Chapter 2

Advanced Functional Membranes for Microfiltration and Ultrafiltration

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Abstract

In the era of freshwater scarcity, the world seeks to limit overexploitation of all accessible resource of freshwater and also to recover potable water by treating wastewater. Various domestic, agricultural and industrial activities lead in generating high amount of wastewater from which water can be recovered for human needs. Over many years, conventional filtration process has gained success to some extent in effluents treatment for disposal. Yet, improvement in filtration process is necessary for advanced wastewater treatment in order to make the whole process handy and cost-effective. The functionality of membrane can be enhanced by incorporating polymers with novel functions in advanced membrane separation methods like microfiltration (MF) and ultrafiltration (UF) for reclaiming potable water from wastewaters, catalysis and biomedical applications. This book chapter mostly focuses on the use of different polymeric substances for MF and UF membrane preparation and their application in various sectors. Basic principle, novel manufacturing techniques for polymeric membrane, process design i.e., synthesis of polymers as designed membrane feedstock, surface modifications, synergistic fabrication of different polymers for advanced functionality, antifouling and antibacterial properties of membrane are also discussed.

Keywords

Filtration, Membrane Technology, Polymer Membrane, Wastewater, Purification, Potable Water

Abbreviations

BOD Biological oxygen demand

CA	Cellulose acetate
CEB	Chemically enhanced backwashing
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibers
COD	Chemical oxygen demand
CPCB	Central Pollution Control Board
HCl	Hydrochloric acid
HNO ₃	Nitric acid
H ₃ PO ₄	Phosphoric acid
H ₂ SO ₄	Sulphuric acid
MF	Microfiltration
MLD	Million liters per day
MW	Molecular weight
MWCO	Molecular weight cut off
NaOH	Sodium hydroxide
NC	Nanocellulose
NF	Nanofiltration
PAN	polyacrylonitrile
PE	Polyethylene
PES	polyethersulfone
PP	polypropylene
PTEE	Poly tetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	polyvinylidene fluoride
TDS	Total dissolved solid
TMP	Transmembrane pressure
TOC	Total organic carbon
TSS	Total suspended solid
RO	Reverse osmosis
UF	Ultrafiltration

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1. Introduction

Water is a crucial need for mankind and thus all human activities are associated with it. It plays a noteworthy role in the socio-economic growth of any population. Most countries around the world are still facing shortage to meet the need of potable water. Even though, water covers almost 71% of the Earth's surface, hardly 2.5% of this amount is fresh water out of which 1% is accessible for consumption and the rest is found in snowfields and glaciers [1]. It is obvious that the world is facing scarcity of freshwater distribution among various industries, urban and rural areas [2]. Consequently, developing countries and agricultural activities are heavily affected by the lack of sufficient water resources for livestock production and irrigation purposes. The evidence of such circumstances is

observed across the world, especially in Asia, Africa, Middle East, and Latin America. On the other hand, freshwater resources takes several years to replenish again which is not sufficient for growing needs of human activities [3]. Therefore, it is necessary to search for an alternative water resource to mitigate the insufficiency of freshwater and that could be sea water, wastewater, etc. Huge amounts of wastewaters are generated everyday domestically, industrially and from agricultural areas with the increasing activities of populations. As per Ministry of Water Resources, River Development and Ganga Rejuvenation, wastewater generation from different industries (Food, dairy and beverages; Textile, bleaching and dyeing; Sugar; Distillery; Chemical, Tannery; Pulp and paper; and others) of India was 501 MLD (million litres per day) [4]. However, based on Central Pollution Control Board (CPCB) generation of sewage was 61948 MLD out of which only 23277 MLD were treated. As a result, around 38000 MLD of untreated sewage was directly discharged into nearby land or water bodies [2].

Generation of wastewater is inevitable as it generates during essential activities of the value chain in all parts of life. Wastewater contains higher concentration of minerals, pathogens and toxic compounds which make it undrinkable and worthless for reuse without treatment. The favorable way of resolving these problems is separation process. UF and MF are the typical pressure driven membrane-based well-established separation system in industrial scale [5]. Such separation technologies are mainly based on the application of polymeric membrane and represent a sustainable approach towards resolving the particulate and macromolecule-based separation process. MF and UF can be a suitable alternative as no chemicals or phase changes are required like other separation methods i.e. adsorption, distillation, fractionation, extraction, etc., [6]. Addition to that, the relative simplicity of operation, less energy consumption, low weight, minimum space requirements, modularity, easy scale-up, and possibilities of carrying out the continuous separation process are the advantages of MF and UF [7, 8]. The utilization of these filtration methods is emerging in industrial scale since the last 50 years. The markets for membrane science are highly diverse i.e., from chemical to medicine or pharmaceutical industry. However, this chapter mainly focuses on wastewater treatment and gas separation by filtration technology.

The objective of this chapter is to discuss the preparation of different polymer-based functional membrane with novel properties and their application in treatment of water and wastewater. It also gives general ideas on synthesis, fabrication and synergistic combination of various polymeric materials in membrane preparation. Basic principle of membrane filtration process, their manufacturing technology, process design, antifouling and antibacterial properties of membrane are also discussed.

2. Basic principle of micro- and ultrafiltration

Filtration is a separation process by which insoluble materials are removed from the gaseous or liquid solution based on their physical as well as chemical properties by use of a membrane or filter [9]. This membrane or filter medium allows the liquid or gas to pass through and retains the solid particles. Therefore, membrane is described as a barrier that segregates two phases from each other by limiting the movements of compounds through it in a control manner [3,10-12]. Such compounds include ions, molecules, and other small particles. The desired products will be either the clarified liquid (also known as ‘filtrate’) or the solid retained/collected in the filter medium (‘retentate’ or ‘residue’) [13]. Filtration is used in many laboratories to minimize the complexity of sample, improve clarity of viscous solutions, and to prepare the sample for analysis. Depending on the filtration method applied, particles or molecules are removed based on their shape, charge or size.

Conceptualization of filtration process by membrane technology was known since 18th century. Unlike other unit separation process in bio-chemical engineering (adsorption, distillation, etc.), the superiority of membrane technology is based on distinctive separation principle, i.e., specific transport phenomena of filter medium. Its degree of selectivity mainly relies on pore size distribution and thus classified as– microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [14-16]. Table 1 illustrates comparison between different pressure-driven filtration processes as per membrane pore size. Fig 1 shows retention and permeation of various sizes of particles via membrane. Membrane technology has recently gained success due to the non-requirement of additives, efficient isothermal performance at low heat and thus less consumption of energy as compared to other thermal separation process. In addition to that, downscaling and up scaling of membrane technology, integration and fabrication into other reaction process are simple. The main objective of membrane technology is to remove bacteria, viruses, organic material, microorganisms, and particulate matter from water, wastewater and polluted gas. However, this excludes the removal of taste, odor and colour of water and gas. The first application of membrane on a large scale was with MF and UF.

2.1 Microfiltration

It is one of most desired separation processes for wastewater treatment and its background was started in 1920s. Commercially available first MF membrane was prepared from nitrocellulose in 1926. Though, in 1940s the usage of MF membranes increases, however, it was little limited in the small-scale industries and laboratories till 1960s. In-line or dead-end mode of filtration is the most commonly used process for MF. Cross-flow mode was introduced in the year 1970s to MF and thus its application increases to large industrial scale. After few years, third type of MF was emerged as semi-dead-end filtration. In 1990-

93, MF/UF was installed for first time in order to treat surface water [17-18]. MF is generally used for the segregation of suspended particles with diameter in the range 0.1 - 10 μ m from a fluid mixture. This range of particles includes a wide variety of natural and industrial materials. The solute separated by MF is typically larger than those separated by UF and NF and thus negligible for RO. The pore diameter and permeate flux is also greater for MF than UF, NF and RO.

Table 1 Membrane separation process based on pore size distribution.

	Particle size (μ m)	Molecular weight (Da)	Pressure bar	Separation mechanism	Particle characteristics	Removable particles	Material retained	Ref
MF	0.1 – 1	10 ⁵ - 10 ⁶	0.5 – 1	Molecular sieve	Macromolecular to cellular	Water, Bacteria, cells, polymers, colloids, humic acids, oil emulsions	Bacteria, suspended particles	[3, 15, 16, 19, 20, 40, 75]
UF	0.01 – 0.1	10 ³ - 10 ⁵	1 – 10	Solution diffusion	Molecular to macromolecular	Small colloids, humic acids, protein, viruses, pesticides, polysaccharides	Glucose, lactose, salt, micropollutants	[3, 15, 16, 19, 20, 35, 76]
NF	0.001 – 0.01	100 - 1000	5 – 70	Molecular sieve	Ionic to molecular	Pesticides, endocrine disruptors, salts	Colloids, macromolecules	[3, 15, 16, 20, 77-80]
RO	0.0001 – 0.001	100	10 – 100	Molecular sieve	Ionic	All contaminants including monovalent ions	Dissolved salts	[15, 16, 20, 81-83]

2.2 Ultrafiltration

UF is a powerful and novel separation process that is used for the fractionation of micro-solutes and water from macromolecules, colloids and protein. It is carried out by a finely porous filter medium (membrane) of size ranging in 50 to 1 nm. The MWCO for UF membranes ranges 1,00,000 to 2,00,000Da [15]. Membranes used in UF are characterized by pore size in the range 0.001-0.1 μ m able to retain species. The retentate for UF includes sugars, polymers, proteins, biomolecules and colloidal particles whereas salts whilst solvent will pass through the membrane. Both MF and UF process mechanism works on the principle of separating the molecules using porous membrane as per their pore size distribution [19]. UF often operated in tangential direction of upstream surface of membrane. However, membrane fouling by protein accumulation is a major limitation of UF membranes.

The required driving force for transport facility through MF and UF filter medium is a pressure gradient which forces the suspended solid and solutes to pass through the membrane where they are accumulated as permeate and retentate. As MF and UF do not typically reject salts, the pressure gradient is very less (1 -10 bar) as compared to RO.

The rejection efficiency R of a membrane is evaluated by:

$$R = 1 - \frac{C_p}{C_r} \quad (1)$$

Where C_p denotes concentration of permeate and C_r represents retentate concentration in mol.m^{-3} . R is the function of pore size, particle size and porosity.

Figure 1 Retention and permeation of particle size via membrane [16, 20]. Redrawn. Permission is taken from Elsevier.

The rejection phenomena of MF and UF membranes are generally demonstrated by minimal molecular weight cut off (MWCO) that is expressed as MW of smallest species retained by the membrane. Alternatively, the permeate flux across porous filter medium is affected by pressure gradient applied on the membrane, membrane resistance and the viscosity of fluid to be passed. The volumetric flux is determined by-

$$Q_v = \frac{P(\Delta p - \Delta \pi)}{l} \quad (2)$$

Where Q_v is volumetric flux, P is co-efficient of permeability, l is membrane thickness in m, Δp and $\Delta \pi$ is hydrostatic and osmotic pressure gradient (Pa) respectively.

Figure 2 Filtration mode for MF and UF membrane [20].

MF and UF membranes can be employed for both cross-flow and dead-end filtration [21] as shown in Fig 2. In dead-end mode, solution is fed perpendicularly across the filter medium under sufficient pressure and rejected particles (retentate) are accumulated on the surface. To maintain the flow, pressure increases to some extent that membrane should be replaced. In contrast, feed solutions are supplied tangentially through the membrane in

cross-flow filtration in order to get clean, particle free permeate [22, 23]. Even though, the infrastructure require for cross-flow mode is more difficult, but membrane lifespan and flux rate are relatively higher than dead-end filtration [24].

Dead-end mode is most favorable choice for batch studies, but for continuous process cake formation occurs due to the deposition of retentate which eventually reduces the membrane flux [25, 26]. This cake layer can be removed by backwashing (flow from opposite direction of feed stream) and thus the operation must be stopped [27]. In contrast, cross-flow mode allows continuous feed stream and the tangential flow direction helps in keeping membrane clean by scouring velocity.

3. Polymeric materials for membrane preparation

Significant advantages of polymeric substances than inorganic materials (metals and ceramic) for membrane preparation in order to execute separation process include:

- high flexibility
- segments and functional groups for specific applications
- high selectivity for target separation
- less expensive
- low energy consumption

MF and UF membranes are usually fabricated by natural polymers such as cellulose derivatives and synthetic polymers i.e. synthetic polymer like cellulose acetate (CA), polypropylene (PP), polyacrylonitrile (PAN), perfluoropolymers, polyamides, polysulfones, polyvinylidene fluoride (PVDF), polyethersulfone (PES), etc. [6]. Lots of literature reviews are reported about the structure and novel functions of advanced polymeric membrane. MF and UF membranes are generally prepared using these polymers and by phase inversion methods [28].

Aliphatic polyamides like nylon-6, nylon 4-6, and nylon 6-6 are extensively used as MF membranes and characterized by good thermal, chemical, and mechanical stability. Amorphous polymers are generally used to prepare UF membranes owing to their convenient resolution and control of small pore size. Polymeric materials which have a glass transition temperature are generally employed. In particular, polyacrylonitrile (PAN) widely used for general aqueous systems because of its resistance to solvents and chemicals, also exhibits relatively low protein binding owing to its hydrophilic properties. Polysulphone (PS), also widely used in the production of UF membranes, has good

mechanical strength and resistance to heat and pH; in contrast it exhibits poor resistance to solvents.

3.1 Biopolymers

Utilization of organic polymers for membrane preparation has extensively increasing due to their unique properties. Their shape, size and structure can be altered as required for a specific application. In spite of not being a novel material for membrane preparation, the renewable characteristics of cellulose are of great interest. In addition, cellulose has stability in wide range of solvents [29]. Nanocellulose (NC) i.e. cellulose nanofibers (CNF) and cellulose nanocrystals (CNC) for MF and UF membranes can be a sustainable alternative towards molecular separation process [30].

3.2 Amphiphilic polymers

Amphiphilic polymers includes both hydrophilic (water loving) and hydrophobic (water-hating) polymers. Though hydrophilic substances are incorporated for the manufacture of MF and UF membrane, but it is not suitable as water molecules act as plasticizers affecting thermal stability and mechanical strength. Crystalline polymer possesses high thermal stability and chemical resistance since the crystalline domain contributes to effect of cross-linking between amorphous domains and hinders the free rotation of polymer segments. MF membranes generally consist of crystalline polymers. Polytetrafluoroethylene (PTFE), poly (vinylidene fluoride) (PVDF), polypropylene (PP), are typical hydrophobic polymers widely used as MF materials. Hydrophobic materials are also widely used to minimize adsorption phenomena which reduce permeate fluxes and create difficulties in membrane cleaning.

3.3 Thermoplastic polymers

Thermoplastic polymers, also known as thermo-softening plastics, are defined as a polymer material which becomes moldable or pliable at a specific elevated temperature and solidifies at low heat. Example of thermoplastic polymers includes polypropylene (PP), polystyrene, polyvinyl chloride (PVC), polyethylene (PE), etc. Superiority of such polymer over other polymeric substance includes:

- These are light weight
- it has high strength
- it is recyclable
- it is high molecular weight polymer
- these can be reshaped by heating and cooling

- intermolecular force acting between polymer chains becomes weak upon heating and thus allows a liquid with high viscosity

4. Membrane filtration technology

Membrane filtration technology is an effectual separation process as compared to other conventional methods and has gained huge interest in industrial scale over last few decades. Besides solid, liquid and gas separation, membrane can also separates negative or positive charge, neutral or bipolar [1]. In the separation process, membrane or filter medium firstly act as a semi-permeable barrier and then it transports the particles through it. As an effective process, membrane technology is most favorable technique for oily wastewater treatment (by separating oil from the wastewater), in fuel cell industries, food industries, pharmaceutical, desalination, etc.

4.1 Membrane characteristics

Membranes are generally thin films. On the basis of its structure, membranes are classified into various categories namely isotropic (or symmetrical), non-isotropic (or asymmetrical), homogeneous and non-homogeneous, porous and non-porous [31]. Table 2 shows various characteristics of membrane applicable for separation process.

Table 2 Characteristics of membrane and membrane technology.

Membrane process	Characteristics	Ref
Separation	Particles, liquids, ions, molecules, gases, etc.	[20, 84, 85]
Flow pattern	Dead-end filtration, cross-flow filtration	[20, 85]
Recycle process	Backwashing	[20, 85]
Shape	Hollow fiber, flat sheet, tubular, capillary, capsule	[29, 31, 84-86]
Preparation method	Phase inversion, sol-gel process, track-etching, extrusion, stretching, micro-fabrication, interface reaction,	[29, 31, 86]
Driving force	Pressure, temperature, concentration, voltage	[29, 84]
Membrane material	Inorganic materials (Ceramics, metal, oxides), Organic polymers, composite materials	[31, 86]
Membrane cross-section	Isotropic, Anisotropic, mixed matrix composite, bi-layer, multi-layer,	[31, 86]
Structure	Porous, non-porous, charged	[84]

Symmetrical membranes are characterized by identical structures and its transport phenomena occur over entire membrane cross-section. Conversely, structure and transport characteristics of asymmetric membrane vary over the membrane cross-section; typically, a relatively dense thin selective layer (0.1-1 μm) is supported by much thicker (100-200 μm) porous substrate. The mass flux is mainly evaluated by the thickness of selective layer, whereas porous sub layer provides mechanical strength and has minimal effect on the separation process. Fig 3 shows a schematic diagram of various types of membranes according to their structure.

An ideal porous membrane is defined as dense polymer made up of cylindrical pores and can be prepared by track-etching. This procedure involves irradiation of a thin polymer layer (about 10 μm thick) with splitting particles from a nuclear reactor or other radiation source. The highly energetic ions penetrate the polymeric film and disintegrate the polymer chains leaving 'tracks' in the membrane material (tracking). In the etching step, the tracked film is immersed in a solution with extremely high or low pH in which tracks are converted into cylindrical pores with a uniform diameter and a narrow pore size distribution. The exposure time of film to radiation controls the number of membrane pore (pore density), while the etching time determines the pore diameter which can range between 0.2 μm to 10 μm . Membrane prepared by track-etching procedure are symmetrical and permeate flux is proportionate to the membrane thickness; consequently, they have to be thinner than asymmetric microporous membranes in order for having comparatively high flux. Polycarbonate and polyester films are the usual materials used for track-etched membranes. The porosity of these membranes is of the order of 10%.

4.2 Membrane process and separation mechanism

Separation process occurs with membrane as a result of gradient through the membrane and thus membrane separation technology may be subdivided into two categories based on gradient types – pressure driven and non-pressure driven. The first category occurs due to the pressure gradient across the membrane which is called transmembrane pressure (TMP). On the other hand, concentration gradient is the base of non-pressure driven membrane filtration; for example, forward osmosis and dialysis. Cross-flow microfiltration, a pressure driven process, has a wide range of application in concentrating, separating, and purifying colloids, macromolecules, suspended particles from mixture.

Passive transport is defined as a type of membrane transport with any requirement of energy for passing the particles across the membrane. Such phenomena occurs as a result of driving force which is created by a difference of concentration, pressure or by an electric field [32]. Table 3 shows the classification of membranes according to passive transport characteristics. On the other hand, active transport phenomena of a membrane require

external energy to pass particles through membrane. It helps to transport molecules which are unable to move against gradient or any other resistance of the process.

Figure 3 Schematic diagram of various polymeric membranes [10]

Table 3 Characteristics of membrane technology via passive transport.

Characteristics		Criteria				Reference s
Membrane type	Non-porous	Micro-porous	Meso-porous	Macroporous		[3, 15]
Pressure required (bar)	15-75	5-15	2-5	1-3		[3, 16]
Pore diameter (d_p)	0.3-0.6	$d_p \leq 2$ nm	$d_p = 2$ - 50 nm	$d_p = 50$ -500 nm		[10, 15]
Concentration	Pervaporation	Dialysis	Dialysis	-		[10, 29]
Transport phenomena	Pressure	Gas separation Reverse osmosis (RO)	NF	UF	MF	[10, 29]
	Electrical fields	Electro-dialysis	-	Electro-dialysis	-	[10, 29]

Non-porous membranes are defined as dense films in which permeate pass through by pressure, concentration or electrical field gradient. It is mostly used for molecular

separation, RO and NF of gas phase. The selectivity and transport rate of a non-porous membrane can be controlled by the interconnection within membrane material and permeate [33]. The efficiency of membrane separation is described by diffusion or solution selectivity. As very limited numbers of molecules or mixtures can transport via non-porous membranes, therefore, high-selectivity of transport characteristics can be achieved. A substitute of molecule-selective technique by non-porous membrane is the application of special transport process i.e., facilitated transport by affine carriers.

For porous membranes, the selectivity and transport rate are affected by size exclusion and the viscous flow. However, the interaction between solute and membrane pore surface gradually minimizes membrane performance. In addition, selective adsorption can be applied with meso- and macroporous membranes as a sustainable alternative approach towards separation process. Porous membranes can be used for very specific separation-based operations as per size and shape differences. It is obvious that membrane selectivity and permeability can be fully influenced by concentration polarization. The trans-membrane gradient significantly decreases with the increase in concentration of rejected molecules or particles on the surface of membrane (membrane fouling). Membrane fouling is the unwanted deposition or adsorption of materials in/on separation layer. High yield, throughput and purity of any product after filtration i.e., ideal membrane performance can be obtained by adaption of process conditions and membrane materials. That is why, optimization of membrane module configuration and process design is necessary before applications.

5. Application of MF and UF polymeric membrane

MF and UF membranes have broad range of applications in wastewater treatment, food industries, pharmaceutical industries, pulp and paper industries, beverage production, etc. [34]. Besides solid, liquid and gas separation, membrane can also separates negative or positive charge, neutral or bipolar [1]. In the separation process, membrane or filter medium firstly act as a semi-permeable barrier and then it transports the particles through it. As an effective process, membrane technology is most successful process for treatment of oily wastewater (by separating oil from the wastewater), in fuel cell industries, food industries, pharmaceutical, desalination, etc. Table 4 shows various applications of MF and UF membranes in the separation process.

5.1 Oily waste water treatment

Wastewater purification is an emerging issue for environmental, social and economic growth of an area and thus for a country. Huge amount of emulsified solution as a part of oily wastewater are produced on daily basis from kitchen, food processing factories, oil manufacturing industries, pharmaceuticals, petrochemical industries, etc. [15]. Separation of oil from solution is necessary and quite challenging. For oily-wastewater treatment, polymeric membrane fabricated with hydrophilic particles can be a great choice for facilitating the separation of oil that can easily pass the water across membrane [1]. MF and UF polymeric membranes are the substantial approach for oil-water separation, however, UF shows better rejection efficiency than MF membranes [35]. Hydrophilic particles embedded in polymeric membrane are able to repulse the oil droplets and allow water to pass through the membrane [36-39]. Sludge of oily wastewater includes phenols, benzofluorene, phenanthrene, aromatic hydrocarbons, toluene, alkanes, benzene, anthracene, pyrene, etc. [40-42]. MF membranes have high flux and thus cause a greater risk oil passage. On the other hand, UF membrane possesses higher recovery of water, lower tendency of fouling formation and easy removal of fouling.

5.2 Food processing industry

Utilization of MF and UF polymeric membranes in food processing industries is an essential tool for separation process and was gained popularity over 30 years. Literature shows that almost 20-30% of total cost for membrane preparation was from food industries. Membrane filtration technology is extensively used for clarification of alcoholic beverages, water purifications, production of protein content rates, clarification of fruit juice, concentration of beverages and fruit juice, recovery of oil-seed protein, sugar recovery from candy, etc. [43].

5.3 Poultry slaughterhouse wastewater

Huge amounts of water are consumed in the poultry slaughterhouse in order to process live birds to meat thereby generating large quantity of wastewater. The estimation of water consumption is around 26.5 litres per bird [44]. The wastewater from this slaughterhouse contains carbohydrates, protein, fats, blood, feather, skins, etc. It is contaminated with grit, inorganic materials, pathogenic bacteria and fecal matters. Therefore, such wastewater is highly rich in BOD and COD.

Table 4 Application of MF and UF polymeric membrane.

Treated items	Type of membrane	Polymer used	Filtration mode	Remarks/Results	Refs.
Oil emulsions	MF	PTEE	Cross-flow	High oil emulsion removal	[39]
Poultry slaughterhouse wastewater	UF	UF-25-PAN	-	99% fats, 98% suspended matters, 94% BOD and COD removal	[44]
Synthetic emulsified Oily-wastewater	MF	PVDF	Cross-flow	95% removal of organic matters	[87]
Vegetable oil factory	UF	UFPHT20-6338 (Polysulphone)	Cross-flow	91% COD, 87% TOC, 100% TSS, 40% Cl ⁻ , 85% PO ₄ ³⁻ removal	[88]
Municipal wastewater	MF	PP, Polysulfonether, Fluoro-polymer	Dead-end	Coliforms and phosphorus removal – removal of contaminants less than detection limit	[89]
Textile wastewater	UF	PVDF	-	20% colour and 60% COD removal	[90]
Oily wastewater	UF-RO	Polyacrylonitrile, polyamide	Cross-flow	Reduction of 100% oil and grease, 98% TOC, 95% TDS, 100% turbidity and 98% COD	[91]
Urban wastewater	MF-RO	Polysulfone	-	Removal of pharmaceutical and pesticides to discharge limit	[92]
Textile wastewater	MF-NF	Polyetherimide	Cross-flow	Indigo blue-dye removal, water recovery 40%	[93]
CO ₂ separation	MF	Poly(ethylene glycol) and poly(dimethyl siloxane)	-	50% removal efficiency	[94]
Refinery wastewater	UF-RO	Polyacrylamide and Polyaluminium chloride	Cross-flow	Rejection of 97% salt	[95]
Metal finishing industry	UF-RO	PVDF	Cross-flow	90-99% removal of different contaminants	[96]

6. Membrane fouling and cleaning

6.1 Membrane fouling

Membrane fouling is the main limitation encountered at the time of practical application of separation process. It occurs when macromolecules, particles, biomolecules, salts, colloids, organic matters, microbes, protein, etc. are retained or accumulated on/in the membrane pores and surface thereby minimizing the performance and permeate flux [45-47]. When foulants (material causing fouling) are settled down in membrane pores then it cannot be removed, thus fouling is considered as an irreversible process. Large amount of foulants deposition causes a formation of cake layer which eventually decreases membrane performance by blocking the pores [48]; however, this type of fouling is reversible [45]. As results, higher pressure is required to free up transportation of particles through membrane. The more the fouling, the higher the pressure desired [45]. Therefore, fouling has adverse effect on overall membrane performance such as huge consumption of energy, decrease in membrane filtration area, more down time, etc.

The correlation between applied pressure and permeate flux is demonstrated by Darcy's law. The flux for an unfouled and fouled membrane is given by equation 3 and 4 respectively.

$$J_w = \frac{\Delta P - \Delta \pi}{\mu R_m} \quad (3)$$

$$J_w = \frac{\Delta P - \Delta \pi}{\mu (R_m + R_f)} \quad (4)$$

Where J_w is permeate flux, μ denotes viscosity of liquid, R_m and R_f represents membrane resistance without or with fouling respectively. It can be seen from equation 4 that, when fouling increases the denominator also increases and therefore the permeate flux decreases.

According to the type of foulants, the membrane fouling can be classified into various categories such as organic fouling, biofouling, colloidal and inorganic fouling [49]. Colloid fouling can be either inorganic, organic or composites. Colloids may include polysaccharides, microorganisms, lipoproteins, biological debris, silts, oils, clay, manganese oxides, iron, etc.

Fouling of membrane is also differentiated by the mechanism of its appearance and thus divided into four types (as shown in Fig 4) -

- Complete pore blocking
- Partial pore blocking
- Internal pore blocking
- Cake layer formation

Figure 4 Comparison between various types of fouling [20]. Redrawn. Permission is taken from Elsevier.

Several factors affecting the mechanism of fouling of membrane are size of solute or particle; structure of membrane (MF and UF membrane); interaction between solvent, solute, and membrane; and membrane porosity. Recently many research work has focused on proteins [50], algae [51], colloidal materials [52], oil [53,54], and organic matter foulants [55]. The functionality of MF and UF membrane solely depends on their fouling

properties and various researchers have improved many strategies for its minimization or removal. One of such strategy includes cleaning of membrane.

6.2 Membrane cleaning

As time passes, foulant materials stick to the membrane surface. Therefore, cleaning is necessary in order to increase the membrane performance i.e., permeability and selectivity by minimization or removal of fouling material. A cost-effective and efficient cleaning process plays a significant role in wastewater treatment. Various physical, chemical and synergistic applications were studied for cleaning of membrane fouling and this depends on the membrane as well as feed solution [3]. Membrane cleaning for MF is quite limited whether many works were reported on UF membrane cleaning. The incorporation of hydrophilic materials into polymeric membrane increases the hydrophilicity which helps in resisting the formation of fouling [31]. This is carried out by immobilization of hydrophilic polymers by plasma or photo parization [56-58], or surface modification [59], or inclusion of hydrophilic polymer to the casting solution [60]. Cleaning of fouled membrane can be broadly classified as chemical, physical, physico-chemical and biological (or biochemical) cleaning [3].

6.2.1 Chemical cleaning

When the membrane fouling is in irreversible condition, chemical cleaning is employed to it. The principle of this process relies on the interaction between membrane material and foulants, cleaning material and membrane, foulants and cleaning material. This basic knowledge helps in selecting the best suited chemical for foulant cleaning [61]. It is considered as the most suitable and efficient method for enhancement of membrane lifespan, product safety and to maintain continuous filtration operation. The effect of such cleaning process includes loosening and dissolution of foulant, avoidance of new foulant creation, and no adverse impact to the membrane materials. During this process, cleaning agents added to the residue at place which helps in weaken the bonds of foulant to material and then cross-flow filtration is applied to remove the fouling. Cleaning agents for chemical cleaning includes chelating agents, acids, disinfectants, bases (or alkalis), surfactants, etc. Each agent has its unique role for application. For example, acids are used for removal of inorganic foulants such metal oxides and salt precipitates. Hydrochloric acid (HCl), nitric acid (HNO₃), sulphuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) are the commonly used acids for chemical cleaning [62, 63]. On the other hand, Alkalis or bases are used for eliminating organic foulants from the membrane. Most commonly used alkali or base is sodium hydroxide (NaOH). However, phosphates and carbonates are also employed for this operation [3,64].

6.2.2 Physical cleaning

Physical cleaning of membrane fouling is a mechanical process and includes pneumatic cleaning, periodic back flushing, ultrasonic cleaning and sponge-ball cleaning. Periodic back flushing applies a pressure in the permeate side to cause a backward movement of fouling material and thus helps in loosening the bond of materials. It is most commonly used for gel and cake layer removal [65]. In the ultrasonication cleaning process, ultrasounds are employed to create agitation in the aqueous medium and thus transmitting energy as of turbulence to the membrane material. Such energy helps in unloading the foulant from the membrane surface. Ultrasonic cleaning is an effective physical cleaning process and mostly depends on the velocity of cross-flow, operational temperature, power of ultrasound wave and duration of pulse [66-68].

As the name suggests, sponge-ball cleaning is carried out by sponge balls (made up of polyurethane) for wiping out the membrane surface. The balls are inserted into the permeator, scrubbed the pores by moving and wipe off the foulants. Pneumatic cleaning includes air scouring and air lifting. In the process, air is supplied under a certain pressure which generates a shear force between the foulants and membrane materials thereby executing the cleaning process.

6.2.3 Physico-chemical cleaning

This cleaning process is a combination of physical as well as chemical process for foulant removal. Therefore, chemical agents are added during physical cleaning process for enhancement of the removal efficiency i.e., better cleaning performance. Chemically enhanced backwashing (CEB) is the most significant process for physico-chemical cleaning process. Another example includes the application of ultrasonication during chemical cleaning which reports 95% removal efficiency [69-70].

6.2.4 Biological or biochemical cleaning

Biochemical or biological cleaning is carried out by utilizing different bioactive agents such as enzymes, a single molecule or enzyme mixture [71-72]. There is a possibility of damage of membrane material during chemical, physical or physico-chemical cleaning, but biological cleaning is less toxic to membrane material thereby considering it as a sustainable cleaning approach [72-74].

7. Recommendation for future research

Membrane technology is gradually achieving huge success in the field of water and wastewater treatment and gas separation. Over past years, numerous works has been done

in this area, however, there is still some limitation and further improvement is necessary. As fouling and huge energy demand is a key limitation in non-equilibrium pressure driven process, constant research is required for achieving a solution of this problem either by incorporating anti-fouling agents to the membrane or introducing a cost-effective pretreatment method. On the other hand, recovery of solute can make the whole process cheaper. Future scope of research must focus on alternative process for recovery of salt-based draw solutes.

Conclusion

There are numerous applications of MF and UF membrane technology for wastewater purification and potable water generation to minimize the scarcity. This chapter summarizes basic principle of filtration methodologies (MF and UF membrane filtration), several polymeric substances for membrane preparations, membrane design and separation mechanisms, their application in various waste water treatment and lastly surface modifications to improve flux, performance and antifouling properties by incorporation of other advanced functional polymeric materials to make the filtration process handy and cost-effective.

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