraulic cleaning under low speed, high pressure and high feed concentration [26, 48]. Hybrid polysulfone membranes were synthesized by incorporation of capsaicin-mimic N-(5-methyl acrylamide-2,3,4 hydroxy benzyl) acrylamide and vinyl triethylene silane. The hybrid membrane was synthesized via microwave assistance and hydrolytic condensation. The hybrid membrane exhibited antibacterial activity and steady permeation flux. The membrane was regenerated with cleaning efficiency of 90% [64].

Dual functional membranes were synthesized having antibacterial and antifouling properties by co-deposition of polydopamine and zwitterionic polymer on polyethersulfone substrate and subsequent immersion in silver nitrate solution [59]. In another study silver-polydopamine was incorporated in polysulfone membrane matrix [58]. Silane coupling agents have been reported to have great mechanical durability and antifouling property. They can react with organic and inorganic substrates and used as dust resistant attachment and to increase tensile moduli of composite materials. Silane composites have wide applications due to their simple nature and versatility. Silanes and capsaicin-mimic moieties bestow polymeric membranes with antibacterial and antifouling properties [64]. Quaternization and surface radical polymerization was employed for development of ultrafiltration membrane containing quaternary ammonium and zwitterionic polymers. These membranes were effective against biofilm formation and had antibacterial properties. The membrane showed higher flux rate and antibacterial activity of 98.2 and 97% against *S. aureus* and *E. coli* [40]. Materials blended in polymeric matrices for enhancement of antibacterial and antifouling properties of the membranes prepared from the latter have been enlisted in Table 1.

The design of multifunctional membranes with exceptional antifouling and antimicrobial properties may require revolutionary surface engineering and production methods to make next generation developments in membrane technology. As summarized in Table 2, in recent years there have been considerable advances in modification of polymer-matrix membranes using macromolecules for water treatment. The integration of macromolecules not only changes the physiochemical properties of membranes (hydrophilicity, porosity, charge density, thermal and mechanical stability), but also give membranes some unique properties based on macromolecules architecture (i.e., linear, crosslinked, branched) and could induce new characteristics and functions based on its synergetic effects. This offers a new dimension for the design and development of the next generation of high-performance polymer membranes [35].

Several challenges still need to be addressed to optimize the design of the organic composite membranes for practical applications at the large scale [35]:

- First, various development methods are currently limited to scientific research by reasons of high costs, difficult operation and scalability and only a small number of methods are ready for commercial use. For example, the fabrication costs of nanocrystals such as zeolite nanocrystal and CNC are high. Besides, during

Table 1 Recent advances in blending modification for enhanced antifouling and antibacterial activities of polymeric membranes (Reproduced with permission form [47])

Functionality	Polymer	Bacterial model	Exposure time	Fouling model
QAC	PVDF	*E. coli, S. aureus*	0–24 h	BSA & HA
			0–24 h	BSA
			3–24 h *E. coli*	–
			6–24 h *S. aureus*	
Chitosan	Starch	*E. coli*	24 h	–
	PEO	*E. coli*	6 h	–
Chitosan-Fe_3O_4	PVDF	–	–	BSA
PEI	PVA	*P. aeruginosa*, *B. subtilis*, *E. coli*, and *S. aureus*	ZOI test	–
Poly dopamine and nisin[a]	PSf	*S. aureus*	24 h	BSA
Poly dopamine and Cu NPs	PVDF	*E. coli*	ZOI test	BSA
Ag-poly dopamine	PSf	*E. coli*	ZOI test	BSA
HKUST@GO (MOF)	CA	–	–	BSA
Ag capped PEI attached PANCMA (MOF)	PES	–	–	SA
ZIF-8/GO (MOF)	PA	*E. coli*	4 h	–
Co-SIM-1 (MOF)	PLA	*P. putida, S. aureus*	24 h	–
COOH-GO	PPSU	*P. aeruginosa*, *E. coli*, and *S. aureus*	6 h	BSA
GO-NH_2	PE/PEO	*E. coli*	24 h	–
GO-PSBMA (zwitterion)	PA	*E. coli*	2 h	BSA
PMBU (zwitterion)	PVDF	*E. coli*	3 and 24 h	HA
HPEI-GO	PES	*E. coli*	24 h filtration	BSA
CTAB@MGO	PMMA/PEG	*E. coli*	ZOI test	BSA
TiO_2	PVDF, SPES	*E. coli*	ZOI test	BSA
SPAES + Cu NPs	PES	*E. coli*	24 h	BSA
ZnO-GO	PSf	*E. coli*	24 h	HA
ZnO	Chitosan, silica	*K. planticola*, *B. subtilis*	ZOI test	–
Oxidized MWNT	PES/SPSf	*E. coli*	6 h	BSA

(continued)

Table 1 (continued)

Functionality	Polymer	Bacterial model	Exposure time	Fouling model
SLS-CNT	PES	*E. coli*	ZOI test	BSA
Sulfonated CNT	PVDF	*E. coli*, *P. agglomerans*, and *P. graminis*	12 h + ZOI test	BSA
HMBA, PEGMA and HEA (comb co-polymer)	PES	*E. coli*	24 h	BSA

[a] In situ polymerization of dopamine with PSf and grafting with nisin. Abbreviations: *CTAB* cetyltrimethylammonium bromide, *HA* humic acid, *HEA* 2-hydroxyethyl acrylate, *HMBA* N-4-hydroxy-3-methoxybenzyl acrylamide, *HPEI* hyperbranched polyethylenimine, *MGO* metallic Ag/ZnO-reduced graphene oxide, *NP* Nanoparticle, *PANCMA* polyacrylonitrile-co-maleic acid, *PEGMA* poly(ethylene glycol) methyl ether methacrylate, *PMBU* poly 2-methacryloyloxyethyl phosphorylcholine-co-methacryloyloxyethyl butyl urethane, *PSBMA* poly sulfobetaine methacrylate, *QAC* Quaternary ammonium compounds, *SA* sodium alginate, *SPAES* sulfonated poly aryl ether sulfone, *SPES* sulfonated polyethersulfone, *SLS* sodium lignosulfonate, and *ZOI* zone of inhibition

regeneration the cellulose degradation causes irreversible damage, loss of its high crystallinity, mechanical strength and high resistance to organic solvents, acids and base materials.

- Second, the process of preparation requires complex multiple steps and involves the use of chemicals, needed special instruments and was time consuming, which restricts their application. Very stable polymers are difficult to dissolve to form casting solution as no crosslinking is available. For instance, polyether ether ketone (PEEK) is stable in most organic solvents, thus sulfuric and methanesulfonic acid are used to prepare the casting solution. The acid used in the solution indicates high hazards to people working in the membrane fabrication process and environmental impact when neutralized prior to disposal. The surface modification techniques such as self-assembly monolayers (SAMs), layer-by-layer (LBL) film deposition, chemical conjugation and plasma treatment is time consuming and involved multiple deposition steps using interacting polymer and their quality highly depends on specific surface properties.
- Third, in most cases the use of these modified membranes requires high stability for long-term operation. The covalent interaction between the membrane and modifiers would make chemical grafting more desirable as compared with the physical surface coating. Moreover, few researches have concentrated on surface modifier stability during cleaning. Indeed, cleaning is a necessary process in the RO process. In practical applications, the acidified, alkaline, or other cleaning environments can result in the degradation of the modifier. Although fouling may not be completely avoided for anti-fouling RO membranes, a lot of research and development are still required in order to develop improved RO membranes for long-term and commercial use.

Table 2 Application of representative macromolecules for the modification of polymeric membranes for water treatment (Reproduced with permission from Nagandran et al. [35])

Macromolecules		Polymers	Membrane process	Applications
Dendrimers	PAMAM	PES	NF	Evaluation of antifouling properties and removal of salts (NaCl, Na_2SO_4) Model foulant: BSA
			RO	Evaluation of antifouling properties and protein adsorption Model foulant: BSA
		SPES	FO	Evaluation of ammonia-selective and anti-fouling capacities for domestic wastewater treatment
	Polyesters	CA	NF	Evaluation of antifouling properties Model foulant: BSA
	Polyethylene glycol	PA	RO	Evaluation of antifouling property and durability against chlorine; Desalination (NaCl)
QACs	[2-(Acryloyloxy)ethyl] trimethylammonium chloride solution (DAC)	PVDF	MF	Evaluation of anti-bacterial property for water/waste water treatment Model bacteria: *E. coli* or *S. aureus*
	Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammoniumchloride (DMOTPAC)			
	Dodecyl dimethyl benzyl ammonium chloride (DDBAC)			

(continued)

Table 2 (continued)

Macromolecules		Polymers	Membrane process	Applications
	Cetyl trimethyl ammonium bromide (CTAB)	PSF-SPES	UF	
	3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC)	CTA	RO	Evaluation of antibacterial properties and removal of salt (NaCl) Model bacteria: *E. coli*, *S. aureus*
Polyzwitterions	Poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PSVBP)	PA	RO	Evaluation of antifouling properties and removal of salt (NaCl) Mixture model: BSA
	Poly (sulfobetaine methacrylate) (PSBMA), poly (4-(2-Sulfoethyl)-1-(4-vinylbenzyl) pyridinium betain) (PSVBP) and poly (N-isopropyl-acrylamide) (PNIPAM)			Evaluating of antifouling and easy-cleaning properties Model foulants: BSA and $CaCO_3$
	N-aminoethyl piperazine propane sulfonate (AEPPS)	PSF	UF	Evaluation of antifouling properties and removal of salt (NaCl and Na_2SO_4) Model foulants: BSA, SA or HA
			RO	Evaluation of antifouling properties and removal of salt (NaCl) for water treatment Model foulants: TA and NaAlg

(continued)

Table 2 (continued)

Macromolecules		Polymers	Membrane process	Applications
	Catechol-functionalized zwitterionic PEG	PVDF	UF	Evaluation of antifouling property and removal of BSA for water treatment
	3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate (DMAPS)	PSF	NF	Evaluation of antifouling properties and removal of salt (NaCl/Na_2SO_4) Model foulants: BSA
	2-(Methacryloyloxy) ethyl dimethyl (3-sulfopropyl)-ammonium hydroxide	PVDF	MD	Evaluation of anti-fouling and anti-wetting of oil emulsions Model foulant: hexadecane emulsion and soy bean oil emulsion
	Poly (2-methacryloyloxyethyl phosphorylcholine) (PMPC)	PSF	UF	Evaluation of antifouling properties for oil–water separations Model foulants: soybean oil emulsion
Chitosan		SPES-PES	FO	Evaluation of antifouling properties removal of salt (Na_2SO_4) Model foulants: SA
		PVDF	MD	Evaluation of anti-fouling properties and removal of salt (NaCl)
			MF	Evaluation of anti-fouling properties for water treatment Model foulants: BSA

(continued)

Table 2 (continued)

Macromolecules		Polymers	Membrane process	Applications
			NF	Removal of inorganic salts and humic acid and evaluation of antifouling Inorganic salts: Na_2SO_4, $MgSO_4$, NaCl, $MgCl_2$, LiCl
Cellulose	Nanocrystalline cellulose	PSF	UF	Evaluation of antifouling resistance against oil molecules deposition for wastewater treatment
		PES		Evaluation of antifouling and antibacterial property for water treatment Model foulant: BSA Model bacteria: *E. coli* and *S. aureus*
		PSF	RO	Evaluation of antifouling properties and removal of salt (NaCl) Model foulant: BSA
	Cellulose nanofibers	PSF	RO	Evaluation of antifouling properties and chlorine resistance for water desalination

(continued)

Table 2 (continued)

Macromolecules	Polymers	Membrane process	Applications
Polydopamine	PSF	UF	Evaluation of antifouling properties Model foulant: BSA
			Evaluation of antifouling properties during oil/water emulsion filtration
	–	RO	Evaluation of antifouling properties and desalination Model foulant: soybean oil

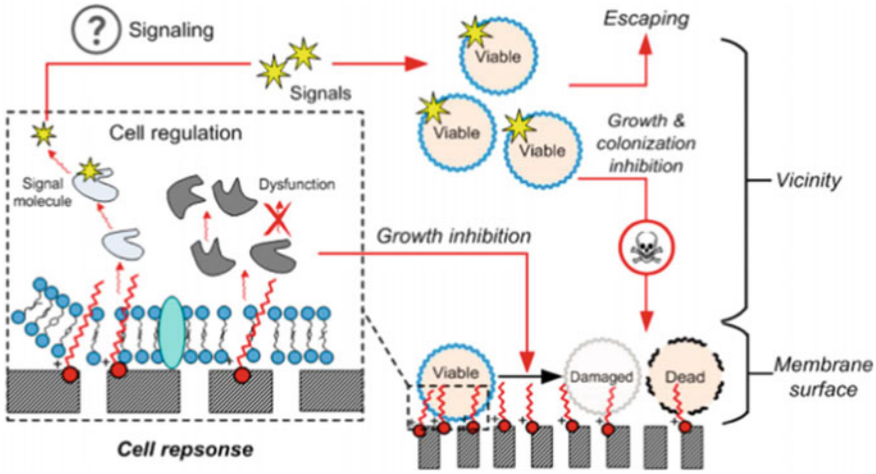

Fig. 6 Schematic representation of antibacterial behaviour at the QAC-blended membrane surface and in the vicinity. SOS response resulting from the contact with immobilized QAC is especially presented in the inset (Reproduced with permission from Zhu et al. [68])

However, direct-contact killing processes have been used restrictively as an antibiofouling strategy. In these processes, dead bacteria serve as substrates for future bacterial colonization resulting in significant membrane fouling. According to a previous study, QAC blended PVDF MF membranes demonstrated sustained antimicrobial potential near the membrane surface [62]. Schematic representation of this process has been shown in Fig. 7. Besides death of the attached bacterial cells, QAC also caused disruption of the cell wall of the dead cells which in turn triggered an SOS response through cell regulation or signalling [68]. This may be considered responsible for retardation and inhibition of biofilm growth. This process of signalling affects both bacteria attached to the membrane surface and present in vicinity. Therefore, these blended membranes offered efficient antifouling potential (as shown in Fig. 6).

6 Characterization of Membrane

Membrane surface activated in terms of charge, hydrophilicity, roughness needs to be characterized before its application. Techniques that are surface sensitive such as like AFM (Atomic Force Microscope), scanning tunnelling microscopy (STM), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), laser scanning confocal microscope (LSCS), electron spin resonance (ESR), neutron reflectivity (NR), and scanning electron microscope (SEM) etc. are widely used for the study of membrane surface modification. But each analytic technique has merits and demerits. Chemical and structural properties of membrane surface can

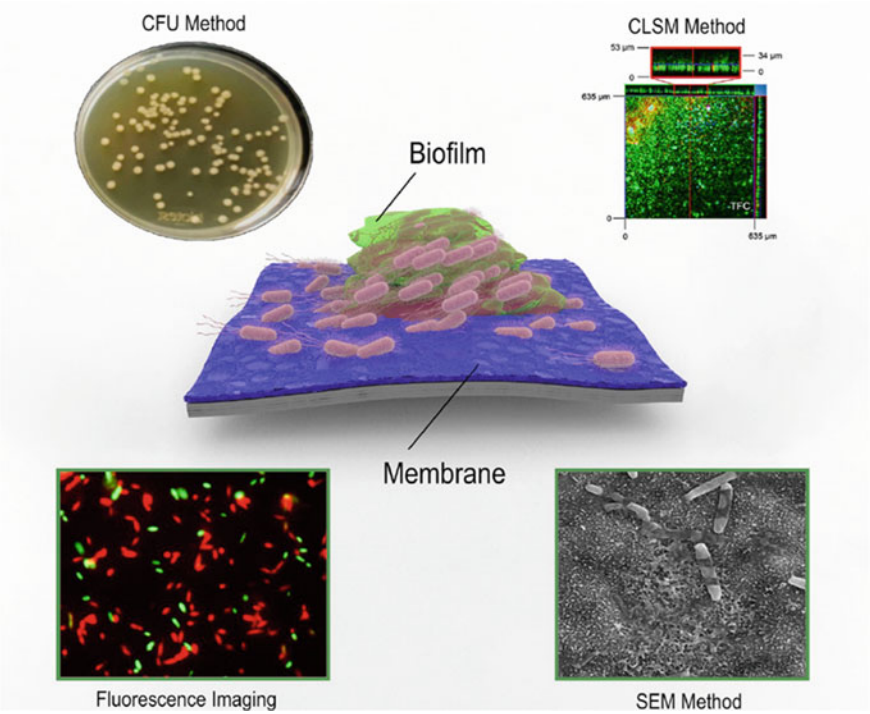

Fig. 7 Biofouling characterization methods; SEM image of *E. coli* on top side of TFC FO membrane, CFU test of TFC FO membrane, fluorescence imaging (Reproduced with permission from Firouzjaei et al. [14])

be obtained from Fourier transform infrared (FTIR) with attenuated total reflection (FTIR-ATR), XPS with energy disperse X-ray (XPS-EDX), and SIMS. Quantitative information of polymeric membranes is obtained from XPS whereas SIMS can provide qualitative information. Porosity, pore size, pore size distribution, pore nodule size can be obtained from AFM. Quick analysis of the membrane surface can be done using FTIR-ATR technique although it is not much surface sensitive. Hydrophilicity or hydrophobicity of the membrane is very important for surface modification and can be determined by contact angle measurement. Surface roughness, porosity, pore size, and pore size distribution also depend on the contact angle of the membrane. Highly porous membranes exhibit low contact angle value even if the membrane is not hydrophilic on the other hand contact angle may be higher if the surface roughness is higher even if the membrane is not hydrophilic. Pore size obtained from AFM analysis may be higher than the actual pore size as AFM measures pore size at the mouth of the funnel shaped pore [65]. Samree et al. [48] used SEM (Scanning electron microscopy) and EDS (Energy Dispersive X-ray) for investigating the membrane modified by TiO_2 NP and Ag NP respectively. Liu et al. [26] investigated membrane porosity using the dry weight method. They evaluated surface compositions of the membrane using XPS (X-ray photoelectron spectroscope). Contact angle goniometer was used for measuring the contact angle of the surface modified hydrophilic membrane. Silver coated nanotube membrane developed by Fan et al. [13] was characterized by SEM, XPS and FTIR. TGA (Thermogravimetric analysis was conducted to determine the thermal stability of the membrane whereas water contact angle was measured using optical contact angle and interface tension meter. Dadari et al. [9] characterized the fabricated nanocomposite membrane using techniques like FT-IR, XRD, zeta potential, EDS, FESEM, and TEM. The membrane was also characterized in terms of contact angle, zeta potential, and porosity analyses. Surface modification was found to be satisfactory in term of hydrophilicity, surface charge, and porosity for the membranes.

7 Characterization of Membrane Biofouling

Monitoring and characterization of biofouling helps identify growth and development of biofilms and monitor cell accruement in turn indicating efficient strategies for mitigating the same [27]. Fouling characterization also helps predict the process specific membrane efficiency. Membrane fouling is monitored and characterized by a large array of techniques ranging from simple visual detection to advanced techniques of microscopy and spectroscopy [14]. Microscopic techniques include atomic force microscopy (AFM), confocal laser scanning microscopy (CLSM), electron microscopy, epifluorescence microscopy (EFM) and light microscopy. Spectroscopic techniques include bioluminescence, fluorometry, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), photoacoustic spectroscopy (PAS), Raman spectroscopy and 3D excitation-emission matrix fluorescence spectroscopy (3DEEM). However, spectroscopic techniques have been rarely applied for biofilm characterization [57]. Hence, it is essential to apply combined microscopic and spectroscopic methods for better characterization of biofilm growth and development [14]. Common techniques for characterization of biofouling have been shown in Fig. 7. Of these methods, CLSM is most widely considered due to its ability to yield high resolution optical images, profiles of porosity-depth and percentage of dead bacteria. CLSM also allows identification of different biofilm constituents like proteins, polysaccharides and both living and dead cells. In this technique, fluorescent dyes are used to stain the membrane. Molecules of the biofilm are then excited with a laser. Fluorescence emitted by the excited molecules are transformed into photons, which in turn are converted to electron signals. These signals are then converted to 3D images with a processor [57].

Bacterial communities fouling membrane surfaces are evaluated using adenosine triphosphate (ATP) bioluminescence assay tests, study of colony-forming units (CFU method) and heterotrophic total plate count [14]. The ATP bioluminescence assay elucidates the activities of living cells and biomass but is unable to yield any information regarding dead cells. Molecular methods like clone library, fluorescence in situ hybridization (FISH) and polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) have also been used to detect and study bacterial communities [14].

8 Model Organism for Studying Antibacterial Property of Membranes

To determine antimicrobial properties of modified membrane gram negative bacteria *E. coli* was used as the model bacteria. The bacteria were grown in TSB (trypticase soy broth) and incubated at 37 °C under shaking conditions. Bacteria grown on the membrane surface were determined by observing under confocal microscope as well as using heterotrophic plate count. After centrifuging at 6000 rpm for 2 min, bacterial stock was resuspended in 1X sterile phosphate buffer saline (PBS) with a final concentration of 107 CFU/mL. For the membrane sample, a 2 cm^2 membrane surface was taken and placed in a Petridish containing bacterial cells and subjected to incubation at 37 °C under shaking conditions for 1 h. Membranes were repeatedly washed with PBS solution to remove any unattached bacterial cells and the placed in sterile plastic container containing 10 mL PBS and sonicated for 7 min to remove unattached bacterial cells. The solution thus obtained was then diluted and added to TSB agar plates under an incubation period of 24 h at 37 °C. Viable cells grown on plates were counted and represented in CFU (colony forming units) [23, 69]. Moreover, viability of bacteria grown on the membrane surface was also determined by bacterial viability kit. Viable and non-viable cells are determined by staining with SYTO 9 and propidium iodide (PI) stain. The membranes were stained and incubated in dark room for 15 min. Membrane surface was washed with PBS to remove any excess stain [56]. Number of dead and live *E. coli* cells was observed under confocal microscope equipped with laser scanning. For excitation of the SYTO 9 stain, laser for EGFP (Enhanced Green Fluorescent Protein) at 495–547 nm was used while for excitation of the PI stain laser for TRiC (T complex protein-1 complex) was used at 566–624 nm. Viable cells stained green while non-viable stained red at 60X magnification [40]. Blel et al. [7] observed the antibacterial property of the membrane surface using square plates and tubular membranes. Square plates used were: one made of alumina, one alumina plate coated with Na-mordenite and another coated with copper exchanged Na-mordenite. Tubular membranes used were: one ceramic tubular membrane, one coated with Na-mordenite and another coated with copper exchanged Na-mordenite. The bacterial cell wall structure largely determines its sensitivity towards metal ions. Gram positive bacteria are more resistant to metal ions because of their thick peptidoglycan layer than gram negative bacteria [56]. *E. coli* was used as a model gram negative bacteria and *S. aureus* as a model gram positive bacteria. Antifouling property of the tubular zeolite membrane was also analysed with *B. subtilis* spores. Zeolite membranes possess high heat resistance and standard procedures for cleaning During the filtration experiments the concentration of *E. coli* was kept constant and the sample of solution was taken and the next day bacterial detection was performed before staring the fresh batch of experiments. Membrane surface modified by Cu-mortenite was inoculated with bacterial cells at 106 CFU/mL and covered with plastic film followed by washing with 10 mL soybean casein digest lecithin polysorbate medium. Number of viable bacterial cells was counted. When plates were subjected to two different bacterial strains, epifluorescence microscopy was used for determining viable and non-viable cells via thw staining method. Experiments were conducted under dynamic flow conditions. Confocal microscope was used for counting bacterial cells and biofilm thickness [7, 56].

E. coli was used as a model strain to measure the quantity of surviving bacteria to understand the real picture of bacterial growth on the membrane surface. Membrane surfaces were taken in cuvettes containing bacterial suspension and incubated at 37 °C for 24 h. They were washed with 20 mL of 0.9 wt% NaCl. The washed suspension was diluted to suitable dilutions and cultured on Luria-Bertini (LB) media and incubated 37 °C for 24 h. Bacterial colonies on the unmodified and hybrid membrane surface was observed. The saline washed membrane suspension was also subjected to staining with 0.1% acridine orange and Propidium iodide and observed under fluorescence microscope. Viable cells appeared green or yellow-green and non-viable cells appeared red. Number of viable cells thus obtained on the membrane was represented as the colony forming unit (CFU/mL). To determine biofilm inhibition by the modified membrane, biofilm inhibition test was performed. Membranes were subjected to *E. coli* growth on the surface in a similar way as that of antibacterial test but incubation time was increased from 24 to 72 h for biofilm formation. Surface attached cells on the membranes were removed by washing with DI water and membranes were then dried in oven (60 °C for 1 h) followed by air drying. Biofilm thickness was obtained from initial and final weight of membranes [18, 48]. Antibacterial activities of hollow fibre membranes were determined by using *E. coli* cultured in Luria–Bertani media and incubating at 37 °C for 24 h and shaking at 100 rpm. Halo zone and flash shaking method were used to determine the antibacterial activity. In the halo zone method, 100 μL of bacterial culture was spread on LB media and placed on hollow fibre membranes. Halo developed around the membrane after the incubation period was over determined the antibacterial activity. Sterilized membranes pre-soaked in PBS solution were immersed in 100 mL of *E. coli* suspension and shaken at 100 rpm for 24 h. Flat colony counter was used to count viable cells. SEM was also used to observe bacterial adhesion on hollow fibre membrane [13]. Dadari et al. [9] observed antibacterial property against *S. aureus* and *E. coli* of modified nanocomposite membranes using colony counting method. Surface sterilized membrane pieces were soaked in bacterial suspension and incubated at 37 °C at 120 rpm for 12 h. The suspension thus obtained was diluted and spread on LB agar plates and incubated at 37 °C for 24 h and the antibacterial rate was determined from viable bacterial colonies.

9 Evaluation of Antifouling Property

To evaluate organic and biofouling properties of the membrane, dynamic fouling experiments were performed. To determine organic fouling, sodium alginate was selected as the model foulant. 250 mg/L of alginate powder was mixed in DI water and used as the feed solution [40]. 3 L of feed was used and operated for 24 h at crossflow velocity of 8.5 cm/s. Permeate flux was monitored using electronic balance. Clean membrane flux was taken to assess loss of flux due to fouling. To assess biofouling, *E. coli* was added to feed the solution at 107 CFU/L under similar filtration conditions. Biofouling activity of TFN membranes were evaluated by storing membranes in a water container for 24 days and 6 months. Antibacterial property of the membranes after 24 h indicated slight presence of live bacteria attached to the membrane surface. After 6 months there was no change in bactericidal activity indicating stable antibacterial activity of MOF crystals that imparts to TNF membranes. The authors concluded the presence of organic ligands and silver sites in the frameworks for its biocidal activity. The organic ligand binds to cations in bacterial cells and causes DNA fragmentation causing cytoplasm outflow and ultimate death [60]. Graphene oxide is used as the filler for modification of membrane surface having antibiofouling properties. Addition of GO increases surface hydrophilicity, negative charge and decreases surface roughness factors that contributes to biofouling. Activated sludge was used to test the antibiofouling properties of GO membrane having mixed bacterial environment. Although initial flux for the GO membrane was lower than the unmodified polysulphone membrane, gradual flux decline was lower in case of the GO membrane. Since GO membranes impart negative charge and bacterial cells also have negative surface charge thus causing repulsion and less attachment on the membrane surface contributing anti biofouling properties [31]. Dynamic biofouling tests were also performed by Ren et al. [46] to observe biofilm growth on water permeability of the membranes developed from in-situ photo-grafting bactericidal and hydrophilic polymers. Surface sterilized membranes were run for experiments using DI water at 6.0 bar pressure in a crossflow system keeping initial permeate flux steady at 25 $L/m^2/h^1$. Dilute LB nutrient solution was used as a feed in the membrane study having quality lower than that of reclaimed water. Bacterial suspension of CFU mL^{-1} was taken for membrane adhesion and incubated at 37 °C for 5 h. Any unattached bacteria were washed with saline solution and the membrane was housed in a module. Permeate flux of the feed nutrient solution and water permeability of the cleaned membrane were noted in a cyclic manner. The biofilm thus formed was stained with BBcellProbe and determined using confocal laser scanning microscopy. They concluded that the surface modified membranes were capable of having antibiofouling property [46].

10 Conclusions

Membrane biofouling is one of the limitations that hampers membrane performance. Traditional methods for membrane surface modifications with material having antifouling properties though have high water permeance can also have a negative effect on long term usage. The reason might be due to the basic deficit in understanding of structural association between the coating materials and performance of the membranes. Many works have been done in reducing membrane fouling. Contact angle is used for measuring surface hydrophilicity of the membranes as more the surface is hydrophilic less will be fouling. On the other hand, surface roughness and membrane pore size affect contact angle measurement. Therefore, the main drawback of surface modification lies in its characterization as no single method exists to determine surface hydrophilicity as a unique property of the membrane chemistry.

Membrane surface having higher hydrophobicity may show antifouling behaviour suggesting other surface chemistry that governs antifouling apart from hydrophilicity. But estimation of surface charge of the membrane is more recognized than surface hydrophilicity and surface roughness. Materialization of AFM for determination of surface roughness at the nanoscale level led to understand the relation between surface smoothness and antifouling behaviour i.e. fouling increases with surface roughness. Though this relation holds good for RO and NF membranes but is yet to understand for other range of membranes, it is also observed that surface roughness enhances permeate flux due to an increase in effective surface area. Change in one parameter causes simultaneous change in other related parameters.

Immobilizing biomacromolecules is a recent attempt to reduce biofouling. Biomimetic surface is an effective means to reduce biofouling. But biomimetic membranes find limited applications in various fields. Formation of a thin film-layer for fabricating TFC RO membrane also finds application due to its antifouling properties. Modifying membranes with metal oxide nanoparticles having antibacterial properties are also proposed. The modified membranes show better mechanical strength, high water flux, more hydrophilicity, porosity and better rejection apart from having antifouling properties. Functionalization of membranes with Ag-MOFs and zwitterions having the highest antifouling capacity, high flux, biocidal activity and permselectivity as compared to naive membranes. Green synthesized nanoparticles used as fillers show antibacterial properties as well as removal of heavy metals. Membrane modifications indeed reduce fouling but to a certain extent and only when the solution is dilute or in the initial stage of the experiment. Once deposition stars to form, fouling may or may not occur as the effect of the solute and membrane interaction gets hampered due to deposition. Though no modified membranes are alone capable of reducing fouling, other factors like periodic membrane cleaning, membrane housing design, devices to reduce foulant deposition can effectively reduce biofouling.

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Chapter 11
Life Cycle Analysis of Polymeric Membrane-Based Processes

Priya Banerjee

1 Introduction

Membranes are semipermeable structures guiding controlled transport of moieties between adjacent phases. As evident from recent research, membranes play a significant role in several advanced processes of separation. Most recent applications of membrane include catalysis [51, 56], energy storage [46], production of green and blue energy [21, 52, 57], membrane bioreactors [5, 27] and processes of molecular separation [such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)] [2, 19]. Membrane based processes have also been widely applied in biological and medical applications like cell culture, dialysis, and drug release [54]. Rapid advancements recorded in the fields of membrane-based processes are attributed to the simple and flexible procedures, energy efficiency, convenient control and scale-up, and environmentally benign nature of the same [15]. Different application necessitates different membrane properties as evident from Table 1.

Membranes reported in recent studies have been mostly prepared from inorganic and organic materials or their composites. These membranes are available in varied configurations like hollow fibres and flat sheets. Of different types of membranes, polymeric ones have received significant attention due to their convenient processes of synthesis, cost effectiveness and small environmental footprint [54]. Polymeric membranes have been reportedly synthesized via different processes like phase inversion, sintering, stretching and track-etching. Of these methods, phase inversion has been most widely investigated for both academic and commercial purposes [22]. Polymeric membranes are produced commercially via solvent or thermal induced phase inversion [31]. Nevertheless, majority of the solvents used for this purpose are

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Table 1 State-of-the-art industrial membrane applications with respective membrane barrier type and separation mechanism, as well as important membrane materials and configurations (Reproduced with permission from Nunes et al. [36])

Application	Barrier type (pore size*)	Separation mechanism	Main materials**	Preferred configuration***
Haemodialysis^{+}	UF	Size exclusion	PSU	HF
Seawater desalination^{++}	RO	Size exclusion (solution-diffusion)	PA/PSU, CA	FS (spiral wound) HF
Brackish water desalination	RO	Size exclusion (solution-diffusion)	PA/PSU, CA	FS
	Dense charged	Ion exchange	Ion exchange polymers	FS
Microelectronics (ultra-pure water)	Dense charged + mixed ion exchange resin	Ion exchange and adsorption	Ion-exchange polymers + mixed anion and cation exchange resin	FS
Water treatment, removal of: colloids, bacteria, viruses, silica, colour, micro-pollutants	MF, UF	Size exclusion	PES, PVDF	FS, HF, tubular
	NF		PA/PSU	FS
Sterile filtration	MF, UF	Size exclusion	PSU, PVDF, PTFE, PP	FS
Food and beverage processing	MF, UF, NF	Mostly size exclusion	PSU, PES, PVDF	FS, HF, tubular
	Dense charged	Ion exchange	Ion exchange polymers	FS
Chloro-alkali electrolysis	Dense charged	Ion exchange, donnan exclusion	Nafion®	FS
Gas separation	Dense selective layer	Solution diffusion	CA, PSU, PDMS	FS (spiral wound, plate and frame), HF
Water electrolysis	Dense charged	Ion exchange, donnan exclusion	Nafion®	FS
Fuel cell	Dense charged	Ion exchange, donnan exclusion	Nafion®	FS
Battery	Porous, optionally filled with electrolyte	–	PP, PE, PTFE, ceramics	FS
Biotech down-stream process	MF, UF, NF	Mostly size exclusion	PSU, PVDF	FS

(continued)

Table 1 (continued)

Application	Barrier type (pore size*)	Separation mechanism	Main materials**	Preferred configuration***
Biomedical diagnostics⁺	Mostly porous	Often only used as scaffold and for capillary flow of analyte	Cellulose derivatives	FS
Biomedical therapy	Mostly porous	Toxin removal, drug delivery and others	PSU	FS, HF

* Pore sizes: MF: >100 nm; UF: 2–100 nm; NF: 1–2 nm; RO: <1 nm

** Polysulfone (PSU), polyethersulfone (PES), polypropylene (PP), polyethylene (PE), poly(vinylidene difluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), cellulose acetate (CA), polyamide (PA), polydimethylsiloxane (PDMS), ion-exchange polymers are typically quaternary ammonium or sulfonic acid functionalized

*** FS: flat-sheet; HF: hollow fibre

⁺ Typically single use

⁺⁺ Typical duration of continuous use >5 years

extremely toxic. Therefore, industrial use of the same are strictly regulated. Every year, more than 50 billion litres of polluted water discharged into the environment is produced as a by-product of membrane synthesis [43]. Approximately 70% of this wastewater is discharged without treatment or diluted with excess water to reduce solvent concentrations below legally mandated discharge levels [43].

Recent research has focussed on the use of *green solvents* for membrane synthesis. Green solvents are environmentally benign solvents, or those derived from biological sources (biosolvents). Few examples of green solvents include Cyrene™ [33], Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv® PolarClean) [20], O-acetyl citrate [54], tributyl triethylene glycol diacetate (TEGDA) [10] and organic carbonates [42]. However, it is also important to ensure that synthesis procedures of these green solvents do not exert any detrimental impact on the environment. Else, the effort invested for developing a sustainable membrane synthesis process using this solvent is rendered redundant.

The parent materials selected for polymer synthesis are of equal concern. Though natural polymers have been gaining attention in recent research, fossil-fuel derived polymers have been widely applied in industrial-scale polymer-based processes, owing to their chemical, mechanical and thermal stability [54]. Effect of complete substitution of fossil-fuel derived polymers by biopolymers on sustainability of such processes is yet to be determined.

Ensuring sustainability of polymeric membrane-based processes necessitates quantitative evaluation of the impact exerted by the same on different concerns like global warming, carcinogenic and non-carcinogenic toxicity in humans, aquatic ecotoxicity, etc. To elucidate the same, life cycle assessment (LCA) has emerged as a primary framework for quantitative determination of environmental impacts exerted by manufacturing processes and resultant products [54]. This approach may be used to understand manufacturing processes including several interacting components and their potential impact on the environment.

2 Improving Membrane Stability

Membrane technology has been established as a competitive process in fields of water treatment and desalination. Nevertheless, this process is faced with both opportunities and challenges in petrochemical, chemical or any other sector where intensification of processes may exert a large impact in terms of economics, energy and environment [36]. Unavailability of membranes having high solvent and thermal stability has limited application of the same in the aforementioned sectors. Development of membranes with improved stability over the next decade is expected to increase the applicability of the same over various sectors [14, 23].

Membranes prepared using cellulose have been widely used for NF of different types of organic solvents [16, 26]. Other polymers used for preparing solvent resistant membranes include poly(arylene sulfide sulfone) (PASS; [7, 39, 40]), polybenzimidazole (PBI, [17]), poly(ether ether ketone)s (PEEK; [11]), poly(oxindolebiphenylylene) (POXI) and polytriazoles (PTA) [36]. Solubility of the highly stable polymers poses a challenge before this field. For example, PEEK dissolves only in strong acids, which are extremely corrosive and inconvenient to handle in a manufacturing environment. Functionalization of these polymers reportedly renders the same solvent resistant [4]. Chemical structures of different solvents and polymers investigated for improving membrane stability have been depicted in Fig. 1.

Crosslinking of polymers also reportedly enhance thermal and solvent stability of membranes [36]. Thermal rearrangement [24] and chemical or thermal crosslinking reportedly facilitates insolubilization of polymers [40]. Besides chemical and thermal resistance, real time application of membranes requires incorporation of the same

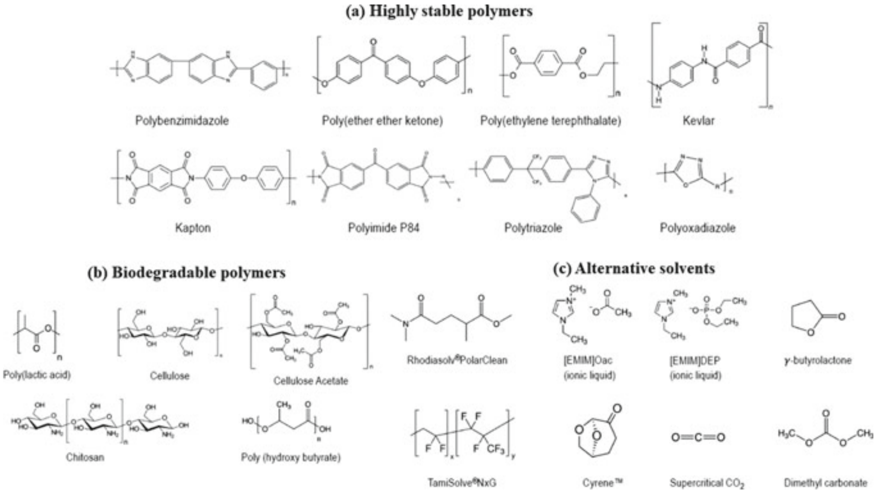

Fig. 1 Chemical structures of polymers and alternative solvents considered for enhancing membrane stability (Reproduced with permission from Nunes et al. [36])

within a module. Therefore, the module needs to demonstrate resistance similar to the membranes.

Besides stability and resistance, achievement of strictly controlled selectivity and acceptable permeation of membranes also pose a challenge before wide scale implementation of membrane-based processes. Processes of grafting and interfacial polymerization are being investigated for membrane supports [23, 49]. Carbonaceous molecular sieves prepared from polymers also demonstrate simultaneous thermal and solvent resistance [25]. Such innovations will enhance applicability of membranes beyond those in practice.

3 Utilization of Renewable Polymers

Over the last 50 years, membranes prepared from polyethersulfone (PES), polysulfone (PS) and polyvinylidene fluoride (PVDF) have been used in various applications. Nevertheless, the concern over environmental impacts of plastic wastes have strongly inspired the concept of recycling. In membrane-based processes, use of biopolymers or recycled polymers may enhance recyclability of membranes. Commercially available renewable and/or biodegradable polymers include poly(hydroxy butyrate)s (PHBs) and poly(lactic acid) (PLA) [36]. Techniques of copolymerization and functionalization of renewable polymers reported in recent studies have been found to alter properties and morphologies of these polymers. In previous studies, copolymers containing distinct polylactide [36] and polypeptide [47] blocks have been used in membrane synthesis. Recent studies have also reported successful interfacial polymerization of renewable building blocks like catechin [1], cyclodextrin [48], and tannic acid [36].

4 Consideration of Alternative Solvents

Membrane synthesis is presently dependant on the use of dipolar organic solvents like dimethylacetamide, dimethylformamide and N-methylpyrrolidone. However, these solvents are banned from usage on a commercial scale due to their toxic effects. So far, the membrane industry has been postponing changes in its procedures. However, stricter environmental regulations will make the use of alternative solvents imperative. The first step would be to opt for non-toxic organic solvents like dimethylsulfoxide (DMSO). According to Alexowsky et al. [3], PVDF MF membranes synthesized via non-solvent vapor induced phase separation (VIPS) demonstrate tunable porosity. Moreover, this process was reported to be fast and scalable. PVDF/DMSO-based membranes prepared via phase separation induced by solvent freezing demonstrated more efficient separation performance in comparison to PVDF membranes fabricated via conventional NIPS processes [50]. Other sustainable solvents include emerging commercial synthetic organic solvents (like methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate) [13, 32], dipolar aprotic TamiSolveÒ [31], ionic liquids [24], plant-based solvents [44] and supercritical CO_2 [36]. Processes based on supercritical CO_2 require equipment specifically used for melt extrusion having extremely accurate pressure control [36]. However, other solvents may readily substitute those presently used in processes of membrane synthesis. Alternative solvents also reportedly enhance membrane porosity and performances [24]. In a recent study, Baig et al. [6] reported the use of water as a solvent and non-solvent in the process of membrane synthesis via phase inversion. In this study, authors efficiently synthesized membranes ranging from MF to NF that demonstrated efficient separation properties. A recent study has also reported synthesis of membranes from recycled polymer (polyethylene terephthalate) having multiple applicabilities [41].

5 Reuse of Membrane Modules

Membrane technologies are widely acclaimed as sustainable separation processes having low energy requirement and low CO_2 footprint. This process is also capable of retrieving valuable resources from wastewater for subsequent conversion to value-added products. However, little attention has been paid to its end-of-life management in terms of disposal, reuse or recycling of membranes and the impact of the waste on the environment. Lifetime of a membrane depends on its application. For example, reverse osmosis (RO)-based membrane elements have a longevity of 3–7 years, beyond which they are disposed in landfills [9]. On the other hand, MF and UF membranes have a life span of 7–10 years. Every year, almost 840,000 membrane elements (accounting for >14,000 tons) are discarded globally and the quantity is growing by the day [36]. Concepts of reuse and recycling incorporated in membrane design helps in reducing environmental impact and cost of these products. Retaining maximum value even after the exhaustion of the product also helps establish a circular economy for these processes. Ideally, in order to be reused or recycled, these membranes should be designed and fabricated with highest possible quality in terms of most efficient performance, minimum aging, antifouling or swelling. Repair or maintenance should be as durable as possible in turn delaying the need for replacement. Life of membranes may be extended by operating the same under mild conditions and optimum transmembrane pressures. Proper monitoring may predict or prevent membrane failure and reduce unnecessary waste or cost.

Research reported over the last decade have investigated methods to reuse or refurbish membrane elements. Regular monitoring of membrane elements includes inspection of brine seal integrity, external damage and fouling, and feed spacers. Data obtained under optimum working conditions are compared with the original data provided by the manufacturers. On the basis of this comparison, it will be decided whether the membrane module will be cleaned, reused or refurbished. For example, RO membranes are refurbished by treating the same with NaOCl solutions.

This treatment results in the removal of the polyamide layer of RO membrane in turn transforming the same to MF, UF or NF membrane [12]. According to de Paula et al. [12], use of such a refurbished RO membrane instead of a new one reduced the cost incurred by 98.9% and prevented production of waste (>2600 kg). If refurbishment is not a feasible option, membranes may be dismantled. They may be removed from their casing and recycled or remanufactured for a different application [37]. Another option is upgradation of the membrane separation performance. This has reportedly been achieved with a "layer-by-layer" fabrication of NF membranes using UF supports [36].

6 Achieving Enhanced Separation Efficiency

Besides permeability and selectivity trade-off, attempts to enhance separation efficiency of membranes should also consider improvements in membrane composition and methods of fabrication. The barrier layer of the membrane should consist of well-defined channels of identical properties and dimensions within a robust matrix that renders stability to the membrane. On the other hand, this layer should be as slim as possible to pose the least resistance it can offer. Materials used for preparation of a membrane are referred to as "building blocks". These building blocks are usually of a specific chemical composition and morphology and possess the ability to give rise to well-defined arrangements consisting of identical or complementary moieties. Arrangement of building blocks are mostly guided by intrinsic properties of the same and rarely by external forces. Building blocks may also be self-assembled in a "bottom-up" approach from individual blocks to large ordered aggregates on the basis of multiple non-covalent bonds or micro-phase separation processes. Solutions or dispersion of these building blocks are similar to membrane preparation processes like film casting or coating. Three different approaches in practice for self-assembly of building blocks are enlisted as follows [36]:

- Fibres (1D), sheets (2D) or particles (3D) having well-defined morphology, dimensions and functional groups interconnect to form a membrane barrier whose interstitial space serves as a porous sieving medium;
- Microphase-segregated non-porous films;
- Liquid-crystalline super-structures containing well-defined pores (Angstrom-scale) either form a membrane directly (as film) or require alignment or fixation prior to serving as one.

7 Circular Economy and Integration Solutions

Aspects of linear economy associated with application of membrane-based processes for wastewater treatment and desalination includes disposal of the following:

- materials (used throughout the process) after the end of their life;
- wastes generated at different steps of the process (including brine, spent cooling water, waste heat, waste sludge, etc.).

Concept of circular economy focuses on using these wastes as resources and reusing these resources for ensuring maximum utilization of resources and minimum generation of wastes [55]. So far, incineration or membrane disposal in landfills have been the most convenient choices for end-of-life management of the same. Every year, more than 8,40,000 end-of-life membranes are disposed by either process [35]. Hence, it is necessary to incorporate strategies of waste reduction in future directions of circular economy guiding membrane-based desalination technologies. Though reuse or refurbishment of membranes have gained importance as viable approaches, they are still faced by certain challenges requiring addressal. Biofouling is one such challenge hindering membrane reuse. The polyamide layer of fouled membranes may be removed by treatment with oxidizing agents (such as $KMnO_4$ or NaOCl). This treatment reportedly transformed RO membranes to UF/NF membranes [28, 34]. This solution reportedly offers great social benefits [45]. Nevertheless, this is not applicable for all membrane types. Success rate of this process of transformation is dependent upon the nature of the polymer layer present in the membrane [55]. Sustainable membrane industry transformation strategies from manufacturing to end-of-life management have been shown in Fig. 2a, b.

8 End-of-Life Management of Spent Membrane Modules

Though a huge amount of waste is generated annually from the membrane-based processes, little attention has been paid to determination of its impact on environment or end-of-life management of membrane modules. Different aspects of membrane waste disposal and management have been shown in Fig. 3a–d. The waste management strategy preferences of the European Directive 2008/98/EC (shown in Fig. 3a) depict the priorities and most sustainable strategies for spent membrane module management. Resource depletion and CO_2 emissions corresponding to each strategy have been shown in Fig. 3b.

8.1 Waste Reduction

The foremost priority is the reduction of quantity of membrane elements wasted. Several methods may be undertaken for the same. Firstly, the membrane should be developed using high-performance polymers having suitable mechanical, antifouling, anti-aging and anti-swelling properties. These properties ensure a long

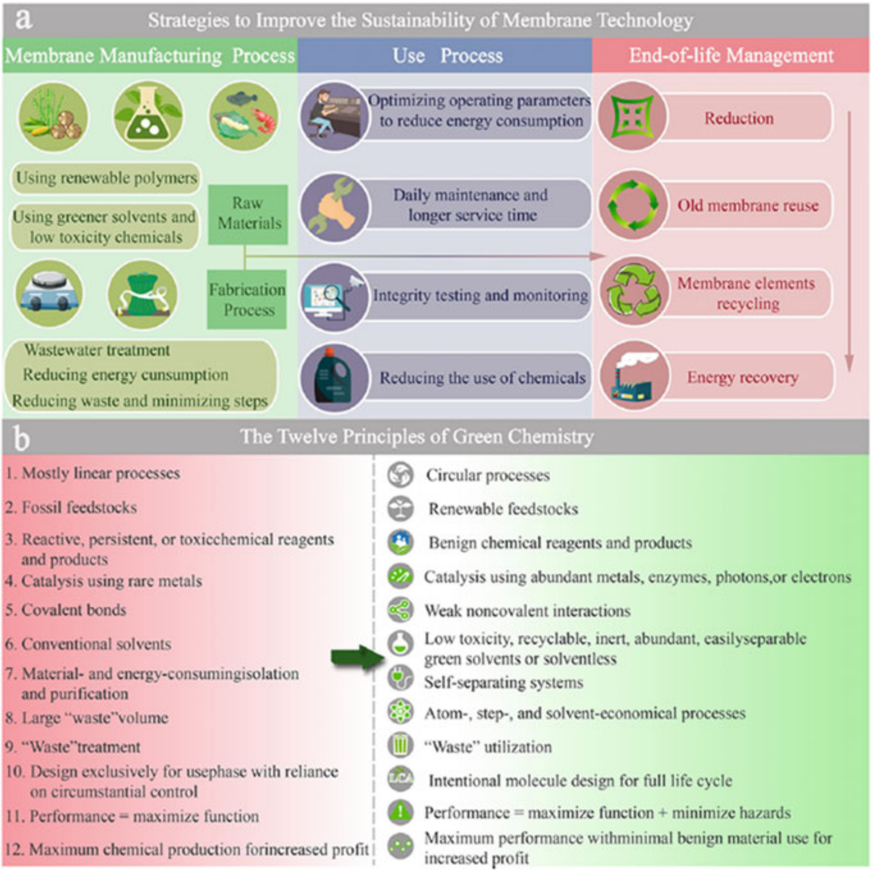

Fig. 2 Sustainable membrane industry transformation strategies from manufacturing to end-of-life management: **a** strategies to improve the sustainability of membrane technology, and **b** characteristics of today's and tomorrow's chemical sectors (Reproduced with permission from Xie et al. [53] Copyright © 2021, American Chemical Society)

life span for the resultant membranes. Secondly, optimization of operational parameters is equally important. Application of membranes under mild experimental conditions and low transmembrane pressure have reportedly extended membrane longevity. Maintenance on a regular basis is also important for determining damaged fibres and their timely repair. Thirdly, biopolymers may be considered as alternatives to petroleum-based ones in processes of membrane synthesis. These polymers are biodegradable and therefore reduce the final volume of solid waste produced [53].

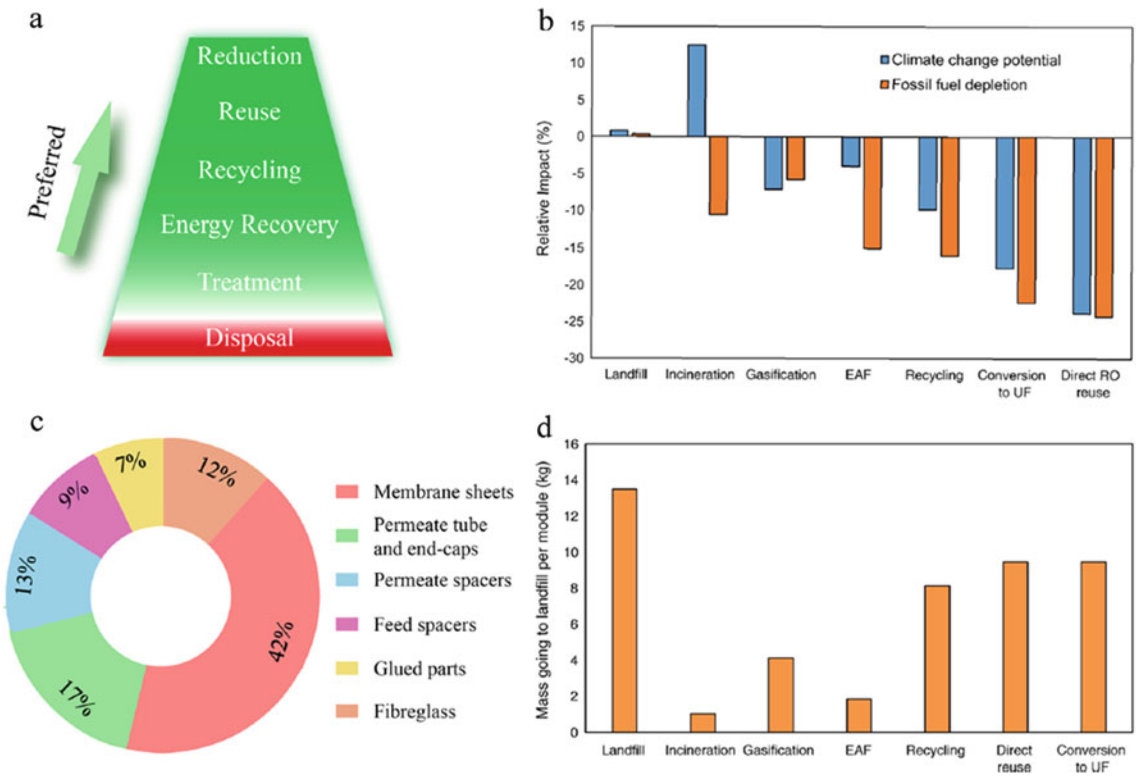

Fig. 3 **a** Waste management hierarchy from most to least preferred options. **b** Greenhouse gas emissions and resource depletion for the disposal of one RO membrane element. **c** Composition of a typical RO membrane element. **d** Mass of waste material requiring landfill disposal for each end-of-life scenarios for one RO membrane (Reproduced with permission from Xie et al. [53] Copyright © 2021, American Chemical Society)

8.2 Reuse of Spent Membranes

Amount of membrane elements wasted may be reduced by reusing the same directly in a lower throughput system. Though these membranes no longer fulfil initial selectivity criteria, they can still yield a high rejection rate (>96%) and therefore be applied for pre-treatment of seawater or selective demineralization of brackish water [53]. Of all strategies employed, membrane reuse entails lowest CO_2 emissions and depletion of fossil-fuel (as evident from Fig. 3b).

8.3 Membrane Recycling

Membrane recycling maybe of direct or indirect type. Direct recycling includes conversion of one type into another type having a lower throughput system. RO membranes have been reportedly converted to NF or UF ones [18, 28]. These converted membranes were successfully applied for pre-treatment carried out prior to advanced wastewater treatment, freshwater production in rural areas and desalination [12].

On the other hand, indirect recycling of membranes involves mechanical and chemical recycling of all plastic components present in membrane elements. Besides PA, PSU and polyesters present in membranes, this also includes PP used in feed spacer, polyester present in permeate spacer, acrylonitrile butadiene styrene used for making permeate tube and end-caps, fibreglass used in outer casing and glued parts made of proprietary epoxy-like materials (as shown in Fig. 3c). All these materials may be extracted and recycled using various methods of mechanical and chemical recycling [8].

Badly fouled membranes may be indirectly reused as supports for recycled anion-exchange membranes. A recent study reported two routes for reuse of fouled membranes, enlisted as follows [30]:

- extraction of polypropylene components for assembly of electrodialysis stacks,
- use as supports in synthesis of anion-exchange membranes.

The anion-exchange membranes so prepared exhibited permselectivity similar to those of commercially available anion-exchange membranes (87%). Moreover, the electrodialysis stacks prepared from fouled membranes demonstrated 84.5% salt rejection.

In approaches to circular economy, recycling is less preferred to reuse as membrane recycling involves further consumption of materials and energy. Nevertheless, recycling is more in keeping with the concept of circular economy than incineration or landfill. Moreover, improvement of membrane antifouling properties also extends membrane lifespan and in turn ensures reduction in both membrane replacement rate and waste generation. Materials used in synthesis of RO membranes, end-of- life options and treatment techniques for reuse of the same have been enlisted in Table 2.

Table 2 Summary of end-of-life options of RO membranes as a case for circular economy (Reproduced with permission from [55])

Membrane type	End-of-life option	Treatment type
Polyamide-polysulfone	Reuse as geotextile in home gardens	N/A
Used RO membranes	Direct reuse as UF and MF filters	Peeling off active separation layer with $KMnO_4$
Polyamide-polysulfone	Reuse as RO pre-treatment membranes and for effluent treatment	Peeling off active separation layer with $KMnO_4$
Used and discarded TM720-400 membranes	Direct reuse as UF and MF filters	Peeling off active separation layer with NaOCl
Used and discarded FILM-TEC BW30-2540	Direct use as nano-filters and recycling via extraction of membrane components	Treated with NaOH, KMnO4 and NaOCl
Thin-film composite LFC-1 membrane	Direct reuse as RO membranes	Treated with NaOH, Na_2-EDTA, SDS and NaCl

8.4 Energy Recovery

In a situation where reuse and recycling of membranes are unable to reduce membrane wastes, energy recovery is considered as a suitable solution for yielding heat energy for generation of electricity or execution of other heat-driven processes [38]. Energy recovery may be carried out through electric arc furnace (EAF), incineration or production of syngas. However, as there is a dearth of selectivity, gas streams may contain considerable quantities of pollutants in terms of CO_2 emissions, dioxins and fly ash. The process of gasification offers greater environmental benefits in comparison to incineration, owing to electricity produced as a result of combustion of syngas produced [38]. Another process of energy recovery includes use of membrane components as a source of carbon in EAFs for steelmaking in order to minimize the consumption of metallurgical coke [29].

8.5 Waste Materials Requiring Landfill

Membrane wastes contain components that cannot be treated (like fibreglass in EAF). It also includes residual wastes produced as a by-product of different treatment processes, waste recovery or recycling (such as slag produced from the gasification and incineration of wastes). These components are ultimately sent to landfills. The mass of waste generated by each end-of-life strategy has been shown in Fig. 3d. Though reuse and recycling of membranes yield prominent environmental benefits, they still give rise to a large volume of waste which necessitates disposal. If the primary priority is to avoid disposal of wastes to landfill, incineration or incineration post membrane reuse/recycling is considered as the best option [55].

9 Challenges and Outlook

It is necessary to implement end-of-life membrane management for ensuring the conversion of a traditional linear process to a circular one. Of all strategies in practice, landfill reportedly exerts the worst impact on the environment. Nevertheless, in terms of mass of waste being generated, incineration produces the least, while membrane reuse is considered second largest after direct landfill. Hence, for arriving at the best scheme for end-of-life membrane management, the selected strategy must consider both the present situation and the final requirement. The best scheme is expected to yield both environmental benefits and economic gains. For identifying the optimal scheme, LCA is used to compare different processes quantitatively. However, most of the studies reported so far have focused only on RO membranes. Faced with the continuous increase in discarded membrane elements, recent research should emphasize on end-of life management of different types of membranes and promote reuse of the spent modules. This will greatly enhance the sustainability of the membrane industry.

10 Conclusion

As evident from recent research, future of the membrane industry is dependent upon process and material innovation, scalability, sustainability, stability of synthesized membranes, feasibility of producing fast models and iterative work with risk-taking visionary industries. However, the membrane technology is faced with several challenges on different levels and sectors. These challenges may be overcome by using materials, solvents and processes that are non-toxic and environmentally benign in nature. A shift towards circular economy may render membrane-based processes sustainable by minimizing both consumption of resources and production of waste. Detailed research is required to identify the best strategy for end-of-life management of membranes used in different applications. This may also include combined implementation of multiple end-of-life management strategies like incineration, reuse, recycling or refurbishment of all types of membranes in use.

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