Polymeric Membranes in Wastewater Treatment

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Abstract

Water covers around 71% of the earth's surface; however, only 2.5% is fresh water available for consumption. Rapid industrialization and increasing human activities, such as the use of fertilizers, mining, and pesticides, add many harmful organic and inorganic pollutants into the water, which endangers fresh water resources and the ecological environment. Various conventional methods for wastewater treatment, including chemical precipitation, physical adsorption, ion exchange, and membrane separation have been present since long times. Among these methods, polymeric membrane separation has become the main focus of attention over the past couple of decades for wastewater treatment, owing to an ease of operation, low energy consumption, and their unique and proficient separation of contaminants which yields high-quality treated water. In addition, these membranes can be used at an increased range of temperature conditions and the recyclability of these membranes is also very promising. Polymeric membranes for wastewater treatment are generally separated into four major categories, based on their performance, characteristics, pore size, and specific separation qualities. These four categories are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). This book chapter will provide a comprehensive summary for readers to understand the progress in the

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L. M. Pandey, A. Hasan (eds.), *Nanoscale Engineering of Biomaterials: Properties and Applications*, https://doi.org/10.1007/978-981-16-3667-7_17

area of wastewater treatment using polymeric membranes and to highlight the recent advances in polymeric membranes and background study of wastewater treatment. In addition, the potential benefits and challenges of utilizing polymeric membranes for wastewater treatment will be briefly discussed.

Keywords

Polymeric membranes · Porous polymers · Wastewater treatment

17.1 Introduction

The connection between human civilization and water has existed throughout the ages, from the first settlements created in fertile river valleys, to the efforts of the United States Environmental Protection Agency (US EPA), the clean water act, and beyond. Water has been utilized across many eras of human civilization as a source of kinetic energy for mills and other mechanical processes, and as a fuel to keep our biological processes operating, such as crop growth and food digestion (Yevjevich 2009). Thankfully, this invaluable resource makes up approximately 71% of the Earth's surface. However, around 96.5% of the water is found in the oceans and is not safe for drinking. Of the remaining freshwater, almost 69% is found in glaciers and ground ice (Shiklomanov 1993).

The limited sources of freshwater are also in danger from various sources of pollution. For example, the US EPA completed a study on the levels of pollution in the water resources of the United States and found that approximately 55% of the mileage of rivers and streams that were tested were deemed impaired, meaning they were unable to support one or more of their designated uses, such as fishing or swimming. Additionally, 70% of the measured lake acreage, 78% of the measured coastal square mileage, and 98% of the miles of measured Great Lakes coastline were determined to be impaired. On top of this, only 62 total square miles out of the 53,332 square miles that were tested of the Great Lakes open waters were found to be able to support their designated uses as they were not deemed impaired (U.S. Environmental Protection Agency (EPA) 2017). Common sources of pollution were mercury, polychlorinated biphenyls, fertilizers, and pathogens. The sources of these pollutants are commonly storm-water runoff, domestic drainage, and industrial discharges (Virgil 2003).

Storm-water runoff can carry oils, gasoline, and other automotive fluids from roads and other urban areas. It can also carry fertilizers, pesticides, and animal wastes from agricultural fields, with many of these providing sources for nitrogen and phosphorous pollution (Virgil 2003). Domestic drainage includes wastewater produced from domestic sources, including what is flushed down sinks and toilets, and is a common source of pathogens and bacteria. Lastly, industrial discharges come in many forms but are typically larger than domestic sources. For example, pulp and paper mills mix clean water with wood chips and chemicals, such as bleach, during their many processes before eventually removing the water from the finished products and returning it to the source. In many of these processes, the water must be cleared of pollutants before being returned to nature (Virgil 2003). This can be done through a variety of mechanical or chemical processes, including filtration through a membrane. These pollutants can cause death or outbreaks of diseases like cholera, hepatitis, and typhoid (Khalifa and Bidaisee 2018).

A number of methods have been used to treat the wastewater from urban and industrial sources in an effort to protect and repair the limited supplies of available fresh water. However, many of these methods produce sludge and other by-products that require large amounts of energy to treat. For example, the entire population of 15,014 publicly owned treatment works in the United States and Puerto Rico taken from the 2012 clean watersheds needs survey were found to produce a total of 13.85 million tons of sludge solids per year (Seiple et al. 2017). The sludge that is produced is typically hazardous, containing by-products from reactants or captured pollutants and pathogens, and requires further, energy-intensive treatment. The energy use of wastewater treatment in the United States accounts for around 2% of the total energy use of the country with a third of that being used solely to treat sludge (Pabi et al. 2013). These numbers will increase as the population grows and as more countries begin to develop their own wastewater treatment systems.

To combat the creation of sludge and the high energy usage, polymeric membranes are being implemented to separate solids and sometimes pathogens from wastewater. Polymeric membranes do not require energy to function, and instead depend on the difference in pressure to drive the wastewater through while impeding the flow of pollutants. Additionally, these polymeric membranes do not create sludge that requires further treatment. This chapter will focus on the use of these polymeric membranes for wastewater treatment while providing a brief discussion on other conventional methods.

17.2 Conventional Methods for Wastewater Treatment

This growing problem of water contamination has a significant influence on the economic development of countries, as well as human livelihoods and the quality of the environment, all throughout the globe. Some pollutants, such as heavy metal ions, do not readily biodegrade and, when ingested, can cause a series of irreversible physiological diseases. For instance, mercury (Hg^{2+}) can damage the central nervous system (CNS) and can cause headaches, stomatitis and gastroenteritis (Tchounwou et al. 2003). Similarly, lead (Pb^{2+}) can cause an inadequate stream of oxygen and nutrients throughout the body, resulting in brain and tissue damage (Daniel et al. 2004). Moreover, cadmium ions can replace calcium (Ca^{2+}) ions in the bones and deter the normal deposition of Ca^{2+} resulting in cartilage disease (Miyahara et al. 1984). Excess arsenic can inhibit the normal metabolism of cells in the body, causing cell wounds and eventually leading to organ damage. Additionally, organic pollutants in water, including fertilizers, plasticizers, pesticides, detergents, pharmaceuticals, oils, and other hydrocarbons, are also hazardous and are mainly derived from agricultural runoff, food and paper industries, and domestic sewage. In order to metabolize these organic pollutants, a large amount of dissolved oxygen is needed, which in turn jeopardize aquatic organisms and their ecosystem (Goktas and MacLeod 2016). Therefore, the removal of organic and inorganic pollutants and the effective treatment of wastewater are vital for the aquatic ecosystem and for the generally health of humanity. In the past, various conventional methods have been adopted for the treatment of wastewater, including chemical precipitation, ion exchange, adsorption, and biological treatment, which are discussed below.

17.2.1 Chemical Precipitation

Chemical precipitation is a method of wastewater treatment in which the dissolved materials in wastewater are turned into solid, insoluble particles through the addition of various chemicals to the wastewater. Specifically, chemical precipitation is used to remove the ionic constituents from wastewater by reducing their solubility using specific counter ions. Chemical precipitation is mainly utilized in the removal of metal cations but can be used for the removal of anions such as cyanide, phosphates, nitrites, and various organic molecules (Brady 2003; Kwon et al. 2012; Kim et al. 2013). Chemical precipitation is typically followed by a solid separation process such as sedimentation, filtration, and coagulation to remove the precipitates. Most of the metal ions are precipitated through hydroxide precipitation but can also be precipitated through carbonate and sulfide precipitation. In some cases, the chemical constituents to be removed must be oxidized or reduced. Phosphates can be removed by precipitation as iron or alum salts, while fluorine can be eliminated using calcium chloride ($CaCl_2$). A chemical precipitation method typically includes four major stages including the addition of reagents, flocculation, sedimentation, and solid-liquid separation. Chemical precipitation is performed in various means as described below.

17.2.1.1 Hydroxide Precipitation

Hydroxide precipitation is a type of chemical precipitation which involves the addition of a suitable hydroxide to the wastewater to form an insoluble metal hydroxide precipitate. The precipitation reaction is illustrated as:

$$\mathrm{M}^{n+} + n(\mathrm{OH})^- \rightarrow \mathrm{M(OH)}_n \downarrow$$

Every metal has a discrete pH value at which the hydroxide precipitation takes place creating the insoluble metal hydroxide. Reagents commonly used for hydroxide precipitation are typically alkaline compounds, such as lime or caustic soda. Although the hydroxide precipitation method has several advantages, including a low cost, simple design, ease of pH control, and an easy removal of the metal hydroxides through flocculation and sedimentation, this method produces a large quantity of relatively low density sludge, which causes dewatering and disposal problems.

17.2.1.2 Sulfide Precipitation

Sulfide precipitation is another chemical precipitation process in which both insoluble sulfides, such as ferrous sulfate, and soluble sulfides, including sodium sulfide and hydrogen sulfide, are used to precipitate the metal ions as insoluble metal sulfides. Sulfide precipitation occurs at neutral pH conditions, as the metal sulfides have a lower solubility than hydroxides below neutral pH and in the alkaline pH range. The basic principle of the sulfide precipitation method is similar to the hydroxide precipitation in which the sulfide is added to the wastewater to precipitate the formed slurry which is subsequently removed through filtration. The formation of metal sulfide is illustrated as:

$$M^{n+} + S^{n-} \rightarrow (MS) \downarrow$$

The benefits of sulfide precipitation over hydroxide precipitation are the reduction in the quantity of sludge generated and the ability to more easily process the sludge to recover the metals which helps offset the cost of treatment. Moreover, the high reactivity of sulfides with metal ions and the insolubility of the metal sulfides are attractive features compared to hydroxide precipitation. However, sulfide precipitation is not viable for all situations because of the toxicity of the sulfide ions and the dangers of hydrogen sulfide (H_2S).

17.2.1.3 Carbonate Precipitation

Carbonate precipitation is generally used to remove metal ions either through converting hydroxides into carbonates using carbon dioxide or direct precipitation using a carbonate reagent like calcium carbonate. The solubility of most carbonates is in between that of hydroxides and sulfides and usually forms easily filtered precipitates. When sodium carbonate is added to water, the basic carbonates are formed as:

$$M^{n+} + CO_3^{n-} \rightarrow MCO_3 \downarrow$$

The precipitated metal carbonates are generated as a sludge and are removed through filtration.

Chemical precipitation offers many advantages as a treatment alternative for removing many industrial wastewater pollutants. It meets stringent discharge criteria and has been used for many years. Moreover, this method is relatively simple and can be used to remove specific components from wastewater with a high degree of selectivity. However, this technique also possesses several limitations, including a high cost, restrictions to its applications, a high energy input requirement, manual oversight, and the generation of large quantities of sludge.

17.2.2 Ion-Exchange Method

Ion-exchange is a wastewater treatment method in which ions of particular species are replaced with ions of analogous charge but of a different species to generate an insoluble resin. In essence, the ion-exchange method is a sorption process coupled with a reversible chemical reaction. The most common applications of the ion-exchange method are the removal of calcium (Ca^{2+}) and magnesium (Mg^{2+}) through "water softening," the removal of bicarbonates through de-alkalization, and the removal of all ions through water desalination. Moreover, the ion-exchange method is also very efficient in removing various toxic heavy metal ions including radium (Ra), uranium (U), chromium (Cr), and several charged atoms or ions such as fluorides, nitrates, sulfates, perchlorates, and iron from wastewater (Al-Enezi et al. 2004). The main component of the ion-exchange method is a microporous exchange resin comprising of small, microporous beads that are insoluble in water and organic solvents. The most widely used base materials for ion-exchange resins are polystyrene and polycarbonate with a diameter ranging from 0.3 to 1.3 mm. These beads are composed of around 50% of a water-dispersed gel-structured material. As the water is homogeneously dispersed throughout the beads, the water-soluble materials and particles can freely move in and out of the beads. Each of the monomers in the polymer beads consists of a specific functional group that interacts with various ions through electrostatic interactions. In general, there are two types of ion-exchange resins: cation-exchange resins, which can remove most of the positively charged ions from wastewater including iron, lead, barium, copper, and aluminum, and anionic-exchange resins, which can remove negatively charged ions including nitrates and sulfates.

17.2.3 Adsorption

Adsorption is another wastewater treatment method, where water is passed through a layer of porous and granulated materials like activated charcoal and zeolites. It relies on a surface phenomenon with a common mechanism for the removal of organic and inorganic pollutants. When the wastewater passes through a highly porous surface, the impurities, such as dissolved organic and inorganic molecules, ions, and salts, are removed. Various physical and chemical interactions between the pollutants and the surface drive the adsorption of contaminants onto the surface. The particles retained at the solid surface are known as the adsorbate and the solid surface on which the adsorbate is retained is known as the adsorbent. The adsorption process is one of the most efficient methods of treatment for the removal of organic and inorganic contaminants from wastewater. The adsorption method has several advantages over other techniques because of its simple design and low investment of initial cost and infrastructure while also meeting stringent water quality standards. Adsorption has garnered the attention of many researchers throughout the years.

The adsorbents used during this process are classified as either natural or synthetic. Natural adsorbents include clay, charcoal, zeolites, and ores (Rashed 2013).

These natural adsorbents have several advantages such as being abundant in nature, relatively cheap, and possessing significant potential for modification to enhance their adsorption capabilities. Synthetic adsorbents are developed from household waste, agricultural waste, industrial waste, and polymers.

17.2.4 Biological Treatment

Biological treatment is typically a secondary wastewater treatment that uses bacteria, protozoa, and other specialized microbes to purify wastewater (Jessica et al. 2013; Liu et al. 2013). In this particular treatment, the microorganisms break down the organic pollutants into smaller pieces which stick together creating a flocculation effect allowing the organic contaminants to settle. Subsequently, the produced sludge is dewatered and disposed as a solid waste. Typically, biological wastewater treatment can be classified into three main categories: aerobic, where the microorganism require oxygen to break down organic matter and other contaminants into carbon dioxide (CO_2) and microbial biomass, anaerobic, where microorganisms break down organic pollutants in wastewater without using oxygen, often forming CO_2, methane, and microbial biomass, and anoxic, where microorganisms use other molecules besides oxygen for their growth. Anoxic biological treatments are commonly used for the removal of additional contaminants that are not possible through the other two methods, such as sulfates, nitrites, and selenates. The amount of organic contaminants that can be decomposed through aerobic biological treatment is measured in terms of the biological oxygen demand (BOD) which refers to the amount of dissolved oxygen required by the microorganisms for the breakdown of organic contaminants into smaller molecules (Tripathi and Shukla 1991). In general, biological wastewater treatment optimizes the natural microbial break down of waste and other contaminants into small molecules, which offers a cheap and efficient additional or alternative method for wastewater treatment (Busk et al. 1989).

17.3 Polymeric Membranes

In addition to these methods, another important and widely adopted method for wastewater treatment is the use of polymeric membranes. Polymers are widely used advanced materials and are found in nearly every material used on a daily basis. The significance of polymers has been highlighted in a plethora of applications in different domains of science, technology, and industry, including as biomaterials (Hasan and Pandey 2015; Hasan et al. 2017, 2018), smart materials (Rather and Manna 2016; Parbat et al. 2017; Vanessa et al. 2018), catalytic materials (Xu et al. 2019; Wang et al. 2017), and the removal of oil spills (Rather et al. 2017; Shome et al. 2019). In addition to these applications, polymers have contributed significantly to wastewater treatment.

Membrane separation technologies for wastewater treatment are increasing rapidly because of pressures from environmental protection laws and the strict regulations on drinking water quality all around the world. Recent advances in membrane-based purification technologies have led to a large utilization of synthetic polymeric membranes for wastewater remediation through the elimination of bacteria, viruses, and other toxic chemicals from the polluted and contaminated water resources. In this regard, the broader applications of synthetic polymeric membranes can be owed to their unique benefits, including the vast number of polymers which allow for the ability to select a specific polymer for the exact separation problem from an existing set of polymers (Visakh and Olga 2016). The removal of selected pollutants and contaminations from the aqueous phase using polymeric membranes can vary significantly and depends on the target pollutants and contaminants as well as several aspects, including the physiochemical properties of the constituents, the condition of operation, and the membrane structure.

To date, a number of polymeric membranes have been developed based on a variety of different components (Anna et al. 2016), such as cellulose acetate (CA), cellulose nitrate, polyethersulfone (PES), polysulfone (PS), polyvinylidene fluoride (PVDF), polypiperazine (PPZ), polypropylene (PP), and polyacrylonitrile (PAN). The first generation of polymeric membrane materials, CA membranes, were produced in 1963 from Loeb and Sourirajan's group and exhibited a high salt rejection with high flux values (Sidney and Srinivasa 1963). They also found applications in a wide range of filtration processes. However, these membranes lacked long-term thermal, biological, and chemical stability, which limits their practical applications in complex conditions including high temperature and extreme pH environments. With the development of other polymeric membranes, PS and PES have emerged among the most common choices for ultrafiltration systems as well as the secondary substrates for nanofiltration and reverse-osmosis processes. These polymeric materials have a high permeability, great selectivity, high mechanical stability, and high chemical resistance. For instance, PES usually has a high glass transition temperature (Tg) at approximately 225 °C and PS shows a high pH stability and oxidation resistance (Souzanchia et al. 2013). However, the main limitation of these polymeric membranes is their intrinsic hydrophobicity, which results in a high biofouling tendency and leads to higher operating costs, shorter lifespans, and irreversible separation performances.

To solve this problem, surface modification tools have been developed to enhance the hydrophilicity of these polymeric materials (Victor et al. 2014). It is generally accepted that increasing the surface hydrophilicity of the polymeric membranes reduces the fouling issues as many foulants, including organic contaminants and proteins, are hydrophobic in nature. There are a lot of methods to develop hydrophilic polymeric membranes, such as the homogeneous physical blending method (Sinha and Purkait 2013; Fan et al. 2014a, b), surface chemical treatment (Xia et al. 2014), and UV irradiation (Vázquez et al. 2005; Gu et al. 2009). Amphiphilic copolymers, like Pluronic F127, can be used as a surfaces modifier and pore-forming agent to prepare antifouling polyethersulfone (PES) ultrafiltration membranes (Zhao et al. 2008). Experimental results have shown that surface modification can be a robust and efficient solution for enhancing the antifouling properties (Rana and Matsuura 2010). Despite various other approaches, including grafting, hydrophilic modification, and etching, chemical modification is still considered to be the most facile and convenient method for surface modification. In the past, various polymers and surface-modified polymers with tunable surface properties have been explored for various applications, such as antibiofouling, nonspecific protein adsorption, and biocompatibility (Hasan and Pandey 2015). For instance, the amine functionalization of polymeric membranes significantly enhances the hydrophilicity and charge of the membranes. A membrane with more hydrophilicity and charge was found to foul less and better reject salts through increasing the electrostatic interactions (Zinadini et al. 2014).

Similarly, the pH sensitivity of polymeric membranes is another property that can be adjusted through a number of techniques. For example, functional polymers, such as polymethyl methacrylate (PMMA) and polyacrylic acid (PAA), can be mixed with polymeric membranes to enhance their pH sensitivity. Additionally, the shrinking and swelling of the pores of the polymeric membranes can be tuned through the deionization of carboxyl groups (–COOH) around their pKa which further enhances the permeability of the membranes (Mikaa et al. 1995; Kang and James 2007). The classic method of preparation for these membranes involves the direct blending of PAA with other polymers, so that the elution of PAA is possible even though it is water insoluble. For instance, Wei et al. reported a blending method to prepare tunable polymeric membranes by combining a cross-linked PAA gel with a PES solution by adopting a phase separation technique (Qiang et al. 2009).

Temperature-controlled water filtration is another class of functional polymeric membranes. A commonly used polymer is poly(N-vinylcaprolactam) (PVCL), a thermally responsive polymer with a lower critical solution temperature (LCST) in the physiological range. PVCL-based microgels can be explored to coat the commercially available hollow fiber membranes used for microfiltration and ultrafiltration-based applications (Daniel et al. 2014). The main advantage of these microgel systems is their versatility which allows them to be applied to almost any kind of membrane application by adopting a facile membrane fabrication process. In this instance, the membranes exhibited reversible, thermally responsive permeability and rejection (Young-Hye et al. 2011). The details of various polymeric membranes used for wastewater treatment, their applications, and methods of fabrication are presented in Tables 17.1 and 17.2.

17.3.1 Classification of Polymeric Membranes and Their Applications

The separation performance of porous polymeric membranes usually depends on the effective pore size of the polymeric membrane and the particle size of the constituent particles in the water. As the pore size shrinks, the driving force behind the process, typically the filtration pressure, increases (David et al. 2018). Polymeric membranes are broadly classified into four major categories, based on their pore size, performance, characteristics, and specific separation potentials. These four categories are

Table 17.1 Summary of the fabrication methods of various polymeric membranes used in microfiltration and ultrafiltration and their applications in waste-water treatment

Materials	Pore size	Method of fabrication	Applications	Advantages	Reference
Microfiltration and ultrafiltration	~0.1–1 µm				
Polyvinylidene fluoride (PVDF)	~1 µm	Block copolymer (PEO-b-PA)	Oil-water emulsion filtration	Significantly low-fouling propensity	Freeman and Pinnau ACS Symposium Series 2004 876:1–23
Polyvinylidene fluoride (PVDF)	~0.05–1.5 µm	Cellulose nanofiber (CNF) based PVDF membrane	Eliminate Fe_2O_3 nanoparticles and CV dyes from water	Ecofriendly	Deepu et al. ACS Sustain Chem Eng 2017 5:2026–2033
PVDF	~0.05–1.5 µm	Dimethyl Isosorbide (DMI) as the solvent, PVDF and polyethersulfone-based membranes	UF and MF for water treatment	Tunable pore size in the range of UF and MF	Francesca et al. ACS Sustain Chem Eng 2020 8:659–668
PVDF	~0.1 µm	Hollow-fiber MF/UF membranes	Drinking water production	Fouling mechanisms were investigated	Katsuki et al. J Membr Sci 2020 602:117975–117984
PVDF	~0.22 µm	Biomimetic coated PVDF UF/MF membranes	Underwater anti-oil adhesion behaviors; water remediation of simulated protein waste-water	Greatly enhanced wettability, good harsh condition tolerance, high filtration efficiency, and excellent fouling resistance	Xiaobin et al. J Membr Sci 2020 591:117353–117361
PVDF	~1 µm	Polydopamine (PDA) coated PVDF ultrafiltration membranes	Bovine serum albumin (BSA) and humic acid (HA) separation	Higher hydrophilicity, water permeation and flux recovery ratio (FRR)	Saraswathia et al. J Environ Chem Eng 2017 5:2937–2943
Polypropylene (PP)	~0.2 µm	Sericin-coated PP-based MF membranes	MF water treatment	High fouling resistance performances	Vishal et al. J Chem Tech Biotechnol 2019 94:3637–3649

PP	~0.2 μm	Pre-coagulation/ flocculation combined with low pressure membrane filtration through polymer	PP-UF membranes for virus and NOM removal in drinking water production	Without pre-coagulation/ flocculation, no (MF) or only minor (UF) virus removal was observed	Fiksdal and Leiknes J Membr Sci 2006 279:364–371
PP	~0.1 μm	Surface deposition of PDA on the membranes	MF membranes for water treatment	Improved fouling resistance performances	McCloskey et al. J Membr Sci 2012 413:82–90
PP	~0.2 μm	Poly[2-(dimethyl amino) ethyl methacrylate] grafted by sequential UV-induced graft polymerization	MF membranes for water treatment	A positively charged membrane surface achieved 100% antibacterial efficiency for tested bacteria	Yang et al. J Membr Sci 2011 376:132–141
Polyethersulfone (PES)	~9.35 μm	Surfactant modification (PSSS)	UF, Flux reduction in PEG and dextran solution	Good fouling resistant properties	Reddy et al. J Membr Sci 2003 214:211–221
PES	~0.5 μm	PDA coated PES UF membranes	UF water treatment	Good anti-fouling ability and enhanced blood compatibility	Chong et al. J Membr Sci 2012 417:228–236
PES	~5–200 nm	PDA coating and PEG grafting	PES-based UF membrane	Good anti-fouling ability	Fang et al, Desalination 2014 344:422–430
PES	~5–200 nm	Poly(ethylenimine) grafting PES-based UF membranes	UF	Good anti-fouling ability and good rejection for proteins	Zhen et al. J Membr Sci 2018 554:125–133
PES/PEG	~30 nm	PEG modified PES-based UF membranes	UF	Enhanced anti-fouling performance	Fan et al. J Membr Sci 2016 499:56–64
Polysulfone (PS)	~10 nm	Polymers, including MC, PVA and PVP	UF	Low deposition of BSA	Kim et al. Desalination 1988 70:229–249
PS	~5–7 nm	Blending with polyaniline nanofibers	UF, bovine serum albumin (BSA) and albumin egg (AE) rejection	High mechanical property and thermal stability	Zhifeng et al. J Membr Sci 2008 320:363–371

(continued)

Table 17.1 (continued)

Materials	Pore size	Method of fabrication	Applications	Advantages	Reference
PS	~0.8 μm	Spray coating of PS/PEG block polymer	UF	Pore sizes, hydrophilicity and UF performances are tunable	Wang et al. Chinese J Chem Eng 2020 https://doi.org/10.1016/j.cjche.2020.05.002
PS	~20–26 nm	PEG-b-PSF-b-PEG block copolymer	TFC FO membrane	Improve the water permeability and antifouling property	Seung et al. NPG Asia Mater 2019 11:8–21
PS	~1.9–7.5 μm	Polypyrrole-polysulfone blend UF membranes	UF	pH responsive behavior	Krishnasri et al. Sep Purif. Technol 2019 5:115736–115750
Polyacrylonitrile (PAN)	~20 nm	NaOH post-treatment	UF	Good anti-fouling property	Xiangli et al. Sep Purif Technol. 2007 3:265–269
PAN	~1 μm	UV assisted grafting polymers, including AA, HEMA, PEGMA, and POEM with various kDa	UF	Low protein-polymer surface interactions	Mathias et al. J Membr Sci 1996 115:31–47
PAN	~6.5 nm	Hydrolyzed ethanolamine-Polyacrylonitrile UF membrane	Dye-water treatment by UF	Excellent anti-dye fouling and a good rejection property for anionic dyes	Jianhua et al. Chemosphere 2020 3:127390–127400
PAN	~2 μm	Synthesized from polyacrylonitrile (PAN) and hydrophilicly modified polyacrylonitrile (HM-PAN)	UF for water treatment	Fouling of protein particles on the blend membranes was able to reduce as the composition of HM-PAN increases	Bumsuk J Membr Sci 2004 229:129–136
Poly(sulfobetaine methacrylate) (PSBMA)	~0.2 μm	PSBMA/PDA co-deposited coating	Application in protein separation	Excellent hydrophilicity, low water flux reduction and high-water flux recovery; good stability in a long-term washing	Rong et al. J Membr Sci 2014 466:18–25

RC-g-PSBMA membrane	~0.2 μm	Atom transfer radical polymerization (ATRP) of a zwitterionic monomer, sulfobetaine methacrylate (SBMA)	Application for protein purification (BSA)	Tunable permeation selectivity	Yong-Hong et al. ACS Appl Mater Interf 2010 2:203–211
Poly (n-isopropylacrylamide) (p(NIPAm))	~20 nm	Co-deposition of stimuli-responsive microgels in the foulant cake layer	Filtrations were done below the lower critical solution temperature (LCST) and temperature was increased to above the LCST for cleaning	Increased fouling reversibility	Canan et al. ACS Appl Mater Interf 2019 11:18711 – 18719
Poly(ethylene glycol) (PEG)	~12.3 nm	Controlled deposition of zwitterionic polymers and PEG	UF	High-performance, antifouling membranes	Kerianne et al. Langmuir 2019 35:1872–1881
Polyacrylonitrile-block-polyethylene glycol (PAN-b-PEG)	~5 nm	Immersion precipitation phase inversion	UF for water treatment	The antifouling ability of the copolymer membranes increased with increasing PEG content in the copolymer	Xiangrong et al. J Membr Sci 2011 384:44–51
Cellulose-acetate (CA)	–	PEG grafting	UF	Modified surface can decrease the fouling tendency	Morao et al. Environ Prog 2005 24:367–382
CA	–	Zwitterionic brushes-modified cellulose membrane	UF for water treatment	Good anti-biofouling ability and cytocompatibility	Liu et al. J Mater. Chem B 2014 2:7222–7231
Poly(vinyl alcohol) (PVA)	~1 μm	Electro-spinning	Selective and high adsorption of lead (Pb(II)) and cadmium (Cd(II)) ions	High adsorption capacity of Pb(II) and Cd(II)	Karim et al. Ecotoxicol Environ Saf 2019 169:479–486

(continued)

Table 17.1 (continued)

Materials	Pore size	Method of fabrication	Applications	Advantages	Reference
Poly(ether ether ketone) (PEEK)	~20 nm	Photo-induced polymerization	Bovine serum albumin (BSA) separation	Good permeability and antifouling performances	Tingjian et al. Mater Today Commun 2020 23:100945–100952
Poly(phthalazinone ether sulfone ketone) (PPESK)	~10 nm	(Atom transfer radical polymerization) ATRP	UF and BSA filtration	Good anti-fouling property	Li-Ping et al. J Membr Sci 2008 320:407–415

Table 17.2 Summary of the fabrication methods of various polymeric membranes used in nanofiltration and reverse osmosis and their applications in wastewater treatment

Materials	Pore size	Method of fabrication	Applications	Advantages	Reference
Nanofiltration and reverse osmosis	~0.5–10 nm				
Poly(m-phenylene isophthalamide) (PMIA)	2 nm	Phase inversion	Chromium (Cr IV) ion removal from waste-water	Enhanced water permeability	Ren et al. J Environ Sci 2010 22:1335–1341
Piperazine	~5–8 nm	Interfacial polymerization	High salt rejection (98%)	Higher chemical stability	Roy et al. Desalination 2017:420 241–257
PVA-Al_2O_3	~3–5 nm	Assimilation of PVA/PAA/GA into the microporous ceramic substrate	Dye waste-water treatment, desalination	Performs at higher pH	Wang et al. AIChE J 2013 59:3834–3842
Polyether sulfone (PES)	~4–6 nm	Electron beam irradiation method	Recovery of 1-(5-bromo-fur-2-il)-2-bromo-2-nitroethane	Above 80% of rejection was observed	Martinez et al. J Ind Eng Chem 2012 18:1635–1641
Polysulfone	~4–10 nm	Interfacial polymerization	Removal of Cr (VI) ions from waste-water	Exceptional chlorine resistance	Hong-mei et al. Desalination 2014 346:122–130
Polymerization of tetraethylenepentamine and 1,3,5-benzenetricarbonyl trichloride with the addition of $CaCl_2$	~6 nm	Layer by layer assembly	Inorganic dye removal	Enhanced chlorine resistance, rejection of various inorganic slats	Fan et al. J Membr Sci 2014 452:90–96
Polyelectrolytes Polydiallyldimethylammonium chloride (PDADMAC) and polysodium-4-styrenesulfoate (PSS)	~7–10 nm	Layer by layer assembly	Removal of inorganic salts from aqueous solution	Rejection of bivalent salts including $MgSO_4$	Law et al. Desalination 2014 351:19–26

(continued)

Table 17.2 (continued)

Materials	Pore size	Method of fabrication	Applications	Advantages	Reference
Cellulose acetate membranes with surface adsorption of ALG/CHI multilayer	~3–8 nm	Phase inversion	Removal of heavy metal ions	Rejection of bivalent ions and various organic impurities	Ramzi et al. Desalination 2011 266:78–86
Amine-functionalized multiwalled carbon nanotubes (NH_2-MWCNTs)/polyether-sulfone (PES) nanocomposite	~6–10 nm	Phase inversion	Removal of bivalent inorganic with high water flux	Increase in hydrophilicity, high stability	Vahid et al. J Membr Sci 2014 466:70–81
Blending of O-carboxymethyl chitosan/Fe_3O_4 nanoparticle on Polyethersulfone (PES)	~7.5 nm	Diffusion-induced phase inversion	Inorganic dye removal from water	Enhanced antifouling resistance and water permeation	Zinadinin et al. Desalination 2014 349:145–154
Polyethersulfone membrane blended with ZNO nanoparticles	~7 nm	Immersion precipitation	Inorganic dye removal	Enhanced antibiofouling property	Stefan et al. J Membr Sci 2012 389:155–161
Polysulfone (PSF) membranes blend with IGEPAL	~8–10 nm	Grafting	Removal of Cd from waste-water	Improved hydrophilicity	Saljoughi and Mousavi Sep Purif Technol 2012 90:22–30
Polyamide membranes modified with poly(ethylene glycol) diglycidyl ether	~3–5 nm	Grafting	Removal of salt with high efficiency	Good fouling resistance	Elizabeth et al. J Membr Sci 2011 367:273–287
Grafting poly (amidoamine) dendrimer (PAMAM) on the polyethersulfone (PES) membranes	~5–8 nm	Grafting	Removal of various types of surfactants with high efficiency	Improved water permeability and antibiofouling	Zhu et al. J Membr Sci 2015 487:117–126
Quaternary ammonium compounds (QACs) grafted on PVDF membrane	~6–8 nm	Atom-transfer radical-polymerization (ATRP)	Waste-water treatment	High inhibition rate	Ping et al. J Membr Sci 2019 570:286–293

Chitosan (CS) was blended with PVDF to prepare mixed matrix membrane	~3 nm	Phase inversion	Reduction of fouling	Improved hydrophilicity	Elizalde et al. Sep Purif Technol 2018 190:68–76
Reverse Osmosis	>0.5 nm				
Silver blended asymmetric cellulose acetate (CA) hollow fiber membrane	~ 0.2–0.5 nm	Jet-wet spinning	Removes dissolved salts and allows water only	Increase in biological stability	Chou et al. Polym Adv Technol 2005:16 600–607
Coating phospholipid polymer on CA membrane	~0.4 nm	Jet-wet spinning	Rejection of biological pollutants	Increase in fouling resistance	Sang et al. J Membr Sci 2005 249:133–141
Polyamide thin film composite (TFC) with triethanolamine (TEOA)	~0.3 nm	Interfacial polymerization	Treatment of industrial effluents	Antifouling against hydrophobic foulants	Yan et al. J Membr Sci 2016 513:108–116
Polyamide TFC over a microporous PES substrate	~0.2 nm	Interfacial polymerization	Inorganic salt removal	Antifouling against hydrophobic foulants	Khorshidi et al. Sci Rep 2016 6:22069–22078
Hollow fiber membrane from cellulose acetate (CA)	~0.3–0.5 nm	Thermally induced phase separation	Antifouling property for humic acid and BSA	High hydrophilicity and high water-permeability	Shibutani et al. J Membr Sci 2011 376:102–109
Polyamide TFC with carbon nanotubes and graphene oxide	~0.4 nm	Interfacial polymerization	Improved fouling resistance towards various proteins and polysaccharides including BSA, sodium alginate	Good separation performance and chlorine resistance	Simcik et al. Sep Purif Technol 2016 167:163–173
Polyamide TFC with aluminosilicate single-walled nanotubes	~0.6 nm	Interfacial polymerization	Removes salt and allows water	Improved membrane performance, long term durability	Kim et al. J Mater Chem A 2015 3:6798–6809
Polyamide TFC with ordered mesoporous carbons	~0.1–0.4 nm	Interfacial polymerization	Higher permeate flux and high rejection of monovalent and divalent ions	Increase in hydrophilicity	Baroña et al. Desalination 2013 325:138–147
Codeposition of dopamine/PSPE coating on polyamide	~0.2–0.4 nm	Interfacial polymerization	Removal of monovalent and divalent salts	Increase in hydrophilicity and limiting protein adsorption	Kim and Deng J Membr Sci 2011 375:46–54

(continued)

Table 17.2 (continued)

Materials	Pore size	Method of fabrication	Applications	Advantages	Reference
Zeolite nanoparticles dispersed polyamide films	~0.2–0.5 nm	Interfacial polymerization	Water purification	High salt rejection	Jeonga et al. J Membr Sci 2007 294:1–7
Copolymer, poly (vinylpyrrolidone)-co-poly (sulfobetaine methacrylate) (poly(VP-co-SBMA)	~0.1–0.3 nm	Copolymerization	Thermosettable materials in a bioinert interface for medical devices	Thermal-tolerant and fouling-resistant	Chou et al. ACS Appl Mater Interf 2015 7:10096–10107
Nano-NaX zeolite embedded into polyamide films	~0.3–0.4 nm	Interfacial polymerization	Desalination	High thermal stability	Fatizadeh et al. J Membr Sci 2011 375:88–95
TFC of polyamide Aminophend/formaldehyde resin	~0.5 nm	Interfacial polymerization	Desalination above 96%	Excellent anti-chlorine, anti-fouling and reuse performances	Wang et al. J Membr Sci 2020 https://doi.org/10.1016/j.memsci.2020.118496
Crosslinking of amine-functional polyamidoamine (PAMAM)dendrimers and PAMAM–polyethylene glycol (PAMAM–PEG)	~0.2–0.5 nm	In situ crosslinking	Salt removal	Low contact angle and high salt rejection	Sarkar et al. J Membr Sci 2010 349:421–428

microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. The utility and applications of these membranes in various filtration techniques are detailed below.

17.3.1.1 Microfiltration and Ultrafiltration

Microfiltration (MF) is classified as a low-pressure process, with an operating pressure typically below 2 bar. The separations using MF operate through filtering and removing the suspended particles or solids, bacteria, protozoa, and, to a lesser extent, algae, owing to the relatively larger pore size between 100 and 1000 nm (Baker 2012). However, microscopic particles, atomic or ionic species, dissolved particles, natural organic matter, and water can pass through the filter membrane (Crittenden et al. 2012), as depicted in Fig. 17.1. These types of polymeric membranes can generally separate macromolecules of molecular weight less than 100 kDa (Siobhan et al. 2002). The MF membranes are commonly used in the sugar and sweetener industry, dairy industries, and in bioprocessing industries. For example, in the dairy industry, the MF method is mainly used to remove the fat from whey in the production of whey protein isolates, in the purification of cheese brine, and in the separation of casein and serum from skim milk.

Ultrafiltration (UF) membranes also operate mainly through filtering; however, UF membranes possess a wider range than MF membranes with a pore size that is generally between 2 and 100 nm. UF is also considered a low-pressure process and typically operate between 0.1 and 5 bar. Additionally, they are dependent on the transmembrane pressure to drive the separation process. These types of membranes are capable of separating large materials, such as colloids, proteins, enzymes, fats, and bacteria, while allowing sugars, salts, and other low molecular weight solids to pass through, as shown in Fig. 17.1 (El-Dessouky and Ettouney 1999). In this separation process, the separation range is expressed in daltons (Da) or kilodaltons (kDa) and is usually in the range of 1 Da or 100 KDa. For instance, Su et al. used the

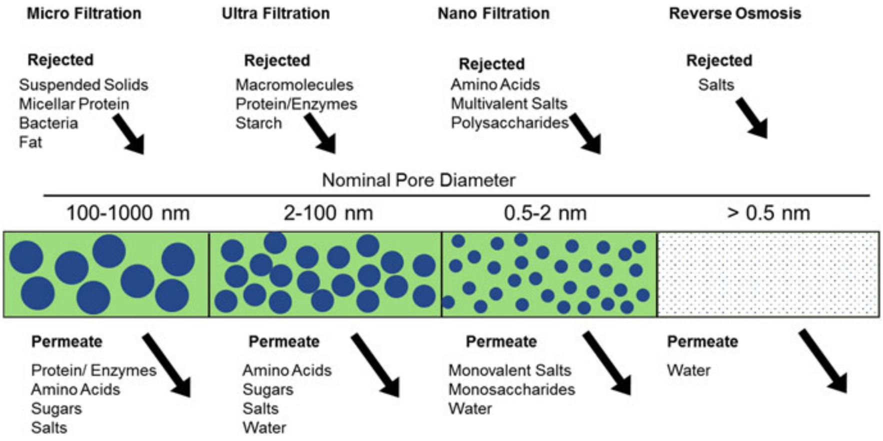

Fig. 17.1 The schematic illustration displays the nominal pore diameter and various pollutants allowed and rejected by various filtration techniques using different polymeric membranes

combination of UF and electrodialysis (ED) for the treatment of a copper slurry (Su et al. 2014). The combined setup of UF and ED removed particles and Cu^{2+} from the slurry through the use of a PVDF flat sheet membrane with a molecular weight cutoff of 30 kDa, corresponding to roughly 4 nm in diameter, while possessing a high mechanical strength.

The elimination rejection achieved by MF and UF polymeric membranes usually depends on the properties of the polymeric membranes and hydrodynamic conditions (Fane et al. 2011). Therefore, interferences in the upstream wastewater treatment process can negatively influence the performance of both MF and UF polymeric membranes.

17.3.1.2 Nanofiltration and Reverse Osmosis

Nanofiltration (NF) refers to the category of polymeric membranes which possess pore sizes in the range of 1 to 10 nm that are operated at high pressure, typically around 3 to 20 bar. The separation range in NF is classified on the basis of rejection of known multivalent cationic solutes including magnesium sulfate ($MgSO_4$) and by the removal of disinfectant by-products including natural and synthetic organic matter (Raymond 1999; Roy et al. 2017). In general, a typical NF membrane can retain the molecules of varying sizes below and above the pore size of the polymeric membranes (Bruggena et al. 2008). The membranes used for nanofiltration are made of polymer thin films which include PET, PS, PES, or PPZ polymers (Lu et al. 2002; Gopal et al. 2006; Tolba et al. 2015). NF membranes can efficiently remove divalent ions, polysaccharides, and small organic molecules while permitting monovalent ions, water, and monosaccharides, as shown in Fig. 17.1. NF membranes operate at lower pressures and have a higher water permeability than reverse-osmosis systems, thus reducing the specific energy consumption. These properties enable the NF membranes to be applicable in wastewater treatment, biotechnology, pharmaceuticals, and food engineering applications. For instance, Ren et al. demonstrated the sustainability of using poly(m-phenylene isophthalamide) (PMIA) NF membranes for the removal of chromium (Cr) ions from wastewater (Ren et al. 2010). The separation mechanism was mainly based on the interaction of Cr(IV) and the negatively charged NF polymeric membrane. Moreover, NF membranes have also been used to treat seawater, where high recoveries of salt water are possible at reasonable pressures as the membrane allows most of the Na^+ and Cl^- ions to pass through while retaining the unwanted sulfate ions (Davis et al. 1996). It is worth noting that previous research has indicated that NF membrane systems can achieve a higher recovery through nonthermal crystallization (Azadi et al. 2016) and can reduce the second level fouling through pre-ozone treatments (Parka et al. 2017).

Reverse osmosis (RO) is another wastewater treatment process that utilizes a semipermeable membrane to remove various ions, unwanted organic and inorganic molecules, and large particles from drinking water. RO membranes possess pore sizes below 1 nm and operate at high pressures, around 5 to 120 bar. RO is a very versatile method that can remove many types of suspended and dissolved chemical and biological contaminants, including bacteria and salts (David et al. 2016), which brands it a great source for use in industrial processes and the production of potable water. Interestingly, salts are highly rejected by RO membranes owing to their sub-nanometer scaled pores, commonly used in the removal of salt from seawater (Argyris et al. 2019). For instance, commercial seawater RO membranes can remove 99.5 to 99.8% of NaCl from the seawater. Important polymers that are being used in RO processes include polyamide, cellulose-acetate, cellulose-diacetate, and cellulose-triacetate (Yang et al. 2019). Furthermore, RO is considered as a complete barrier for pathogens, bacteria, and other microorganisms that are harmful to infants and the elderly. For instance, in a previous study of RO based wastewater treatment, it was found that neither *Escherichia coli* nor viruses were detected in the permeate after filtration through the RO polymeric membrane (Tama et al. 2007). Moreover, RO membranes were further found to be beneficial in eliminating high molecular weight organic constituents, such as humic acid and fulvic acid (Rodriguez et al. 2009).

17.3.1.3 Challenges Associated with Polymeric Membranes

Although wastewater treatment using polymeric membranes has shown great potential, there are still several technical challenges that need further investigation and research. Some of the challenges are detailed as below:

1. Polymeric membrane fouling and scaling will lead to the increase of water cost. Fouling and scaling are the accumulation of materials deposited on the polymeric membranes. They usually result in pore clogging and, eventually, decreased flux. Therefore, a regular and periodic cleaning of the polymeric membranes is inevitable, and the expenses associated with filter changes is another hassle that can increase costs.
2. The selectivity of the polymeric membranes to specific waste materials is very important, which is restricted depending on the membrane surface charge and the pore size. However, they require a large amount of energy to maintain high pressure during purification in practical applications. In addition, the fouling-driven decline in polymeric membrane permeability leads to a reduction in the flux. This increases the pressure needed to keep a normal level of flux. Hence, the performance under constant high pressure is a substantial challenge for wastewater treatment using polymeric membranes.
3. Some of the polymeric membrane filtration techniques require some pretreatment methods for some heavily polluted wastewater. These pretreatments include the addition of chemicals or the use of other treatment methods, both of which increase the cost of using polymeric membranes.

17.4 Outlook and Conclusions

Global water scarcity is growing rapidly in many regions of the world due to an increase in human activities and the growth of agricultural and industrial needs. On top of this, unmanaged wastewater streams have caused the pollution of many existing fresh water sources. Problems with water are expected to grow in the coming decades and water scarcity is expected to appear in many new regions, including those that are currently water rich. Hence, the treatment and reuse of wastewater is a critical issue. In this chapter, we have discussed various conventional methods including chemical precipitation, ion exchange, and adsorption for wastewater treatment. However, these methods have various limitations including a high cost, restrictions to their applications, a high energy input, and the generation of large quantities of sludge during treatment.

In addition to these conventional methods, another class of water treatment using polymeric membranes has been extensively studied and used in a number of applications, including wastewater treatment. Moreover, we have conferred in detail that the separation performance of porous polymeric membranes usually depends on the effective pore size of the polymeric membrane and the size range of contaminants present in water. As the pore size shrinks, the separation process requires a higher driving force, which is typically the filtration pressure. Moreover, we have discussed the four major categories of polymeric membranes of wastewater treatment, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, based on their performance, characteristics, pore size, and specific separation qualities. Their applications in wastewater treatment were discussed briefly in this chapter. Additionally, the benefits of polymeric membranes include a series of outstanding properties, such as high flexibility, excellent chemical and mechanical durability, high permeability of water, chemical species selectivity, and efficient removal of waste products. Hence, the development of polymeric membrane technology has allowed for the next generation of water supply systems to advance beyond the conventional and traditional methods with a more affordable price and higher efficiency.

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