CHAPTER

3

Recent Progresses of Ultrafiltration (UF) Membranes and Processes in Water Treatment

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OUTLINE

3.1 INTRODUCTION

Ultrafiltration (UF) refers to the filtrated separation of particles in the colloid-size range [1–5]. In the UF process, the transfer of the dispersed phase ("solute" in its most general sense) through the membrane pores is much less than the "solvent" for one of several reasons [6–9]:

A. Due to adsorption (primary adsorption).
B. Due to size exclusion (sieving).
C. Due to deposition on the surface (cake formation).

By using a membrane surface, UF can separate dissolved macromolecules and tiny suspended particles from a fluid feed with the range of pore size between 1 and 100 nm, which means that UF is between microfiltration (MF) and nanofiltration (NF) [10–12].

The UF membranes can concentrate the large components of the feed fluid on one side of the membrane, as the microsolutes and the solvent are depleted as they can move through the membrane [8, 12, 13]. The UF membrane acts as a selective barrier retaining molecules with molecular weights higher than a few thousand of Dalton (macrosolute), while molecules with the small sizes (solvent and microsolutes) move freely through the membrane pores. The UF membrane is often rated, somewhat randomly, by the molecular weight cut off (MWCO), that is, UF membranes have a molecular weight cut off (MWCO) between 1000 and 1,000,000 [9, 12, 14, 15].

Compared to a reverse osmosis (RO) membrane, a UF membrane is used with lower operating pressure to retain larger solutes. The range of 1–10 bars is the typical operating pressure for UF. Generally, UF membranes are classified as an asymmetric membrane with a porous sublayer and a thin top layer, which governs the UF separation performance. A UF membrane is often operated in a tangential flow mode where the feed stream sweeps tangentially across the upstream surface of membranes

as filtration occurs, thereby maximizing flux rates and membrane life [16, 17]. Some of the UF membrane properties are pore size, pore size distribution, surface pore size, rejection, flux, percentage of porosity, solvent resistance, temperature stability, flux decline and pressure resistance. Retentivity is critical, and the skin plays a principal role in the UF membrane performance. The internal pore blockage should be prevented to maintain and provide a high flux rate [18–21].

UF is a pressure-driven membrane transport process that has been applied in a small laboratory scale as well as in a large industrial scale. The interest has grown in recent years to use UF for the separation of dissolved molecules of different sizes and properties. Depending on their pore size, UF technology is applied for essential separation processes such as filtration of colloidal suspensions, treatment of product streams in the food and beverage industry, recovery of useful material from coating or dyeing baths in the automobile and textile industries and treatment of industrial wastewaters, also in medical, biotechnological industries, paper industry, and the dairy industry [22–25].

3.2 RECENT PROGRESSES IN UF MEMBRANE DEVELOPMENT

The membrane separation process is known to be useful for the desalination of seawater and brackish water, wastewater treatment, removal of toxic substances from drinking water, and production of ultra-pure water for the semiconductor industry. UF, NF, and RO filtration have been successfully applied for the removal of colloidal particles, turbidity, dissolved organic matter (DOM), and microorganisms. This advanced technology can produce water quality better than the current regulatory requirements and therefore can replace conventional clarification and filtration methods [26–28].

Asymmetric polymeric UF membranes have to satisfy strict operating parameters requirements such as solvent resistance, pH resistance, chemical resistance, thermal and mechanical stability; also high selectivity, flux, high durability (most extended possible life) and low cost of material on the market today [29–31]. Recently, five different polymeric membranes, including two MF and three polyacrylonitrile UF membranes, were compared for the treatment of industrial wastewater. MF membranes showed higher permeability and less rejection while UF membranes optimal results [28, 32].

3.2.1 Material Selection for Polymeric UF Membrane

In the fabrication of mixed matrix UF membranes, particles/nanoparticles should be compatible with membrane polymer. When the casting solution is prepared, loading of particles or nanoparticles in the polymeric

solution should be set at an optimum value for avoiding particle agglomeration at the skin layer and sublayer of the UF membrane. Therefore, the selection of particles and nanoparticles is a great deal of interest for all researchers who produce mixed matrix UF membranes [9, 33–37].

In fact, the degree of entrapment of particles/nanoparticles in the polymer matrix depends mainly on the compatibility between polymer and particles/nanoparticles. The loading of particles/nanoparticles usually enhances the membrane performance, but the membrane performance gradually deteriorates if the particles/nanoparticles are not strongly entrapped in the membrane. Therefore, the material selection of particles/nanoparticles and polymers available in the market is one of the most important aspects to be considered in UF membrane fabrication [33, 37–39].

3.2.1.1 Polymer

Polymer plays an essential and ubiquitous role in many technologies, including UF, and is separated into numerous classes according to their physical and chemical properties. Polymer morphology plays a significant role to determine bulk physical properties by which the behavior of the polymer as a continuous macroscopic material is determined. In fact, chemical properties of polymer determine the bulk physical properties as well through the interactions between polymer chains working via various physical forces. In a much larger scale, their chemical properties determine how the bulk polymer interacts with other chemicals and solvents [13, 40, 41].

At present, some synthetic polymers such as polyether sulfone (PES), polysulfone (PSf) and polyvinylidene fluoride (PVDF) are used for UF membrane. On the other hand, before the evolution of polymer synthesis, natural polymers were used. Due to the serious concerns over the environmental effects and awareness that petroleum resources are limited, the use of biodegradable polymers produced from extensive sources such as cellulose, chitin, and starch has significantly increased. Accordingly, this type of polymers has been widely commercialized in membrane filtration technology [39, 42, 43].

3.2.1.2 Nanoparticles

Particles and nanoparticles, when incorporated in the polymeric phase of UF membranes can significantly increase the UF performance. Currently, carbon nanotubes (CNTs), graphene, clays, carbon molecular sieve, metallic oxide, zeolites are known to be effective for removing organic compounds when incorporated in the polymeric membrane. Nanostructured materials are highly capable of decreasing the toxicity of organic pollutants to an allowable level owing to their large surface area and uniformity in size. As discussed earlier, the compatibility of particles and nanoparticles with the polymer matrix is essential. Therefore, finding novel and potentially powerful particles and nanoparticles is always a challenging task for membrane R & D [32, 44–48].

3.3 POLYMERIC UF MEMBRANE CONFIGURATIONS

Polymeric membranes of different shapes such as flat sheet, hollow fibers, and nanofiber sheet (see Fig. 3.1) have been used for submerged UF membrane. Hollow fiber membranes have always shown higher efficiency and longer lifetime; however, flat sheet membranes are easier to use in UF [49, 50].
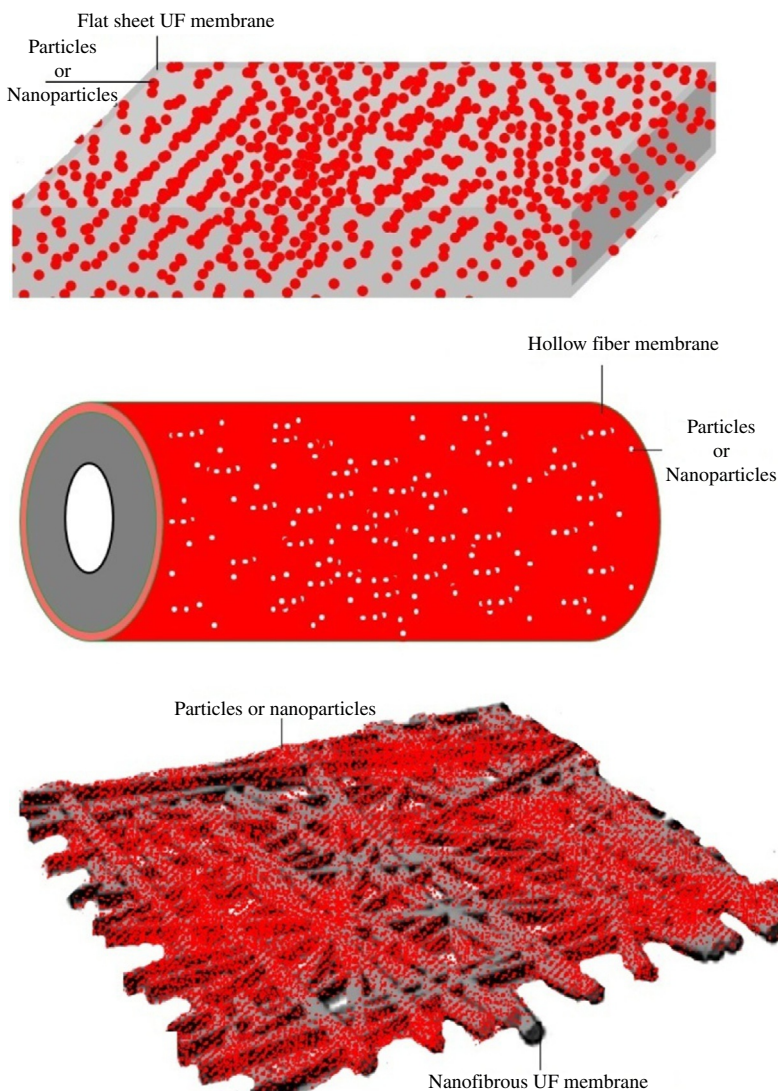

FIG. 3.1   Various UF membrane shapes.

Recently, nanofiber mat has been used for UF membrane, but not many data are available for this kind of membrane [51].

3.3.1 Flat Sheet UF Membrane

The membrane can be produced as flat sheets or hollow fibers. To fabricate a flat sheet, a polymer solution is spread on a support glass plate using a casting knife. On the other hand, hollow fibers provide a higher surface area per unit volume of membrane modules [52–55]. The flat sheet membrane and hollow fibers can be prepared by using a casting technique and a spinning technique, respectively [56, 57].

The casting of flat sheet membranes is a well-established phase inversion technique. First, a polymer is dissolved in a suitable solvent or a mixture of solvents and nonsolvent (in phase inversion) to form a homogeneous dope solution. The dope solution is then cast on a suitable support such as glass plate or nonwoven polyester sheet using a casting knife. As depicted in Fig. 3.2, the casting knife is made of a metal blade moving on two runners that can provide a gap between the blade and support accurately [58, 59]. This gap determines the thickness of the membrane produced. A pneumatically controlled flat sheet membrane casting system has been developed by combining semi-technical hand-casting knife and pneumatic system.

This system offers an easier casting operation by controlling several casting variables such as shear rate and forced convection residence time. Then, the cast film is instantly dried, or the solvent is partially evaporated before the cast film is immersed into a coagulation bath. The resultant membranes were used in commercial plate-and-frame and spiral wound systems [10, 60].
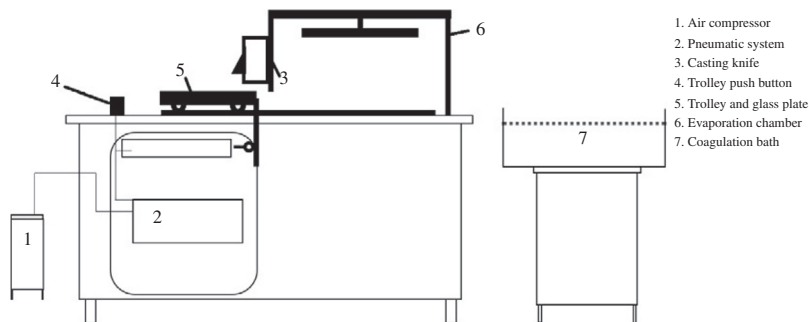

1. Air compressor
2. Pneumatic system
3. Casting knife
4. Trolley push button
5. Trolley and glass plate
6. Evaporation chamber
7. Coagulation bath

FIG. 3.2   Flat sheet membrane casting equipment.

3.3.2 Hollow Fibers UF Membrane

Hollow fibers were fabricated by the spinning process, which involves the extrusion of a polymer solution through an annular spinneret. Hollow fiber membranes can have either dense or asymmetric structures depending on the way the gel filaments are solidified [61–63]. Melt spinning usually obtains a dense structure while solution spinning (phase inversion) is used to obtain an asymmetric structure. A hollow fiber spinning system is shown schematically in Fig. 3.3. The fibers are almost instantaneously formed as the polymer solution leaves through the spinneret. The spinneret consists of two concentric capillaries; outer capillary and central capillary. The outer capillary has an outer diameter of around 400 μm and an inner diameter of approximately 200 μm while the central capillary has a diameter of about 100 μm. The polymer solution is forced to come out of the outer capillary and air, or a secondary solution is simultaneously delivered through the inner capillary. Typically water is delivered through the inner capillary when asymmetric hollow fibers are spun [9, 64–66].

3.3.3 Nanofibrous UF Membrane

A UF electrospun nanofibrous membrane is a novel technology for removing organic contaminants in the wastewater by membrane adsorption, offering an alternative option to the effluent treatment. In particular, electrospun nanofibrous membrane looks promising due to high permeation and rejection rate, when they can be used many times via appropriate desorption after each test [67]. For this reason, electrospun nanofibrous membranes have come to the forefront of R & D recently as one of the most

1. Solution tank
2. Gear pump
3. Syringe pump
4. Spinneret
5. Conceptive chamber
6. Coagulant bath
7. Treatment bath
8. Wind-up drum
9. Controller
10. Internal coagulant
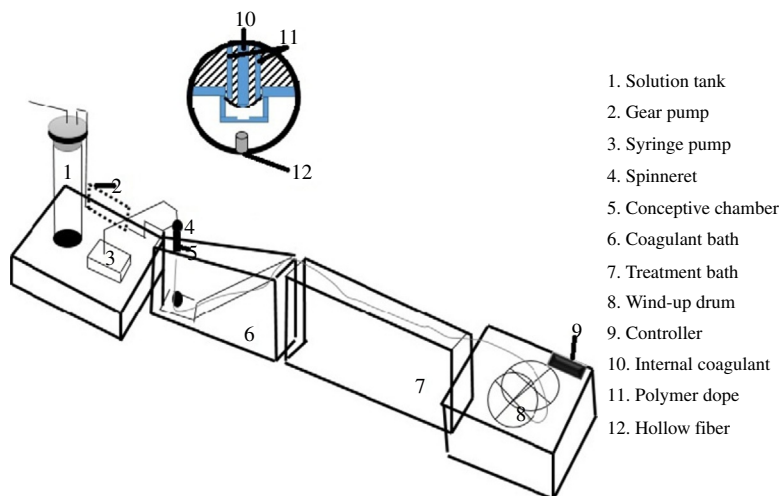11. Polymer dope
12. Hollow fiber

FIG. 3.3   Hollow fiber spinning system.

efficient techniques to remove the organic pollutants from wastewater at lower operating costs. However, the incorporation of suitable and compatible particles and nanoparticles, as adsorbents, is the most challenging parameter to use electrospun nanofibrous membrane for membrane adsorption. In several studies, a hot pressing technique has been used for enhancing the compactness of the membrane or nonwoven supports and via pressure and heat of hot press system [68, 69] (Figs. 3.4 and 3.5).

3.3.4 Mixed Matrix Membranes

Mixed matrix materials (MMMs) are structured with functional particles embedded within a polymer matrix. These materials are also known as heterogeneous or hybrid materials. Selection of particles and polymer
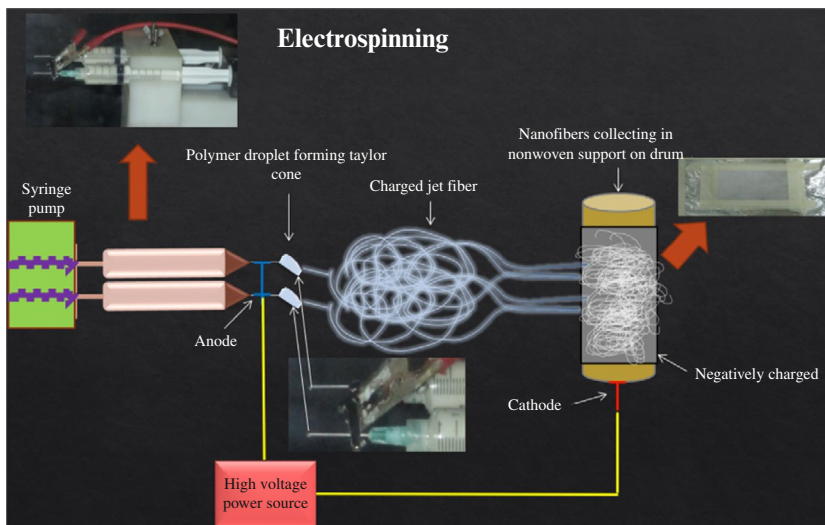
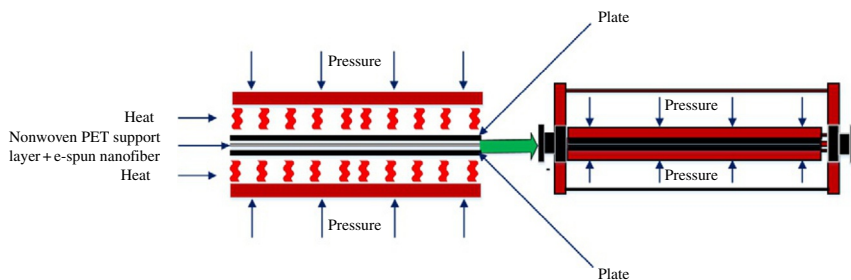

FIG. 3.4   Electro-spinning procedure.

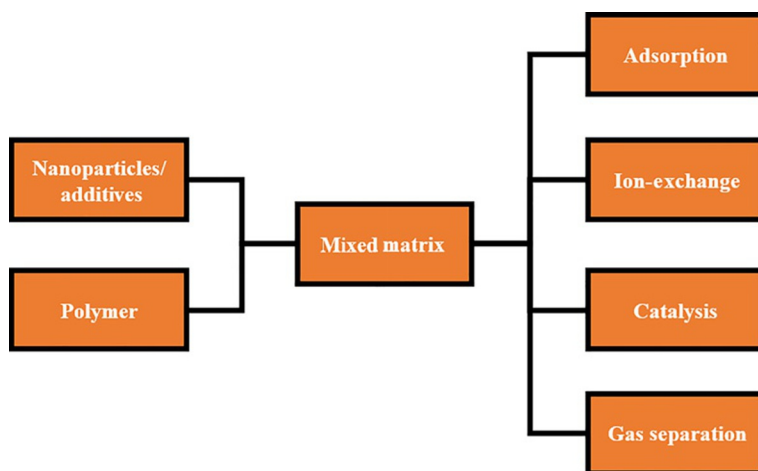FIG. 3.5   Illustration of the hot-pressing method.

FIG. 3.6   Schematic representation of the mixed matrix membrane.

binder or polymer matrix will determine its function such as adsorption, catalysis, ion-exchange or separation membrane [9, 70–74]. The concept of mixed matrix membrane is schematically presented in Fig. 3.6. MMMs are formed by dispersing molecular sieve entities into a polymer matrix [75–79]. Fig. 3.7 illustrates the structure of a mixed matrix film. In Fig. 3.7, the molecular sieves are uniformly distributed within the polymer matrix. It is believed that this emerging approach synergistically combines the best features of both phases and simultaneously to compensate the weakness in each medium [80, 81]. In a molecular sieves-polymer mixed matrix system, the high selectivity benefits of the molecular sieve are
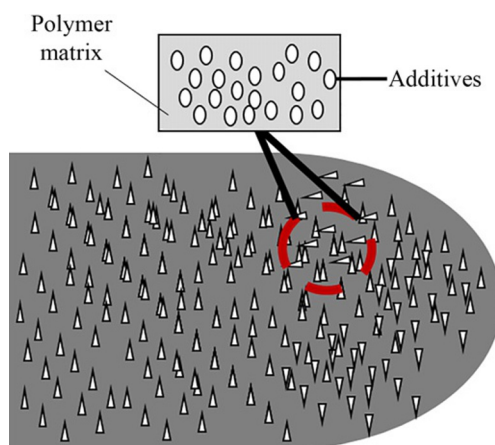

FIG. 3.7   A schematic diagram of an MMM film.

combined with desirable mechanical properties and economical process-abilities of polymers. In turn, the costly processing and severe mechanical problems in purely molecular sieving membranes can be overcome, and the limit in the trade-off between productively and selection of polymer materials can be surpassed [82–84].

3.4 FOULING MITIGATION

3.4.1 Fouling Type and Methods to Control Fouling

The decrease in the permeation rate during membrane process, called fouling, is recognized as the main problem in the application of membrane technologies. Several types of fouling can occur in membrane systems including inorganic fouling, particulate and colloidal fouling, organic fouling, and biofouling [31, 85, 86]. Pore blocking and cake formation are considered as the two primary mechanisms of membrane fouling while other factors such as adsorption, particle deposition within the pores, and formation of the cake layer affect membrane fouling through the modification of either or both mechanisms. Pore blockage increases the membrane resistance, while cake formation creates an additional layer of resistance to permeate flow. The severity of these phenomena depends on the nature of the particle, the operating conditions such as pH, ionic strength, pressure, and particle concentration and the nature of the membrane. Development of effective methods to control fouling is based on an understanding of the fouling mechanism and the influence of the process parameters on the membrane fouling. To discuss approaches to mitigate membrane fouling we will first outline the main particularities of this process [87–91].

Generally, for MF and UF, two types of fouling phenomena are distinguished. The first is macrosolute or particle adsorption, which refers to the specific intermolecular interactions between the particles and the membrane that occur even in the absence of filtration. It is usually irreversible, adhesive fouling. In water treatment applications, the foulants are usually adhesive due to hydrophobic interactions, hydrogen bonding, van der Waals attractions, and extracellular macromolecular interactions among others. The second type is known as filtration-induced macrosolute or particle deposition, which is often reversible, nonadhesive fouling, where the accumulation of cells, cell debris, and other rejected particles on the top surface of the membrane is prominent. It occurs as external fouling or cake formation. Reversible fouling resulting from cake formation was found to be only weakly dependent on membrane surface chemistry; in contrast, irreversible fouling exhibited a marked dependence on surface chemistry [92, 93].

Membrane fouling is an incredibly complex physicochemical phenomenon. Usually, several mechanisms are involved simultaneously. Thus, in case of protein-containing solutions, it was suggested that it began with protein aggregates depositing on the membrane surface, thereby blocking its pores. Disulphide linkages, van der Waals forces, electrostatic interactions, hydrophobic interactions, and hydrogen bonding all contributed to membrane fouling by a proteinous substance, mostly through adhesive fouling [94–96]. On the contrary, for filtration of river water, cake formation on the surface of the membrane resulted in more pronounced UF membrane fouling than the adsorption of small substances inside the pores of the membrane. UF membrane fouling was dominated by the cake layer formation attributed to the accumulation of dissolved organic materials and suspended colloids in the raw water. The particles are driven to the membrane surface by the flow of permeate to form a cake layer on the membrane unless the shear rate is very high to prevent cake formation. The undetachable cake layer accumulates on the membrane and results in fouling in the long term [97–99].

Biofouling is another major problem, which destroys the structural integrity of the membrane, and this leads to subsequent irreversible membrane damage, shortens membrane life, increases operational and maintenance costs, and reduces efficiency. It is initiated by irreversible adhesion of one or more bacteria to the membrane surface, followed by growth and multiplication of the sessile cells at the expense of feed water nutrients. It can eventually form a confluent lawn of bacteria, otherwise known as a biofilm on the membrane surface. Chemical properties of membrane surface, its roughness, pore shape, and size distribution are found to be the main factors controlling the biofouling potentials [100, 101]. The complexity of membrane fouling predetermines the exploiting of a variety of approaches to control this adverse process. Here these approaches are categorized under four main topics: (i) Pretreatment of feed; (ii) Membrane materials/surface modification; (iii) Operating parameters; and (iv) Cleaning procedures. Approaches discussed in the first three topics are focused on preventing or mitigation of the membrane fouling, whereas methods of the fourth topic are assigned to cope with consequences of the membrane fouling [102–104].

3.4.2 Cleaning Method

This is a standard method of reduction of membrane fouling employed in cross-flow filtration processes. Cross-flow filtration techniques in membrane technologies have been employed on a global scale for the removal of particles, colloidal species, and microorganisms but the principal limitation lies in the flux decline associated with particle formation on the

membrane, thus hindering mass transfer. Backflush was used to eliminate particle deposition, which allowed efficient flux recovery [31, 45, 105].

In MF, high feed/retentate velocities are used to reduce cake formation and concentration polarization. As well, it is a common practice to pump filtrate back through the membrane into the feed channel to give a periodic backwash. This lifts the deposited material off the surface of the membrane. The backwash pressures need to be greater than the operating filtration pressure. The efficiency and effectiveness of this technique are limited to surface deposits removal from the membrane. It becomes ineffective with strong adhesion of deposits and if there is any pore fouling. Periodic backwashing improves membrane permeability and reduces fouling, thus leading to optimal, stable hydraulic operating conditions. Air backwashing in submerged membrane reactors can increase the flux up to fivefold. When the technique is carried out at a faster rate, it is known as backpulsing or backshocking. Backpulsing is a cyclic process of forward filtration followed by reverse filtration [87, 106–108].

Reversal filtration involves a reversal of the flow through the membrane by changing the orientation of the trans-membrane pressure (TMP). More rapid backwashing has been claimed to be more effective, and backpulses are of short duration and may be operated continuously or periodically [109–112]. They are particularly useful with colloidal suspensions and with streams requiring protein transmissions through the membrane. The backpressure is applied in an extremely rapid pulse every few seconds throughout the process. The reverse flow removes the particles that are reversibly deposited on or within the pores of the membrane, while the foulants are swept off the membrane via the cross-flow. These actions subsequently reduce fouling and improve permeate flux over time. Cross-flow filtration with rapid backpulsing has been studied in-depth by many groups in different membrane/foulant system, who documented the method as an effective means of controlling fouling and increasing permeate flux for nonadhesive foulants that exhibit reversible fouling. The use of rapid backpulsing was also studied extensively [29, 113–115].

3.5 SURFACE MODIFICATION

Surface modification has been potentially used to minimize the fouling on the membrane surface and maximize the membrane performance regarding permeability and solute rejection. The primary parameter which plays an essential role in membrane surface modification is the use of materials with a favorable effect on the structure of membranes such nanoparticles and nanotubes or some adsorptive materials [116].

Alternatively, modifying membranes and membrane surfaces aim at fabrication of antifouling membranes by inhibiting microbial growth on the membrane. The proper membrane material selection can also improve the membrane and membrane surfaces concerning antifouling behavior, which consequently reduces cake layer formation and concentration polarization and overall fouling reduction. Many marketable and commercial membranes are made of PES, polyvinylidenefluoride (PVDF) and other hydrophobic polymers due to their high chemical, thermal and mechanical properties [116, 117]. On the other hand, hydrophilic nanoparticles are often used to be blended with the hydrophobic polymer. Hence, the combination of hydrophobic polymer and hydrophilic nanoparticles can enhance the membrane performance significantly, as reported by many researchers [32, 107, 116, 118–120].

Other methods can be used to change the hydrophobic surface to hydrophilic. They are (i) coating and (ii) grafting. In the first method, the membrane is immersed in the coating solution. The second grafting method is a kind of immobilization, where hydrophilic species are grafted on the membrane surface from grafting solutions [121, 122]. Another type of membrane grafting is done by photo-induced grafting, which is mainly used for functionalization of membrane surface due to their numerous features. Its advantages are the low cost of the process operation, selective absorption of UV light without affecting the bulk polymer, mild reaction conditions and permanent alteration of the membrane surface with facile control of the chemistry [107, 120, 123–126]. In fact, many researchers have recommended a combination of surface modification and cleaning procedure to increase the permeability and separation performance of the membranes which reduces the fouling on the membrane surface due to bacterial suspensions, clay suspensions, and oil emulsions [31, 127].

3.6 RECENT PROGRESSES IN UF MEMBRANE AND UF MEMBRANE PROCESSES

UF is increasingly used in water treatment due to a decrease in membrane prices, improving module design, operability, and economics of membrane separation processes. Furthermore, as the regulation for chemical and biological contaminants in water have become more stringent, membrane processes including NF, UF, and MF have been utilized as treatment alternatives to replace conventional processes which employ chemical coagulation for removing dissolved species and filtration for removing suspended species. MF has been used in water treatment for removing suspended solids (larger than 0.1 μm). MF has also been used by water utilities in place of conventional processes where treatment objectives are suspended solids control and microbial removal. However,

MF cannot achieve a reliable degree of dissolved organic control while UF does. Denitrification can be done by physicochemical treatment techniques such as RO, ion exchange and electrodialysis. Pesticides on the other hand usually require activated carbon treatment or oxidation by strong chemical agents. Lyonnaise des Eaux, a company in the water treatment business, developed an industrial scale MBR system to remove pesticide by combining biological denitrification and powdered activated carbon adsorption. UF has been used to remove many contaminants [128–130].

UF can be a very promising liquid-solid separation process as it can remove particulates and macromolecules in the range of 0.02 μm to 1 nm. Although UF has a broad molecular weight cut off (MWCO) range, it is less effective in removing low molecular weight organic matters. A combination of UF and coagulant or absorbent has been proven to remove organic matters in water significantly. However, MWCO is not the only factor that will determine the membrane rejection. Factors such as membrane characteristics, feed properties, operational conditions, pretreatment procedure, module configurations, solution chemistry and the presence of other solutes have been reported to influence the membrane performance. UF membranes are made from various types of polymer, but two most common membrane materials are PS and cellulose acetate (CA). There were 34 UF plants in operation or under construction worldwide having a total capacity of 34 million gallons per day [130–132].

3.6.1 Antibacterial Membrane

Since the 1990s, MF was evaluated by water supply agencies as a cost-effective alternative to the conventional pretreatment for desalination by RO. However, because an MF membrane can remove substances larger than 50 nm and bacteria while bacteria and virus pass through, many researchers have turned to UF, which allows removal of 3 nm or larger substances, and subsequently reduces the biofouling problem of RO membrane. Furthermore, the disinfection process (via UV, ozonation, or chlorination) after the membrane filtration process is also recommended as a secondary bacteria control barrier and distribution system protection [133]. The other promising way is to incorporate an antibacterial agent into polymeric membrane so that removal and disinfection can be carried out simultaneously in a membrane.

Recently, Moslehyani et al. reported that the key advantage of an antibacterial membrane is the enhancement of antibacterial action by the incorporated antibacterial agent. When the feed solution comes to contact with the membrane surface, the antibacterial agent is released to disrupt the bacterial cell wall membrane. Therefore, membrane filtration and

disinfection occur simultaneously. As a result, a biofilm covers the membrane surface creating a newer, smoother and more antiadherence surface, further enhancing the antibacterial capacity of the membrane. It is known that the smoother surface is less prone to fouling due to the decreased interaction between the colloidal particle and the surface [6].

Antibacterial compounds are defined as a synthetic or natural compound that destroys bacteria or suppresses their growth or their ability to reproduce. There are many antibacterial products commercially available for cleaning and hygienic purposes. In addition, the invention of loading/incorporating antibacterial agents into our daily needs such as clothing, soap, containers for food-packaging, and water filtration system is frequently undertaken. Water treatment and effluent disinfection using membrane technologies have been in growing interest due to the environmental factor as compared to the common disinfectant, chlorine. Therefore, the combination of membrane technologies and the relevancy of the incorporation of an antibacterial agent such as silver is an area of interest [8, 11, 134]. Factors affecting bacterial attachment and transport are summarized in Table 3.1.

TABLE 3.1 Factors Affecting Bacterial Attachment and Transport

Factor	Effect on transport and attachment
Ionic strength	Attachment increases with higher ionic strength due to electrical double-layer size reduction
Clay-content	Attachment increases with high clay content due to the larger specific area of adsorption
Oxygen limitations	Oxygen-limited biofilms exhibit lower shear removal rates but higher sloughing
Charge on media	Attachment of negatively charged bacteria will be high in positively charged media
Flow rate	Higher flow rates reduce bacterial attachment
Nutrient concentration	Bacterial size is reduced in higher nutrient concentrations
Bacterial size	Smaller bacteria may interact with media less and may not be removed by filtration as easily as bigger bacteria. On the other hand, larger bacteria have been shown to move faster than small bacteria
Cell concentration	At low cell density, attachment is favored. Bacteria tend to move from high concentration areas by a tumbling diffusive flux
Bacterial motility	Motile bacteria may migrate faster than nonmotile bacteria through chemotaxis
Water content	Bacteria move faster through the unsaturated soil of higher water content

3.6.2 Adsorptive Membrane

Contamination of drinking water with heavy metals is a significant public health concern worldwide. For example, the presence of lead in drinking water has been reported in more than 70 countries. Millions of people, mainly in developing countries such as India and Bangladesh, are at high risk due to contamination of ground and surface water. In the aqueous solution, heavy metals are colorless and odorless, and it is not easy to detect them visibly. Because of this, its contamination is a serious concern for the environment and living creatures. It is known that long-term exposure to drinking water contaminated with heavy metal can cause various kinds of cancers. Conventional technologies to remove heavy metal ions are chemical precipitation, coagulation and flocculation, ion exchange and membrane filtration. Membrane filtration processes such as NF and RO are also known to be effective to eliminate arsenics (As). However, they consume high-energy due to the requirement of high pumping pressure. The pore sizes of MF and UF are too large to remove the dissolved metallic minerals. Thus, the inconsistent and/or incomplete removal of heavy metal by conventional technologies has urged to search for efficient, environmentally friendly, and low-cost treatment technology for hazardous decontamination [68].

Recently, Moslehyani et al. reported that electrospun adsorptive nanofiber membrane (EANM) is a novel technology with a high potential to remove heavy metals from drinking water due to EANM's high permeation rate and adsorption capacity, particularly when they can be used multiple times via appropriate desorption. For this reason, EANMs have come to the forefront of R & D recently as one of the most efficient techniques to remove arsenic at low operation cost. However, the use of suitable and compatible adsorbent particles is the most challenging parameter in the preparation of highly efficient EANMs [135].

## 3.6.3 UF Photocatalytic Membranes

Photolysis as a critical component of photodegradation technology has been studied for the last few decades. The reaction scheme implies that an interface is formed between the (solid) photocatalyst and a liquid or a gas phase containing the reactants. Particularly, understanding the mechanisms and kinetics of photocatalytic membrane process is the most significant part of the whole process [136–138]. A photocatalyst is a semiconductor that converts the light energy to the chemical energy of the electron-hole pairs. Therefore, a suitable energy bandgap together with chemical and physical stability, nontoxic nature, availability, and low cost should be considered when a solid photocatalyst is chosen [138–140]. In general, the photodegradation has three main products including nonreacted (similar to the initial feed), intermediate product,

and final product [45, 141]. To understand the mechanism of photodegradation is necessary to understand the role of the ultraviolet radiation in the photocatalytic reaction. In the photocatalyst, there is a conduction band and a valence band separated by a bandgap of energy. When the photocatalyst is exposed to ultraviolet photons, whose energy ($h\nu$) is higher than or equal to the bandgap, the transfer of an electron occurs from the valence band to the conduction band to create electron-hole pair [138, 142–144]. The lowest energy level of the conduction band corresponds to the reduction potential of the photoelectrons while the highest one corresponds to the oxidizing power of the electron holes as is illustrated in Fig. 3.8.

When no electron and hole scavengers are available, the input energy is dissipated as heat within a few nanoseconds by recombination.

Several steps involved in the photocatalytic reaction are given below with an example of typical photocatalyst TiO_2.
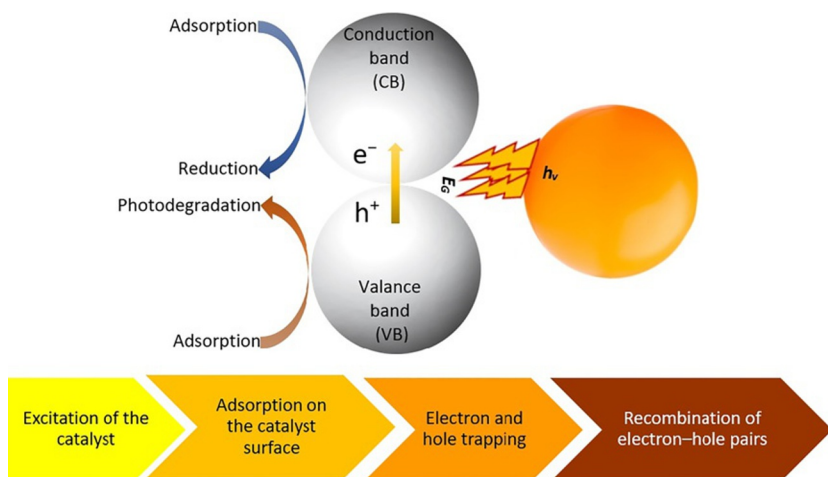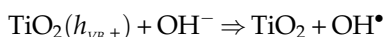
I. Photocatalyst excitation

$$TiO_2 + UV(h\nu) \Rightarrow TiO_2(e_{CB-} + h_{VB+})$$
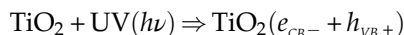
II. Photocatalyst adsorption

$$TiO_2(h_{VB+}) + H_2O \Rightarrow TiO_2 + H^+ + OH^\bullet$$
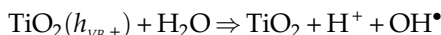
$$TiO_2(h_{VB+}) + OH^- \Rightarrow TiO_2 + OH^\bullet$$

FIG. 3.8   Photocatalyst mechanism during photodegradation.

III. Photocatalyst electron-hole trapping

$$TiO_2(e_{CB-}) + O_2 \Rightarrow TiO_2 + O_2{}^{\bullet-}$$

$$O_2{}^{\bullet-} + H^+ \Rightarrow H + O_2{}^{\bullet}$$
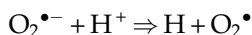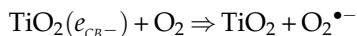
IV. Photocatalyst electron-hole pairs recombination

$$e^- + h^+ \Rightarrow heat$$
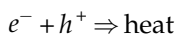
Many organic reactants accept hydroxyl radicals generated in the photocatalytic adsorption process in water, which act as electron donors when they are oxidized. Thus, the organic reactants are degraded to the intermediate substrate and further decomposed into carbon dioxide and water [136, 145–147].

As well, photocatalytic reaction process is described by the following three steps [148, 149]:

  I. External mass transfer of reactant to the solid photocatalyst surface.
 II. Internal mass transfer via intra diffusion of a photocatalyst.
III. Organic compounds decomposition by diffused photocatalyst.

Moslehyani et al. [98] constructed photocatalytic membrane reactor (PMR) to study oil-water treatment. In the photocatalytic reactor, UF membrane was used to retain the unreacted oil while TiO_2 photocatalyst was suspended in the feed. PMR is a novel method for oily wastewater treatment, and its performance in the degradation of toxic hydrocarbon compounds and purification of oily wastewater looks very promising.

3.7 SUMMARY

The water and wastewater industry has been faced with many challenges over the last three decades and is currently looking for economical methods of treatment. The removal of particulate matters by chemical and physical methods is commonly used for the treatment of drinking water as well as the surface water sources. More focus is nowadays placed on membrane technology for water treatment, where the choice of membrane, module configuration, process and operating parameters, and pretreatment among others are essential to make the process most effective. Membrane processes are very promising due to their potential to remove particles, including microorganisms, organic pollutants, inorganic salts, and to achieve biologically stable water by reducing microbial regrowth in the distribution system. Among others, UF is considered as the most

efficient and economical process among all types of membrane technology that is used for water and wastewater treatment.

Acknowledgments

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