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Importance and Significance of UF/MF Membrane Systems in Desalination Water Treatment

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Abstract

The proposed chapter addresses a comprehensive overview of the history and future outlook of ultrafiltration/microfiltration (UF/MF) membrane for desalination water pretreatment. Known theories on UF/MF membrane formation from phase inversion (Dr/wet) systems can be prolonged to define the consequences of high or low molecular weight additives. Also, direct material reengineering and surface modification for high-performance anti-fouling of UF/MF membranes are also highlighted. Before the modern final polymeric film, the characterization techniques, particularly molecular weight cut-off, pore size, pore size distribution, and microbiological activity classification, on to the UF/MF membrane surface were presented, respectively. Lab scale to commercial scale UF/MF membrane configuration and market size of UF/MF membranes for pretreatment desalination are described. The significance of UF/MF provided here as an unconventional approach for desalination water pretreatment is in contrast with the current conventionally used technologies. The recent development made in the integration of established desalination processes, such as spiral wound reverse osmosis (SWRO), multi-stage flash (MSF), multi-effect distillation (MED), electrodialysis (ED) desalination, and UF pretreatment, is addressed. Finally, the influence of UF/MF on desalination water pretreatment step on to the energy cost of desalination process system is discussed.

Keywords: desalination, microfiltration, post-treatment, ultrafiltration

1. Introduction

1.1. An early history of UF membrane

Almost every chemical process involves at least one separation or purification step, and the chemical industry has developed a range of separation techniques to facilitate recovery of the required products. In recent years, membranes and membrane separation techniques have grown from laboratory tool to an industrial process with considerable technical and commercial impact. Instantly, the membrane processes are faster, more efficient, and economical than conventional separation techniques, particularly for desalination water treatment. Among all the membranes process, UF/MF membranes have the largest variety of applications in various industries, because it is a separation technology of high efficiency and low energy consumption [1].

The permeation of water by a thin sheet of animal bladders (diaphragm) was introduced by Abey's Nollet in 1755 (France), and the phenomenon of water permeation was named as osmosis [2]. Later on, Dr. Adolf Eugen Fick from Germany has introduced diffusion law and was developed the first high-pressure synthetic membrane made from nitrocellulose in 1855 [3]. After 50 years, Dr. Bechhold from Germany developed first low-pressure cellulosic membranes (collodion), which is prepared by impregnating filter paper with glacial acetic acid. The first such low-pressure membranes were produced in 1907, and Dr. Bechhold revealed the term "Ultrafilter" collodion membranes. Since for Bechhold's original membranes were introduced and applied protein solutions by forcing at several pressures against to the atmospheric pressure through his collodion membranes [4]. After Dr. Bechhold breakthrough in UF/MF membrane, there has been continuous effort to develop improved UF membranes, which have resulted in many diverse types of such membranes [5]. Further early developments, principally Zsigmondy and Bachmann [6] and Ferry [7] improved on Bechhold's membrane fabrication method, Elford developed graded porosities UF membranes having the properties "Gradocol" [8]. By the early 1930s, microporous cellulosic membranes such as cellulose nitrate, cellulose di/triacetate were commercially available [9, 10]. With further growth of UF/MF synthetic cellulosic membrane during 1950s, the synthetic membrane technology was commonly available for removal of bacteria, virus, dextrin, protein from water, in addition to salinated water cleansing, respectively. But, the little flux was the main drawback of such Bechhold's type membranes. These deficiencies put together are too costly and practically inappropriate. The period of cost-effective feasible membrane advancement, which was started in the late 1950s and prolongs to this date, may be divided into two time periods. The first generation was from 1959 to 1970 of cellulose acetate integral asymmetric membranes, and the second generation started from 1971 to 1984 of noncellulosic asymmetric membranes [10, 11].

The significant development in artificial membrane technology began in the 1960s and to be headed toward the growth of new UF/MF membranes materials. These events allowed for wider industrial and commercial application of UF/MF [10, 11]. In 1962 Loeb and Surirajan developed a new method of polymeric membrane fabrication, called dry/wet phase inversion process. After the breakthrough of phase inversion the history of the synthetic membrane were entirely changed which was active properties regarding mechanical strength, membrane morphologies, and ten times higher performance than the earlier membrane. **Table 1** shows the first contribution to UF membrane development [10, 11]. The beginning of

Inventor	Development	Year
Bechold	Prepares collodion membranes of graded pore size measure bubble point and use the term ultrafilter	1906
Zsibmondy and Bachmann	Patent collodion filter (German Patent 329-060)	1918
Filter GmbH	Commercializes ultrafiltration membranes	1926
Reid and Breton	Selection of cellulosic material for membrane making	1959
Loeb and Surirajan	Cellulosic acetate integral-asymmetric membranes	1960
Amicon by Koch	Market laboratory-scale UF membranes develop polysulfone, PVDF membranes	1966
Amicon by Koch	Make first UF hollow fiber membrane	1967
Abcor by Koch	Installs commercial tubular UF plant (electro coat paint)	1969
Romicon by Koch	Introduces hollow fiber capillary UF plants	1973
Abcor by Koch	Commercializes spiral wound UF modules	1980
Abcor by Koch	First commercially significant ceramic membrane	1988

Table 1. Key historical development of UF membrane from Market laboratory - scale to commercial scale [10, 11].

thin-film-composite (TFC) polymeric membranes started during 1963, initiated by a research institute and one of its first employees, Peter S. Francis [11, 12]. A significant discovery was made in the art of thin-film-composite membranes by Cadotte in 1970 with the beginning of large-scale commercial polymeric membrane. Cadotte invented two innovative techniques of TFC membrane based on interfacial polymerization and solution coating methods [12]. During 1970–1990, the researchers developed important methods of membrane materials synthesis, membrane fabrication process, membrane geometry, separation, and purification processing techniques. Also during 1985, the synthetic commercial membrane entered into a new era, and by the end of 1990, the MF, UF/dialysis, nanofiltration (NF), RO, ED, and gas separation membranes technology have grown steadily at the industrial level. Moreover, by the end of 19th century, the advancement of membrane growth has enhanced performance, steadiness, and provided lower operating costs, making membranes the preferred technology in the water treatment industry as well as in the food and pharmaceutical industries [1, 10, 13].

1.2. Theoretical background of UF/MF

UF/MF membranes [14, 15] have a porous barrier structure that retains components by a sieving mechanism and used for separation of solutes from the feed solution. The water flux in MF and UF is proportional to the applied pressure (Darcy's law). A pressure gradient (0.5–5 bar) across the membrane transports the solvent through, while the substances larger than the pores are rejected. It is agreed that the important process involved in UF/MF is one of sieve action, tricky by adsorption and other consequences are emerging from the unusually large ratio of

pore length to pore diameter in all pressure-driven membranes. The principle of the pure water flux into the UF/MF membranes is due to the capillary pore diffusion model and the mean pore radius can be calculated by Hagan-Poiseuille equation [15, 16],

$$\bar{r} = \left(\frac{8 J_{\mu} \Delta x H_p}{\varepsilon} \right)^{\frac{1}{2}} \quad (1)$$

whereas \bar{r} is a mean pore radius, J_{μ} shows pure water viscosity, Δx is membrane thickness, H_p is hydraulic pressure, and ε shows membrane porosity.

However,

$$H_p = J_p / \text{TMP} \quad (2)$$

whereas, J_p shows water permeation, and TMP presents transmembrane pressure (ΔP).

Combine Eq. (2) into Eq. (1),

$$\bar{r} = \left(\frac{8 J_{\mu} \Delta x \text{TMP} \tau}{\varepsilon J_p} \right)^{\frac{1}{2}} \quad (3)$$

The leading theory of fluid flow through UF/MF membrane in an ideal condition such as consistently sized pores in the membrane, negligible concentration polarization, no fouling, respectively. **Figure 1** summarized the theory of transport phenomenon and fluid dynamics of an UF membrane. Also the pore size, some other factors such as interactions between UF feed components and membrane matrix play a significant role in the transport through the membrane [10, 17–19].

Sakai [19] reported that the Eq. (3) is directly relating to the membrane structure. Sakai and co-worker also indicated that Verniory et al. improved the UF/MF membrane transport parameters. Among membranologist, it has been widely proven that UF/MF membranes flux and rejection are depended upon their structure. Nakao [19–22] has reported that in the case of known relation between flux and rejection, the membrane structure can be characterized

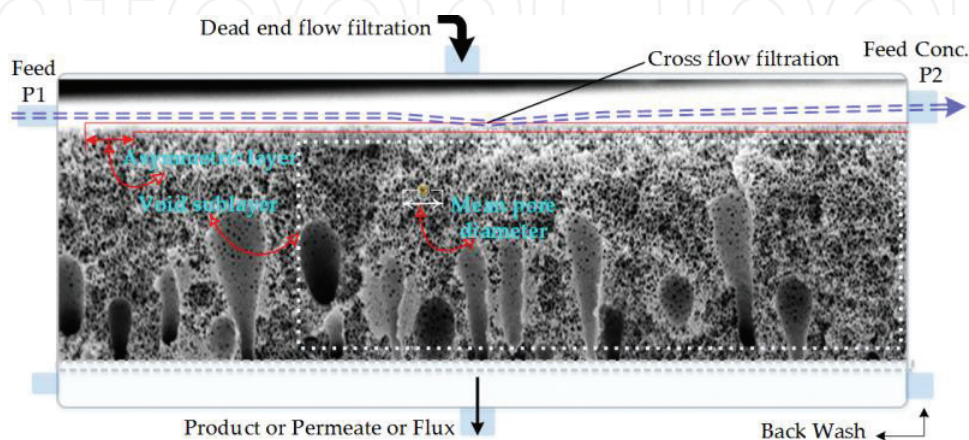


Figure 1. Predicting flux from pore statistics using Hagen-Poiseuille Equation [17].

such as thickness, pore size, pore radius, pore volume, pore density, and tortuosity, respectively. However, Sakai successfully investigated the qualitative attempts to account for tortuosity (τ) in the pore model. Tortuosity τ perhaps described the ratio of pore as,

$$\tau = \frac{\text{Mean path length}}{\text{Membrane thickness}} = L/\Delta x = W_c/\Delta a > 1 \quad (4)$$

where W_c is present water content, which approximates the pore volume in the membrane.

$$J_p = \left(\frac{\varepsilon \cdot d_p^2 \cdot \Delta P_T}{32 \Delta x \cdot \mu} \right) \quad (5)$$

When Eq. (3) is used to calculate the mean pore radius, it becomes complicated because of the introduction of tortuosity, and the result is larger than that obtained from Eq. (1). Unfortunately, it is impossible to determine the pore sizes of asymmetric membranes with the aid of Hagen Poiseuille equation (3), which makes it necessary to use, for this purpose, the data of more complicated methods [23]. Among all above methods, the most informative are the means of electron microscopy, gas pycnometer, which give the possibility to determine pore sizes and pore size distributions (PSD) of asymmetric membranes [18, 24–27].

2. Significant development of low-fouling UF/MF membranes lab scale to commercial scale

Synthetic polymeric membranes can be divided into hydrophobic and hydrophilic classifications, and structure can also be classified. Structural classification is critical because it is the structure which determines the separation mechanisms and the membrane application [10, 28, 29]. Membranes can be further classified as symmetric or asymmetric [10, 29]. The symmetric membranes can be porous, cylindrical porous, and homogeneous (nonporous). The asymmetric membranes can be porous, microporous with top layer, and composite that is consisting of a porous substrate with a dense top layer. The thickness of the top layer in asymmetric membranes is in the range of 0.1–0.5 μm and is supported on a porous sub-layer with a thickness of about 50–150 μm [10, 11, 29]. The development of pressure-driven membrane technology was began after Loeb-Surirajan and Riley et al. [30, 31] and Cadott discovered about the three following significant developments [12],

- i. Ability to fabricate particular selective membrane that has high permeation, essentially ultrathin, dense layer, surface barrier layer, integrally supported by a thick, porous, spongy structure and was able to produce at commercial scale.
- ii. Ability to form polymeric membranes into compact, high-surface-area, economical membrane configuration.
- iii. TFC or ultra thin film (UTF) able to be laminated on microporous or porous support layer.

Modern membrane technology began in late 1990s, the development of polymeric membrane chemistry and processing techniques are used in membrane fabrication. With the developments

in polymeric membrane materials, manufacturing technologies, and water treatment processing systems have made this technology an efficient, economical for water treatments, and competitive with traditional water treatment methods [10, 15, 29]. Recently, UF/MF membranes have been succeeded for a range of industrial applications [32]. Each application enforces precise specifications on the membrane material and membrane structure. The revolution in understanding the origin of these structural elements of Loeb and Surirajan phase inversion process was obtained by Wienk et al. and Wu et al. [33, 34],

- i. Thermodynamic calculation and kinetics of phase separation of polymer/solvent/nonsolvent.
- ii. The role of additives, both high- and low-molecular weight, on membrane formation.
- iii. Theory behind macrovoids porous and nodular structures formation.

The latest development revealed "next generation" of membrane materials for UF/MF focus onto:

- i. Well-distinct configuration as 'tailored' membrane materials.
- ii. Innovative processing of polymers for membranes, particular neatness of membrane industrialized.
- iii. Superior functional polymer membranes, qualifying the integration of active barrier structure with 'customized' approach of interactions.
- iv. Groundwork of nanoparticles mixed matrix membranes for the synergistic allying of different functions by different polymeric materials.

Also, the development is involved in both organic and interpenetrating multiphase structures with excellent transport properties, agreement to allow membranes with superior chemical/thermal stability, fouling resistance, organic solvent resistance, and unusually high permselectivities and permeabilities [35]. Such kind of polymeric membranes may well circumvent many of these limitations. Similarly, recent developments in UF/MF membrane module design, including rotational membrane devices and cycled flow fluid management for fouling control, use of low-cost refractory monoliths as membrane supports, and use of electric potentials to minimize the fouling rate on to the membrane surface [24]. Today, almost 98% of cross-flow membrane systems installations use polymeric UF/MF membranes [13, 36].

Principally, almost all commercial membrane lifespan faces two serious issues due to natural phenomena during separation (solute) and purification (fluxes/permeate) such as concentration polarization (solute) and fouling. A typically asymmetric polymeric membrane as shown in **Figure 2** has random pore sizes. Therefore, concentration polarization plugging up on membrane pores and fouling is happened due to the living microorganism adhesion, gel layer formation, and solute adhesion at the membrane surface (see **Figure 1**) [37, 38]. Several researchers and manufacturers have revealed that the natural phenomenon is responsible for restricting the permeate flux during cross-flow (i.e., permeation followed by cleaning). Throughout the early stage of filtration process within a cross-flow rotation, concentration polarization is one of the prime causes for flux reductions [39, 40].

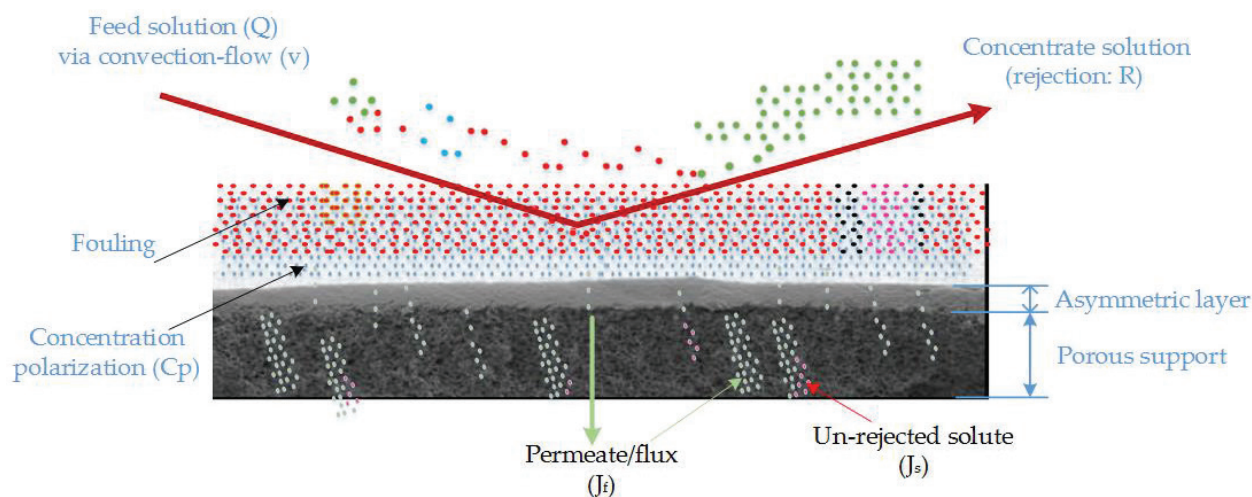


Figure 2. Typical cross-flow process with asymmetric membrane [17].

Commercial scale polymeric UF/MF membrane systems run in a continuous cross-flow mode, where backwash and cleaning operation interchanges with the normal operation. The decrease in the flux for pure water from cycle to cycle, because of fouling, the flux decline within a period due to concentration polarization, and the average flux under steady state level. The latter is also decreasing from cycle to cycle, suggests irreversible solute adsorption or fouling [41–43]. And of the solute retained on a membrane surface leads to increasing permeate flow resistance at the membrane wall region. Strategies to minimize the effect of fouling can be divided into two groups: avoidance and remediation. The remediation is to clean up by the cleanup process, is usually done by chemical cleaning at regular times [44], and this is necessary for all membrane processes in nearly all applications. However, large differences in the cleaning frequency can be found, ranging from daily to yearly, depending on the concentration of foulant and the pretreatment. A large number of cleaning agents are commercially available. The choice of optimal product depends on feed characteristics. Acid cleaning is suitable for the removal of precipitated salts, such as CaCO_3 , whereas alkaline cleaning is used to remove adsorbed organics. Nearly, all cleaning products contain detergents. Another remediation technique often used in UF/MF is backwashing or back pulsing. A short pulse of water or air from the permeate side to the feed side efficiently removes all fouls blocking the membrane pores [45]. This principle is often applied in a dead-end or semi-dead-end filtration. It is possible to avoid fouling by using adequate pretreatments, such as coagulation precipitation, or slow sand filtration [10, 15, 29, 46].

2.1. Material selection for UF/MF fabrication

Recently, UF/MF membranes become an innovative and dominant technology and have been extensively used in many areas, including wastewater treatment, protein separation, dialysis, and dairy industry [47]. However, the most common applications of UF/MF in downstream processing are protein concentration (i.e., solvent removal), buffer exchange and desalting, virus removal and clarification [41]. Since, the improvements of UF/MF technology to make membrane water treatments economically competitive with traditional water treatment methods

[10, 29, 32], the use of these membranes has increased exponentially for the downstream process of sea water desalination (SWD). Also, the UF/MF membranes employed in SWD have gained significant attention as these methods are efficient in removing the turbidity, the particles, and the microorganisms present in wastewater [10, 29]. With the improvements in this technology to make membrane for separation and purifications economically competitive with traditional separation methods [10, 17, 45], the use of these membranes has increased exponentially.

It has been established that the porous structure and hydrophilicity of UF/MF play crucial roles in membrane manufacturing processes [29, 34, 48]. A suitable porous membrane should be excellent in permeability, hydrophilicity, and chemical resistance to the feed streams. An asymmetric membrane is a good option for high permeability. Thus, currently, much effort is being devoted to improve the performance of the existing membranes regarding anti-fouling properties, high mechanical strength, and excellent chemical resistance. To make a porous or microporous membrane, some mineral or ceramic membranes have been developed. However, polymeric membranes are yet mostly used [49, 50]. Therefore, different polymeric materials have been used for UF/MF membranes and investigated at lab scale to be commercial with changing results, as not all of them produce membranes with suitable performances [50]. Nevertheless, since the first membrane cellulosic and noncellulosic materials were described by Reid and Breton in late 1959 [51], numerous materials have been developed to improve the capacity and performance of membranes filtration [11, 17, 29]. For a given treatment stream, a particular polymeric membrane material can be selected from an assortment of candidates. Till now, there are more than 130 materials (cellulosic, noncellulosic polymers, composite, and inorganic) that have been used to manufacture membranes [11, 17]. The range of materials from which it is possible to create some form of artificial membrane structure is extensive. Each year, number of research papers in polymer and membrane science present many new examples of materials that demonstrate semi-permeable qualities at some scale. However, only a very limited number of these potential candidates make it to the commercial environment [1, 52–54]. Very few materials possess the structural and chemical properties necessary to render them suitable for application in industrial scale membrane processes. **Table 2** shows the various hydrophilic and hydrophobic polymers used for membrane production at lab scale to commercial scale [11, 17, 29, 53]. Furthermore, typical commercial hydrophilic co-polymers are made of polyethylene oxide (PEO), crystallizable polyamide (PA), nylon or aliphatic polyamide (PA6 and PA66), polyurethanes (PU), and polyester (PET). These materials can be used to make a hydrophobic polymer more hydrophilic. Hydrophobic polymeric materials such as PC, PSF, PES, PVDF, PI, PEI, Ar.PA, polyether ether ketone (PEEK), and PAN, are also conventional polymeric materials for the preparation of UF/MF membranes [10, 17, 29, 55].

Among all those materials, CA, PSF, PES, SPES, PAN, and PVDF are the most commonly used polymers for UF/MF membranes at lab scale to commercial scale [1, 17, 29, 52]. Generally, PSF, PES, and polycarbonate (PC), respectively are produced by aromatic bisphenol intermediates such as bisphenol-A-PSF, tetramethyl bisphenol-A polysulfone (TM-PSF), bisphenol-B polysulfone (PSF), and their modified form such as sulfonated polysulfone (SPSF), and sulfonated polyethersulfone (SPES) have been used extensively to fabricate UF/MF [11, 17, 54]. **Figure 3** shows several types of aromatic bisphenol intermediates used for PES, PSF, and polycarbonate (PC) preparation [56]. Typically, all these thermoplastic base materials can easily be dissolved

Hydrophilic polymers			
Poly(vinyl alcohol)	PVAL	Cellulose and its derivative	
Poly(vinyl chloride)	PVC	Cellulose acetate	CA
Polyamide	PA	Cellulose triacetate	CTA
Poly(acrylic acid)	PAA	Cellulose acetate butyrate	CAB
Poly(ethylene oxide)	PEOX	Cellulose acetate propionate	CAP
Polyacrylonitrile	PAN	Cellulose nitrate	CN
Poly(vinyl acetate)	PVAC	Cellulose propionate	CP
Poly(vinyl butyral)	PVB	Ethyl cellulose	EC
Poly (p-hydroxystyrene)	PHS	Carboxymethyl cellulose	CMC
Hydrophobic polymers			
Polysulfone	PSF	Polytetrafluoroethylene	PTFE
Polyethersulfone	PES	Polyethylene	PE
Poly (vinylidene fluoride)	PVDF	Silicone	Si
Polycarbonate	PC	Polyphenylene oxide	PPO
Polypropylene	PP	Polyphenylene sulfide	PPS
poly(methyl methacrylate)	PMMA	Polystyrene	PS

Table 2. Commercial available hydrophilic and hydrophobic polymers for membrane production [11, 17, 29, 53].

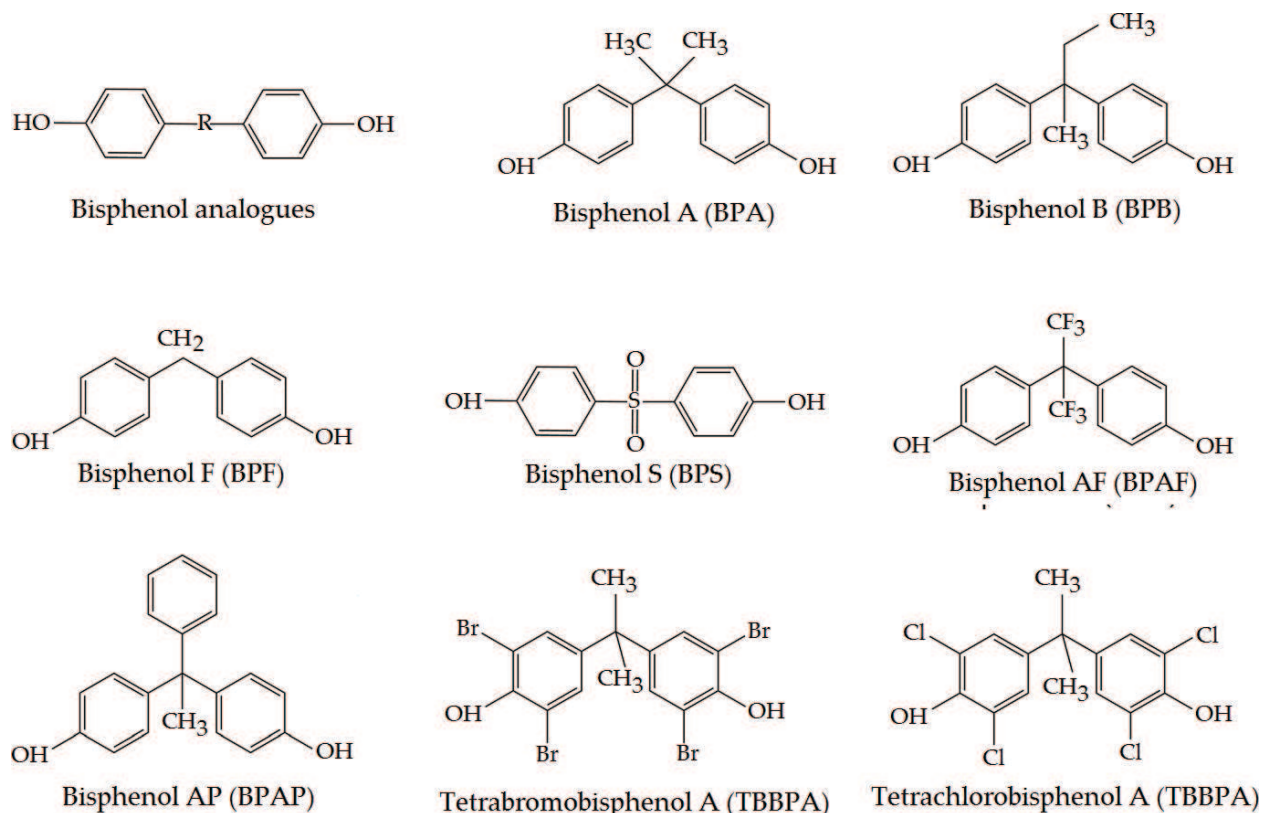


Figure 3. Chemical structure of aromatic bisphenol intermediates of PSf, PES, and PC [55].

in aprotic solvents and produce membranes with excellent thermal, hydrolytic, and mechanical stability properties in both hot and wet environments. **Figures 4** and **5** show chemical structures of CA, CTA [56, 57], and thermoplastic polymers [17, 58–62], and **Table 3** summarized the leading manufacturer of polymer used for membrane fabrication. Almost more than 90% of membrane manufacturer are producing PSF, PES, TM-PSF, SPSF, SPES, PVDF, and PAN membrane in a wide range of UF/MF applications. To prepare membranes for the liquid separation processes using repeated applications with either hot water or sterilization to keep the membrane clean [11, 17, 63]. Sulfonated polyethersulfone membrane has been customized to be drastically more hydrophilic than standard PES, PSF membranes [29, 42, 58–60, 62, 63]. It is biocompatible and has highest opposition to fouling by hydrophobic compounds such as fats, lipids, anti-foams, and other similar highly fouling substances [1, 10, 32, 42, 60, 64].

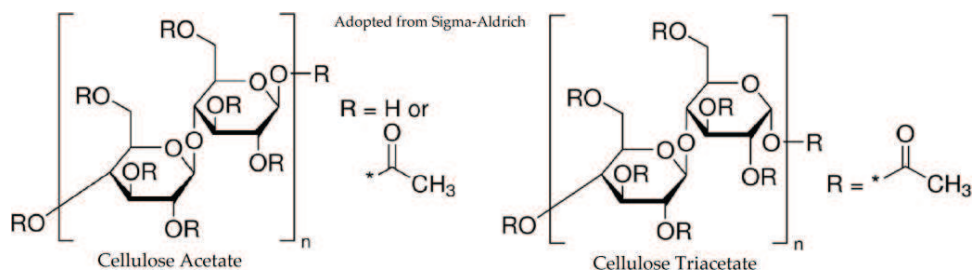


Figure 4. Chemical structure of commercial CA and CTA [56, 57].

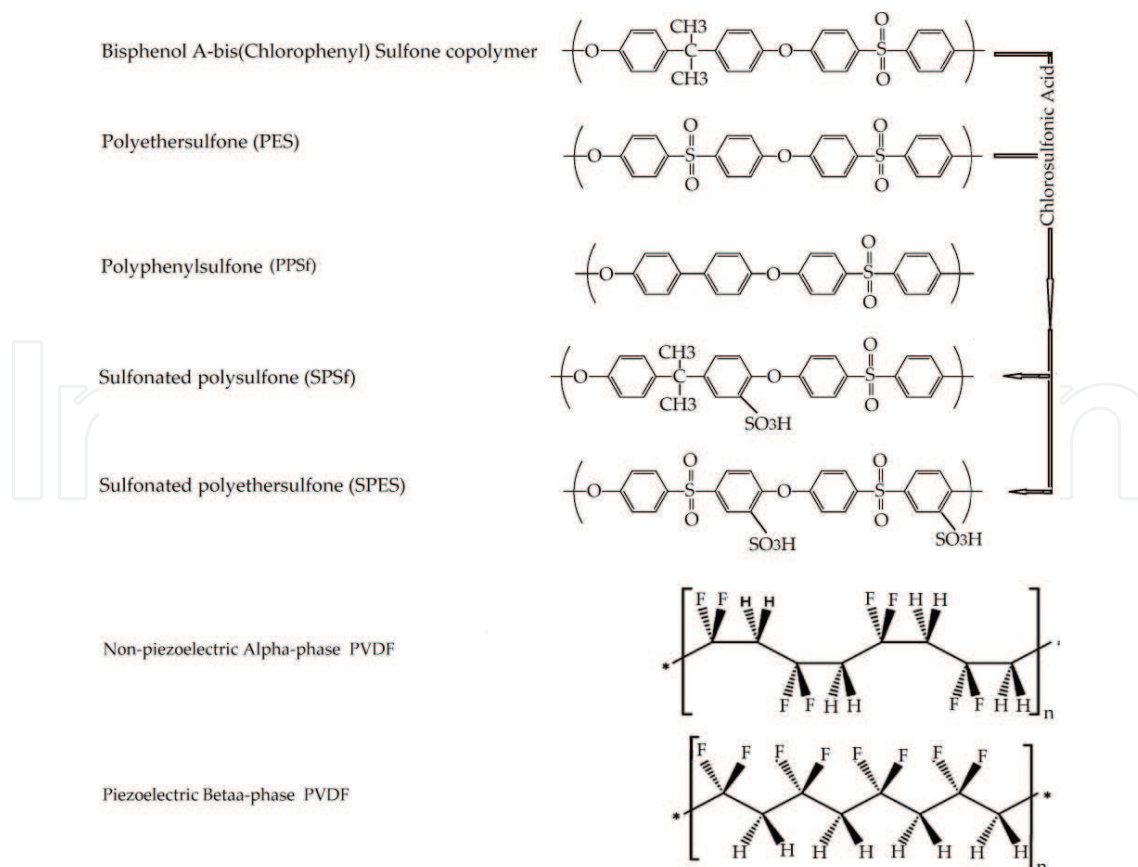


Figure 5. Chemical structure of hydrophobic PSF, PES and modified hydrophilic SPSf, SPES [58, 59].

Manufacturer	Product name	Trade mark	WA	TM	Tg	MW	
			%	MPa	oC	g/mol	
BASF	Blend GF45	1010 G9	0.65%	15,500	216	np	
	PESU	E 1010 NAT	0.80%	2650	222	np	
	PESU	E 2010 SW Q31	0.80%	2650	225	np	
	PESU-CF30	E 2010 C6	0.60%	22,000	225	np	
	PESU-GF20	E 2010 G4	0.60%	7300	225	np	
	PESU-GF20	E 2010 G4 MR	0.60%	7301	225	np	
	PESU-GF30	E 2010 G6	0.60%	9800	225	np	
	PESU	E 2010 HC	0.80%	2650	225	np	
	PESU	E 2010 MR	0.80%	2650	225	np	
	PESU	E 2020 P	1%	2650	2250	4800	
	PESU	E 2020 P SR	1%	np	np	55,000	
	PESU	E 2020 P SR	1%	np	np	55,001	
	PESU	E 3010	0.80%	2650	228	np	
	PESU	E 3010 MR	0.80%	2650	228	np	
	PESU	E 6020 P	1%	2650	225	75,000	
	PESU	E 7020 P	1%	np	225	92,000	
	PESU+PTFE	KR 4113	1.50%	11,000	225	np	
	PPSU	P 3010	1.20%	2270	220	np	
	PPSU	P 3010 MR	1.20%	2270	221	np	
	SOLVEY	Udel PSU	P-1700	0.30%	2480	174	np
Udel PSU		P-1720	0.30%	2480	174	np	
Udel PSU		P-3500 LCD	0.30%	2480	174	np	
Udel PSU		GF-110	0.29%	3720	179	np	
Udel PSU		GF-120	0.29%	3720	180	np	
Udel PSU		GF-130	0.20%	8690	181	np	
Veradel PES		3000 P	0.50%	np	np	np	
Veradel PES		201 NT	0.50%	2100	np	np	
Solvey Solef		PVDF	6020	0.04%	1700	-40	np

Manufacturer	Product name	Trade mark	WA	TM	Tg	MW
			%	MPa	oC	g/mol
Sumitomo chemicals	Sumikaexcel PES	3600P	0.43%	2550		
		4100P	np	np	np	np
		4800P	np	np	np	np
		5200P	np	np	np	np
		5003P	np	np	np	np

np: not provided.

Table 3. Membrane polymer manufacturer.

2.1.1. Surface chemistry and choice of additives

The significance of all pressure-driven membranes particularly UF/MF rely on the properties of their surfaces. As reviewed above and has been proven that the thermoplastic polymers specifically PSF, PES, SPES, PVDF, and PAN are dominant materials for membrane making at retail level [10, 17, 63]. However, surface contamination which may lead to deterioration in membrane performance is also known to be governed by the membrane surface properties and obstacle in membrane performance. Therefore, the membronologist has been paid much attention to the membrane surface modification and were identified theoretical and phenomenological reasons behind the hydrophobic reasons of thermoplastic polymers [17, 29, 32, 64, 65]. Also during 50 years, membronologist has developed very innovative methods to modify the hydrophobic membrane surface into hydrophilic. Zeman and Zydney [66] have reported that almost 50% of all MF and UF membranes traded by 1996 were surface-modified. Moreover, many numbers of high cited research manuscripts and books have been published regarding membrane surface modification techniques. Mittal¹ has compiled highly cited work in several volumes entitled "Polymer Surface Modification: Relevance to Adhesion." Pinnau and Freeman [65] edited a book of a membrane-based symposium entitled "Advanced Materials for Membrane Separations" [62]. In this book, relevant topics covered in the 2001 ACS Symposium summarize recent advances in various research areas for development of novel materials used in membrane separations. Benham and Kinstle [67] edited ACS symposium entitled "Chemical Reactions on Polymers," the topics included as one of the greatest active fields in polymer science because of its unique ability to produce specialty polymers with desirable chemical and physical properties through modification of readily available polymers [58]. Xu and co-authors [68] published a very comprehensive book on surface engineering of polymer membranes, squeezes those processes which alter membrane surfaces to improve their in-service performance. The book shows the basics of the surface design of UF/MF polymeric membranes, together with membrane surface modification, to minimize fouling, to modulate hydrophilic and hydrophobic. Also, improve biocompatibility, act as a diffusion barrier, provide bio- or chemical functionalities, mimic a biomembrane, fabricate nanostructures, or directly improve the esthetic appearance of the membrane surface. Xu and co-authors [68] also described general techniques of surface modification of membranes

via functionalization and macromolecule immobilization methods for membrane surface modification.

Morao et al. [69] also reported a comprehensive literature work on surface modification plans that include ion-beam irradiation [70]. Mulder, Pinnau and Freeman said plasma treatment or grafting [29, 66] and UV-induced grafting [67] on a polymeric membrane surface. Several other authors also reported chemical sulfone enrichment [60, 71], chemical dehydrofluorination by alkaline solution [71–73], coating temperature-sensitive polymeric brushes [74], and grafting with pH- and ionic-strength-sensitive polymeric brushes [10, 29, 72, 74]. Moreover, researchers has been used several other techniques such as, the irradiation-induced grafting [75], physical adsorption of water-soluble polymers [76], a formation of Langmuir-Blodgett films [77], thermal grafting of a hydrophilic polymeric surface coating [78, 79], and photografting with UV irradiation [68], respectively. All these surface modification techniques are usually applied on hydrophobic-casted surface and these are complicated and expensive and require at least one additional step in the membrane preparation process [68]. Besides, the physical techniques, all the methods mentioned above allow the membrane surface to be modified without affecting the bulk properties too much when appropriate conditions (the modification time) are selected. Technically the modification of thermoplastic or thermoset types of UF/MF membrane surface by using physical techniques revealed are easy, economical, green, and improved surface properties. However treating polymeric membrane surface by physical method resulting unstable and mechanical strength drawback [80–82].

Typically, several methods have been widely used to fabricate synthetic membranes using all mentioned polymers (See **Table 2**). The principle of synthesis is to transform the polymeric material using a convenient method to achieve a polymeric membrane structure with a significant morphology for a distinct separation. The techniques that are being employed for the preparation of artificial membrane are phase inversion, stretching of films, irradiation and etching of films, track-etching, sintering of powders, sol-gel process, microfabrication vapor deposition, and coating [11, 29, 33, 49, 81]. The ultimate morphology of the membrane film or fibers will deviate significantly based on the properties of the selected polymeric materials and the operational conditions. The majority of membranes at the lab to commercial scale are prepared by controlled phase inversion process, i.e., dry/dry, dry/wet, and wet/wet; yet, preferably, the dry/wet phase inversion techniques are the most useable process currently [1, 29, 33, 49, 81]. Consequently, polymeric membranes are formed by the so-called phase inversion techniques, which include the main steps of Refs. [33, 49, 81] are:

- a. Dissolving the polymer together with pore-forming additives (either organic or inorganic) in an aprotic solvent (preferably NMP, DMAc, DMF, DMSO, acetone, etc.).
- b. Flat sheet casting the resulting solution as a thin film on the surface of nonwoven PET fabric.
- c. The solution is spinning the self-support as a geometry of capillary or hollow fiber.
- d. Dipping the spun hollow fiber or cast film in a polymer nonsolvent bath.

2.2. Comprehensive characterization of UF/MF membrane

The most significant methodological problem in engineering and fabricating of pressure-driven membranes is “tailoring” of membrane surface function into hydrophilic or hydrophobic together with anti-fouling properties, uniform structure, and pore forming properties for the selective sieving process [62, 81, 83]. Therefore, the characterization of surface chemistry is an essential tool in membrane science and technology, because it is well known that membrane performance depends not only on feed hydrodynamics and steric hindrances but also on membrane surface (hydrophobicity, hydrophilicity, and membrane surface charge) and membrane-solute(s)-solvent chemical interactions. Moreover, without characterization, the synthesized pressure-driven membrane cannot predict their properties mainly pore size or molecular weight cut-off (MWCO); thus, it is only a tool for membranologist to emphasize the significance of prepared polymeric membranes. Nevertheless, to tailor UF/MF membranes and eventually use the most important polymeric membrane for a final application, most important membrane has to determine the attribute of MWCO, pore size distribution, using independent characterization methods [10, 11, 29]. Among these are:

i. Surface functionalization analysis

- (a) Contact angle
- (b) Fourier transform infrared (FTIR)
- (c) X-ray diffraction

ii. Structural analysis

- (a) AFM and SEM/EDX
- (b) Membrane equilibrium water content (EWC) and porosity

iii. Performance evaluation

- (a) Membrane affinity test
- (b) Molecular weight cut-off (MWCO)
- (c) Pore size and pore size distribution
- (d) Solute rejection curve

2.2.1. Surface functionalization analysis

2.2.1.1. Contact angle

As reviewed above that the surface hydrophilicity of selected polymer is a major component to predict the membrane affinity with permeate and anti-fouling properties of UF/MF membranes. Hydrophobic polymeric membranes have nonpolar groups and lower surface free energy; this can prevent contact with water and can push out the water molecules adjoining it [36, 75, 84]. The majority of membranologists and manufacturers are using the hydrophobic polymer as a base polymer for UF/MF fabrication. The relative hydrophobicity and hydrophilicity of membrane surface can be

qualitatively determined by computing the contact angle of a water drop deposited onto the surface, which has commonly been used to assess the wettability and interfacial energy of the substrate surfaces [76]. **Figure 6** summarized several types and most suitable hydrophobic and hydrophilic thermoplastic polymers for membrane constructions [17, 58–61]. In **Figure 6**, among all polymers, sulfonated polymers are hydrophilic form of PSF, and PES and their contact angle almost 50% lower than virgin polymer [85]. Typically, contact angle measurements should be made inside an enclosed chamber to stop airborne particles and establish an equilibrium vapor pressure of the liquid tested, which is especially preferable when the test liquid is volatile. It has been observed that evaporation can cause the fluid front to retract and that a retreating or an average contact angle is recorded unintentionally. However, the inherent inaccuracy of the direct measurement technique and the use of liquids with high boiling points make the enclosed chamber unnecessary in many cases.

Therefore, the contact angle of the surface of the membrane can be measured at ambient conditions using the contact angle to water the produced membranes was measured by the sessile drop method [85–87]. Sample coupons at horizontal dimension ($2.5 \times 6 \pm 0.5$ cm) should be prepared by cutting the membranes sheet at random locations. Then, the sample should be placed on a glass plate (active surface of the membrane must be upward) and fixed with a double-sided tape. A drop of double-distilled water ($5 \mu\text{l}$) should be placed on the surface using a microsyringe (Hamilton Company, Reno, NV). The position of the moving bed can be adjusted manually so that the water drop will be fitted to the scale when projected on the screen. After a fixed deposition time (10 sec), the image will be recorded. To measure the contact angle, the height-width method can be used. For the reason that this approach gives reliable data for contact angles less than 90° . The contact angle should be measured at five different spots on each membrane sample so as to ensure reproducibility of data.

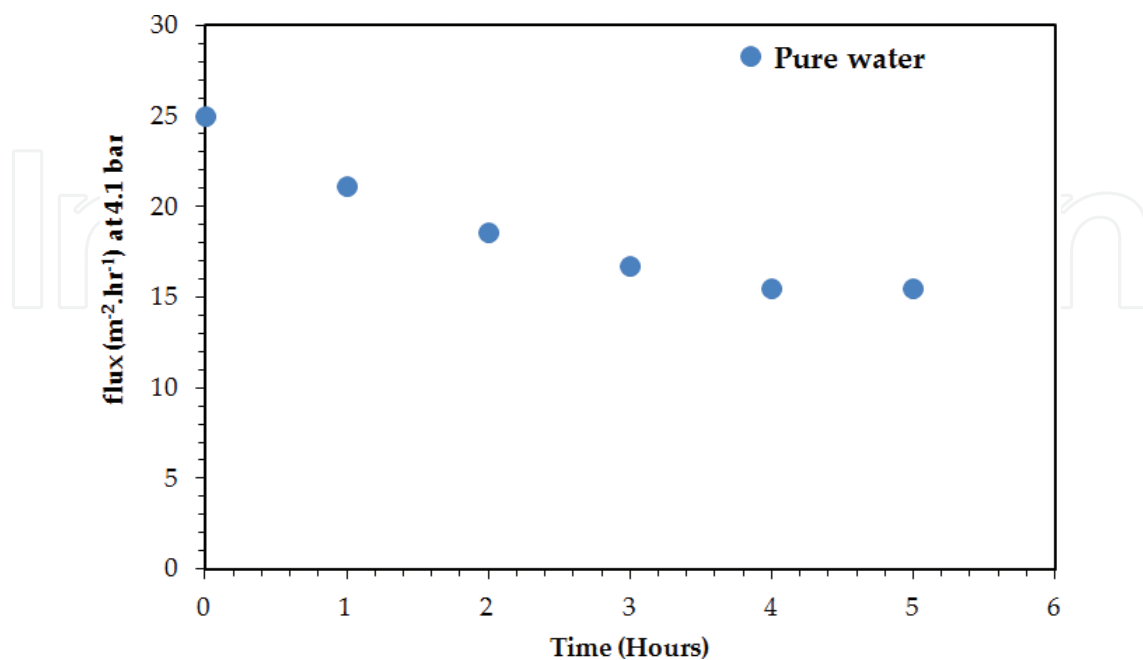


Figure 6. Membrane hydraulic resistance against pressure with respect to time.

2.2.1.2. *Fourier transform infrared (FTIR)*

The analysis of polymeric membrane films in transmission using FTIR is particularly a consistent method for assessing the significant properties of polymers due to additives for achieving quantitative information on modified polymer used for the membrane [53, 88]. There are different methods of polymer sample handling used with FTIR, together with diffuse reflectance (DRIFTS), attenuated total reflection (ATR), and correct specular reflectance/reflection absorption. Established methods of sample holding are more helpful than others for particular specimen types. To analyze and achieve a high-quality spectrum of a sample, it is important to know which handling technique works best for the sample type. Since, FTIR scanning is too responsive, therefore, before analyzing membrane samples make sure the sample should be free of contamination. Therefore, before scanning membrane sample should be clean with 1:1 alcohol/DI-water and then dry in nitrogen chamber at 50–60°C (subject to base polymer properties) for 24 h. Typically, almost all ATR accessory equipped with a Zinc selenide (ZnSe) and diamond crystal at a nominal incident angle of 45°, yielding to 12 internal reflections at the membranes surface with 16 scans at 4 cm⁻¹ resolution and ratio to background spectra recorded in the air at abscissa 350–4000 cm⁻¹ [17].

2.2.1.3. *X-ray diffraction (XRD) techniques*

X-ray diffraction method is nondestructive analytical techniques, which reveal information about the crystal structure, chemical composition, and physical properties of materials. Also with the help of XRD, the membranologist can be identified unknown material during membrane modification particularly while we use nanoparticles during dope solution preparation and membrane fabrication and can be compared its crystal structure to that of a standard database [83]. XRD can also be used to identify the presence of multiple phases where different crystalline compounds coexist [89].

2.2.2. *Structural analysis*

2.2.2.1. *AFM and electron microscopy*

Atomic force microscopy (AFM) is a comparatively a vital tool for membranologist to understand the surface roughness of membrane. As compared to scanning electron microscopy (SEM), AFM is capable of producing images both in air and liquid without conducting the membrane. Besides, the samples do not require any chemical etching or conductive metal coating. However, due to membrane surface roughness, it is often difficult to obtain a pore size distribution. Nevertheless, since the discovery of AFM, it has been used broadly for investigating the surface roughness of UF/MF membranes [26]. Moreover, a significant attribute of AFM is its tendency to measure force interactions as a function to look into surface separation distance [90]. All AFM measurements can be carried out using multimode AFM with a Nanoscope IIIa controller and contact mode OTR8 silicon nitride probes (Olympus, from Japan, Bruker, USA, Agilent, USA). Before scan polymeric membrane samples, the probes should be wiped in argon plasma [90]. Membrane samples can be fixed to the metal sample discs using epoxy resin. Measurements should be carried out under ambient conditions

using the contact mode of imaging. The surface roughness morphology at 2D and 3D topographic images can be extracted. The roughness analysis of mean roughness (R_a), the root mean square of data (R_z), and the average difference in the height between the five highest peaks and the five lowest valleys (R_y), as well as regarding the diameter of the nodules [27] of prepared membrane and additives such as BSA, PEG, and PVP, etc. Z is described as the difference between the highest and lowest points within the given area (nm).

Membrane imaging with scanning electron microscopy (SEM), transmission electron microscope (TEM), and field-emission scanning electron microscopes (FESEM) has become standard method to investigate membrane morphology or structure and the mechanism of membrane formation [91, 92]. However, all these microscopic samples required one additional step of the metal coating before scanning, but a metalization of the membrane sample is necessary to yield high-quality images and for the visualization of the pore structures [93]. Kim et al. [91], have revealed that polymeric membrane coating is essential at low voltage for conductivity and high voltage for contrast. Also, Kim et al. [91], have revealed that FESEM has proven essential tools for membranologist to examining both surface morphology of finely porous membranes and the fouling process in membrane research. Several researchers [26, 27, 94–96] has combine AFM with SEM together with solute transport data and were determined UF/MF membrane pore size and pore size distribution. Earlier researchers used AFM to study the UF/MF membrane surface structures [96–99] and to interpret the mechanisms of fouling in membrane processing [85].

To analyze polymeric membrane with SEM/FESEM, the sample should be washed with ionized water and dried in vacuum oven at 50–60°C. Also, to get an efficient cross-sectional morphology, the membrane samples must be ruptured in liquid nitrogen [46]. The sample needs to be electroconductive for current, and it can be done by coating them with a very lean layer of about 1.5–2.0 nm using gold or gold/palladium, platinum metals. Also, polymeric membranes sample must be capable of upholding at high vacuum and should not change the space. Polymers, metals, and crystals are usually little problematic and keep their structure in the SEM [89].

2.2.2.2. Membrane equilibrium water content (EWC) and porosity

Equilibrium moisture content or water uptake or water swelling is considered to be an essential tool to characterization factor as it indirectly shows the degree of hydrophilicity or hydrophobicity of a membrane [17, 100–102]. EWC is directly related to the porosity, and UF/MF membrane and the porosity play a vital role not only in also characterizing in important in membrane application. Therefore, some researchers have described the porosity and numbers of techniques have been suggested to estimate membrane porosity [35, 103–108]. Some of them give information on the overall membrane porosity. Nevertheless, the porosity of the membrane can be measured by the gravimetric method, and by apparent density method as reported several researchers [11, 100–107]. According to this approach, the average membrane porosity is determined as the overall void fraction, calculated as the volume of the pores divided by the total volume of the membrane. Perfectly dried membrane samples were weighed with a precision balance. Membrane samples, then, immersed in pure water for

24 h and weighed again. The overall porosity (ε) was calculated using the following formula (Eq. (6)):

$$\varepsilon = \frac{(M_{\text{wet}} - M_{\text{dry}})}{A \Delta_x} \times 100 \quad (6)$$

where M_{wet} is the wet membranes, M_{dry} is the weight of dry membranes, The volumetric porosity,

$$\varepsilon = \frac{V_e}{V_w} = \frac{V_w - V_d}{V_w} = 1 - \frac{V_d}{V_t} \quad (7)$$

$$\varepsilon = 1 - \frac{\rho_m}{\rho_p} \quad (8)$$

where V_e is the empty volume of the membrane, V_d is the dry volume of the membrane, V_w is the wet volume of the membrane, ρ_m shows membrane density, and ρ_p is the density of base polymer used for UF/MF membranes fabrication.

Porosity via pycnometer calculation as follows,

$$\varepsilon = \frac{[M_{\text{dry}} + P_l - (P_l + M_{\text{wet}})]}{\rho_m V_t} \quad (9)$$

Where M_{dry} is the weight of dry membrane, P_l is the weight of pycnometer totally filled with the pure liquid, such as pure water, kerosene, toluene, etc., and $P_l + M_{\text{wet}}$ is the weight of pycnometer filled with liquid and membrane. The density of membrane shows ρ_m [17, 103]

2.2.3. Performance evaluation

2.2.3.1. Membrane affinity test

Typically, the primary characterization of any membrane is their performance and rest of all above characterization are depended on and to support the performance. Theoretically, the permeate (flux) of any substance per unit driving force which is "transmembrane pressure" is directly proportional to the permeability of the material. Before evaluating UF/MF membrane for protein or waste water treatment, it is critical to examine the membrane affinity test of the pure water. Thus, in membrane affinity, the hydraulic resistance (R_m) is one of the important properties to study the membrane compatibility with clean water against transmembrane pressure (ΔP) with respect to time [11, 95]. To characterize the membrane hydraulic resistance (R_m) and compaction, the pure water (de-ionized water) flux of membranes can calculate at different transmembrane pressures (ΔP) later than compaction. Yasuda and Tsai [100], revealed that after earlier time, the initial flux would be started after the pressurization of a test cell. The de-ionized water permeates usually dropped severely in the starting and flattened steady

state after about 6 to 8 h. The resistance of the membrane, R_m , can be examined from the slope of water flux vs. (ΔP) graph, and **Figure 7** shows R_m vs. flux with respect to time.

Following equations can be used to calculate the membrane resistance and membrane compaction against pressure [11, 102]:

$$J_w = \frac{\Delta P}{R_m}, \text{ where } \Delta P = \pi_m - \pi_b \quad (10)$$

$$J_w = \frac{\Delta W_p}{\rho A \Delta t \Delta P} \quad (11)$$

Where R_m shows membrane hydrodynamic resistance and can be determined by the slope of the water vs transmembrane pressure (ΔP) difference graph, π_m is the applied pressure on the membrane (driving force), π_b is the osmotic pressure, and ΔW_p is the permeate weight. The difference, Δt is an interval of time, A is the membrane active surface area, and ρ is the density of permeate.

2.2.3.2. Molecular weight cut-off (MWCO)

Technically, UF/MF is a pressure-driven process designed to remove large macromolecule ($>0.001 \mu\text{m}$ for UF and >0.1 for MF) from selected solution (see **Figure 8a**). MWCO is a pore characteristic of membranes and is related to rejection for a given molecular weight of a solute and the value frequently used by membrane manufacturers to describe their porous UF/MF membranes. Dextran, PVP, PEG, and BSA of a range of molecular weights are often used to rate the MWCO of UF/MF membranes [11, 17, 29]. For example, a membrane that can remove dissolved solids with molecular weights of 150+ has a molecular weight cut-off of 150. **Figure 8b** [17] shows a retention vs. molecular mass curve and membranes with this particular MWCO

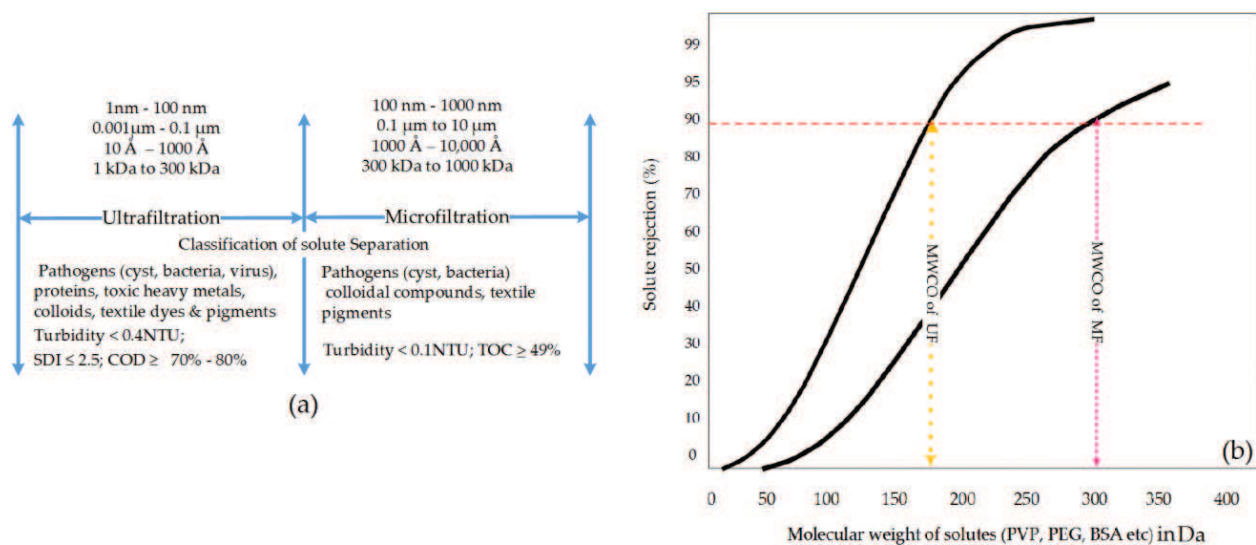


Figure 7. Classification of solute separation and MWCO of UF/MF [17].

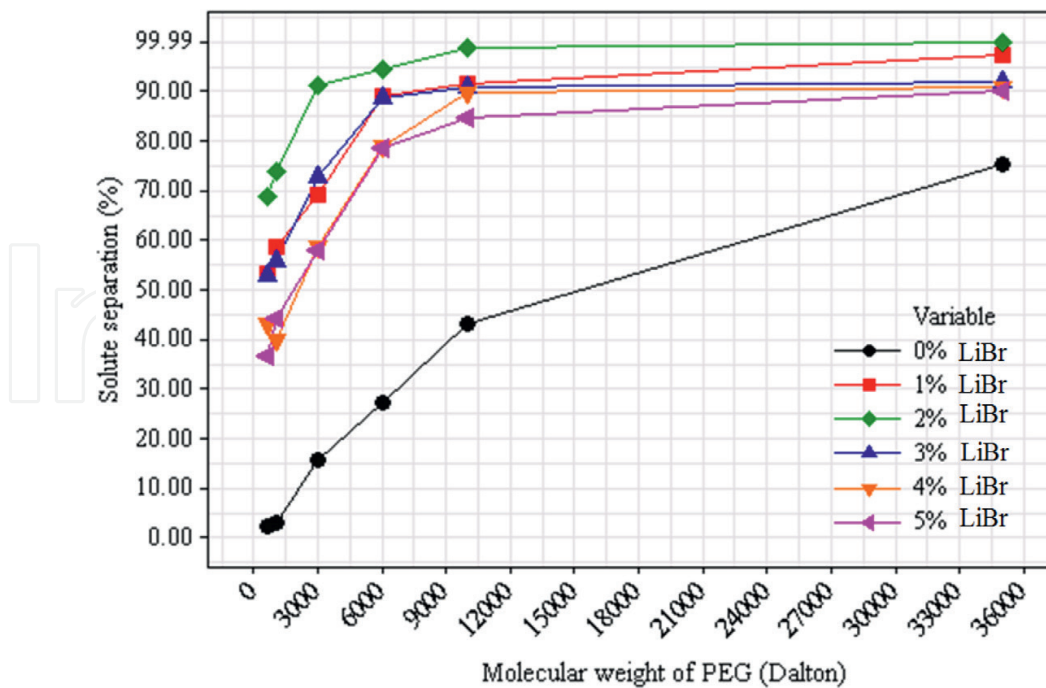


Figure 8. A typical rejection curve, variable shows UF membranes with and without (0%) additives [17].

would be appropriated for applications. Theoretically, UF and MF have the same chemistry and same phenomenon except for pore size difference. **Figure 8a** [17] shows a pore size or MWCO differences between UF/MF membranes. Typically, UF membrane has pore sizes in the range from 10 to 1000 Å and is capable of retaining species in the molecular weight range of 300 to 500,000 Daltons, while MF pore size is usually almost 100 times higher than UF. Typically, the value of MWCO is defined as the molecular weight (MW) which is rejected by 90%. The molecular weight has a linear relationship with the pore radius or pore size of a membrane [10, 11, 25–27, 108]. In general, the MWCO of a membrane is determined by the identification of an inert solute, which has the lowest molecular weight and has a solute rejection of 80–100% in steady state UF experiments. The permeate solutes (bovine serum albumin or polyethylene glycol or PVP) concentration can be determined using UV-vis spectrophotometer at a wavelength of 280 nm. Theoretically, solute rejection performance for UF/MF membranes is usually illustrated as the observed amount of rejection, and it can be defined as,

$$\text{Solute rejection (R)} = \left[1 - \frac{C_p}{C_f} \right] \times 100 \quad (12)$$

Whereas, C_p and C_f are the solute concentration in the flux and feed, respectively. In UF/MF macromolecular solutions, the concentration polarization phenomenon always happened. As a result of this phenomenon, the solute concentration at the membrane surface C_s is higher than for UF/MF membranes; therefore, it is expressed as the true rejection, R_t , and it can be evaluated as:

$$R_t = \left[1 - \frac{C_p}{C_m} \right] \quad (13)$$

The value of C_m can be calculated using the boundary layer resistance (BLR) model for the permeate flux. In BLR, the permeate flux is expressed as the following Eq. (14):

$$J_w = \frac{\Delta P}{\mu_O(R_m + R_{bl})} \quad (14)$$

Insert Eq. (10) in Eq. (14)

$$J_w = \frac{\pi_m - \pi_b}{\mu_O R_{bl}} = \frac{\pi_b}{\mu_O R_{bl}} \quad (15)$$

where R_{bl} is the hydrodynamic resistance of the boundary layer to the flow of solvent defined as:

$$R_{bl} = \int_0^\delta P_s(x)^{-1} dx \quad (16)$$

If the relationship of transmembrane pressure as a function of solute concentration is known, then the value of C_m can be determined from Eqs. (14) and (15).

2.2.3.3. Pore size and pore size distribution

Typically, the average pore size, pore volume, pore size distribution, pore density, pore geometry, and properties of UF/MF porous membranes are imperative. Also, it is vital to the development of new kind of membrane [19, 21, 23] but also a great help in selecting and using membrane correctly and fast in the application. Kaneko [106] and Nakao [21, 22] has comprehensively reviewed and described various kind of pore size and pore size distribution methods. Sakai was also discussed and provided a general description of the concept of pore size and pore size distribution method for UF/MF. Calvo and co-authors [104] have reported comprehensive reviews on almost all pore size and pore size distribution methods used for UF/MF. However, recently among all the methods, the membranologist is using true solute rejection data and MWCO (solute rejection curve) for pore size and pore size distribution method.

2.2.3.4. Solute rejection curve

The variations of solute rejection with solute molecular diameter yield and shaped curve as illustrated in **Figure 9** (MWCO) and **Figure 10** (log-normal). **Figure 9** suggests that the relation between solute rejection and solute diameter is described by log-normal probability function as reported by several authors [22–27] and yields a straight line on a log-normal probability graph as shown in **Figure 10**. If the solute rejection correlates with solute diameter by the log-normal probability function, this relationship can be expressed as:

$$R_t = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^y e^{-u^2/2} du \quad (17)$$

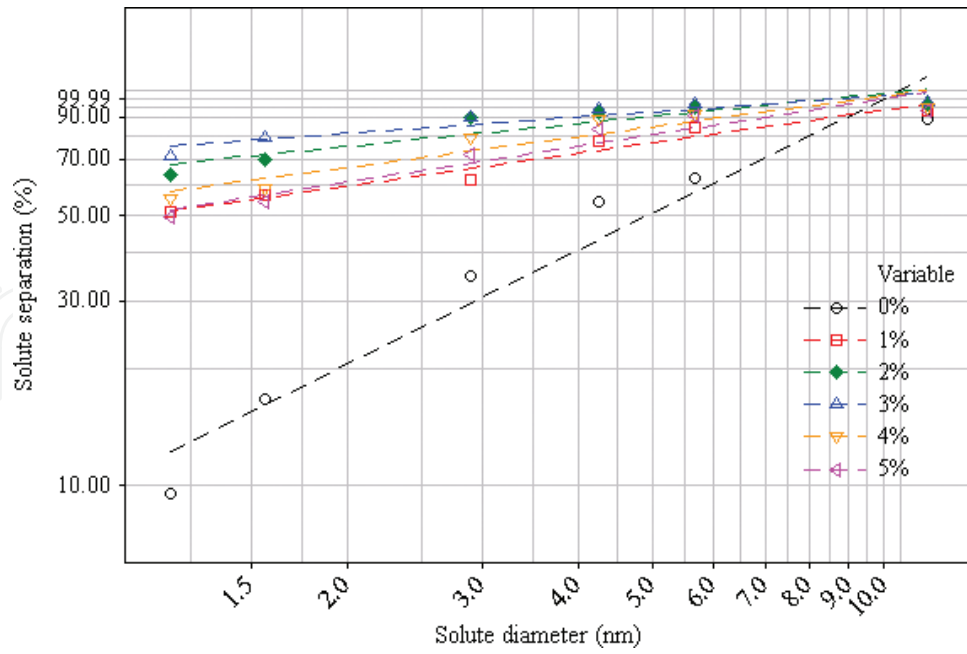


Figure 9. A typical rejection curve on log normal probability graph, variable shows PES UF membranes with LiBr (1%-5%) and without additives (0% LiBr) [17].

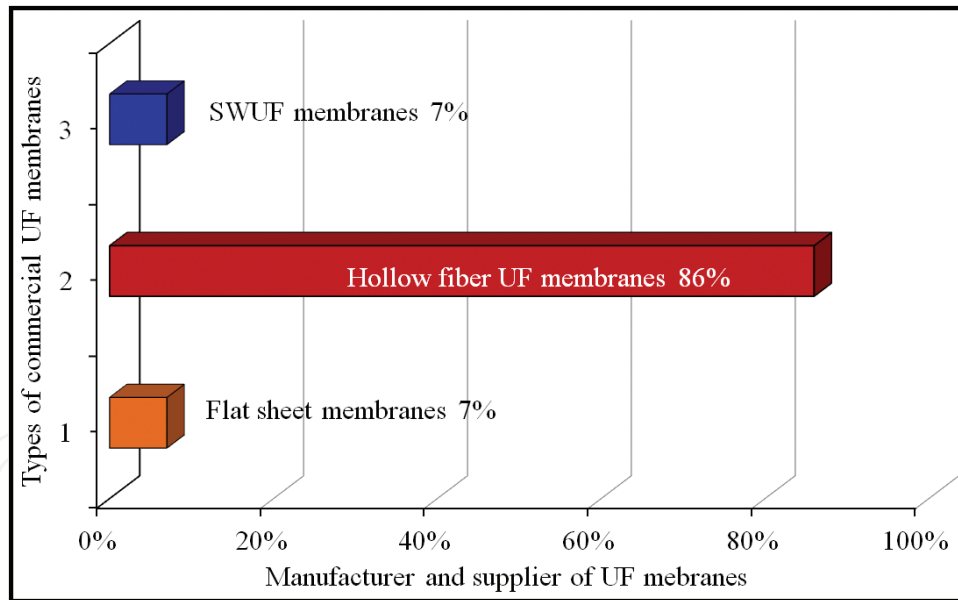


Figure 10. Recent status of commercial HF membranes [63, 108].

$$y = \frac{\ln D_s - \ln \bar{D}_s}{\ln \sigma_s} = \frac{\ln D_s - \mu}{\ln \sigma_s} \tag{18}$$

Where D_s is the solute diameter, μ is the geometric mean diameter of solute at $R_t = 50\%$, and σ_s is the geometric standard deviation about the mean diameter. According to the Eqs. (17) and

(18), a straight line in the form of solute yield among R (solute separation in %) and D_s (solute diameter) on a log-normal,

$$R(R_i) = A + B(\ln D_s) \quad (19)$$

Where, A and B are the intercept and the slope, respectively. From this log-normal plot, mean solute size (D_s) can be calculated as D_s corresponding to $R = 50\%$ can be determined from the ratio of D_s at $R = 84.13\%$ and 50% [26, 27, 106]. By ignoring the dependence of solute separation on the steric and hydrodynamic interaction between solute and pore sizes [25, 26], the mean pore size (D_s) and the geometric standard deviation (σ_g) of the membrane can be considered to be the same as that of solute mean size and solute geometric standard deviation. From Eqs. (18) and (19) and the tables of statistics that were presented by Michaels [25], μ and σ_g are evaluated as:

$$\mu = \ln \bar{D}_s = (\ln D_s)_{R=0.5} = -A/B \quad (20)$$

$$\sigma_g = \frac{(\ln D_s)_{R=0.84} - (\ln \bar{D}_s)_{R=0.159}}{2} = \frac{1}{B} \quad (21)$$

2.3. UF/MF membrane configuration and components

To minimize the operational in desalination process, beach well-intake pretreatment is used [10, 14, 28, 32, 36, 46, 109]. However, this is not always precisely promising and not liable to headway due to operating cost. Thus, the pressure-driven membrane processes such as MF, UF, and NF are now the new drift in deceitful n RO or MSF pretreatment systems [46]. Microfiltration (MF) is an open technique for the removal of suspended solids and for lowering the silt density index (SDI). Energy consumption in MF is relatively small so that the total costs for the MF pretreatment are comparable to the beach well intake [83, 84, 109–112]. Whereas, the cost for a corresponding conventional pretreatment is more than double. MF provides an RO feed water of high quality, with (slightly) lower COD/BOD, and smaller SD1 in comparison to the untreated seawater, although there is a significant influence on the feed water quality [111–114]. Good quality seawater may be used for large SWRO plants with a minimal pretreatment and at relatively low cost.

To minimize the energy cost, scaling inhibitor, and fouling lessening, respectively for the useful of the RO, and MSF treatment practice of MF and UF optimizes only the pretreatment given lower capital and operating costs, or on a wider variety of sources [83]. Besides, the implementation of NF as a pretreatment, on the other hand, will lead to a breakthrough in the application of RO or MSF because it has implications for the desalination process itself and not only on the quality of the feed water. Turbidity, microorganisms, and hardness are removed in the NF unit, as well as a fraction of the dissolved salts [14, 109]. The worldwide market for UF membranes has moving parallel with RO, grown to nearly \$3.3 billion in 2016 from \$3.1 billion in 2015. The market is expected to increase at a 5-year compound annual

growth rate (CAGR) of 6.9% from 2016 to 2021, increasing to nearly \$4.6 billion in 2021 [115, 116]. Thus, the world demand of UF is parallel moving with RO membranes. As described above that majority of membrane manufacturer and supplier currently prefer hollow fiber membrane components for UF and MF application. Recently, MF/UF membrane systems have enjoyed exceptional growth, producing high-quality feed waters to downstream RO systems and as stand-alone filtration methods for a variety of applications. Therefore, the majority of fresh water treatment plants are preferred low-pressure hollow fiber membranes elements configuration [63, 113, 114]. **Figure 10** summarized the recent status of hollow fiber membrane elements as compared to SW setup and flat sheet elements [63, 108]. Several types of HF elements configuration are available commercially depend upon types of water treatment or other applications. **Figure 11** summarized the HF elements for a configuration such bundles, using a simple technique or spiral winding techniques that better shell flow distribution and lower mass transfer resistance [108, 111, 117]. Fiber crimping also has been introduced to reduce mass transfer resistances. The introduction of fluid into the shell region of these devices has received significant attention as it can impact performance significantly [108].

Commercially, available in microfiltration and ultrafiltration, and the tubular membranes operate in tangential, or cross-flow, a configuration where process fluid is pumped along the membrane surface in a full action. Several membrane manufacturer and suppliers provide several offers of strong choice that are effortless to control and clean, serving many industrial and municipal applications [63, 108]. The major demand of HF element configuration is usually the strict quality requirement of pharmaceutical, food industry. Besides, HF is also suitable for wastewater treatment, gas separation, etc. **Figure 11** also shows several types of tubular membrane configuration, and **Figure 12** revealed top seller of UF/MF membrane configuration. Tubular membrane elements easy procedure, high suspended solids, and concentrate product competent and often to greater end-point concentration degrees without plugging, making them ideal for recovering wastewaters, and clarifying juices [63, 108, 111].

2.4. Commercial UF/MF materials

Currently, several membrane configurations are available commercially. **Table 4** lists some of the commercially available membranes for UF [1, 17, 63]. The membranes itself must satisfy some mechanical, hydrodynamic, and economic requirements [17, 63]. Automatic membrane condition means the ability to provide the necessary physical support for the membrane including the capacity to undergo the required pressure drop and any back flushing. Hydrodynamic membrane requirement means minimizing pressure drop through the device and thus reduce pumping costs [52, 118]. The solute mass transfer is optimized, and thus, concentration polarization is reduced. Particulate plugging and dead spots for clean design are minimized. Economic membrane requirements reduce membrane packing densities, manufacturing costs, permit easy access for cleaning/replacement and provide sufficient chemical resistance [45, 52, 63, 110, 115]. Recently, Millipore Corporation from the USA has introduced their new generation of UF membranes. These membranes are based on new casting processes that provide void-free membranes and high process flux with enhanced product retention and significantly increased mechanical resistance. These membranes have been commercialized under the trade names of Biomax (void-free PES family) and Ultracel



Figure 11. Commercial available hollow fiber membrane elements configuration.

(void-free composite regenerated cellulose family). Applied membrane Inc from the USA is a leading supplier of RO and UF membranes systems and water filtration elements under the AMI label for over 25 years. Previously, FILMTEC produced a broad range of CA thin composite membranes ranges for RO. Dow/FILMTEC is currently commercializing UF membrane series M-U4040 PES and MU2540 PAN for pharmaceutical, food beverage, and wastewater treatment [17, 52, 63].

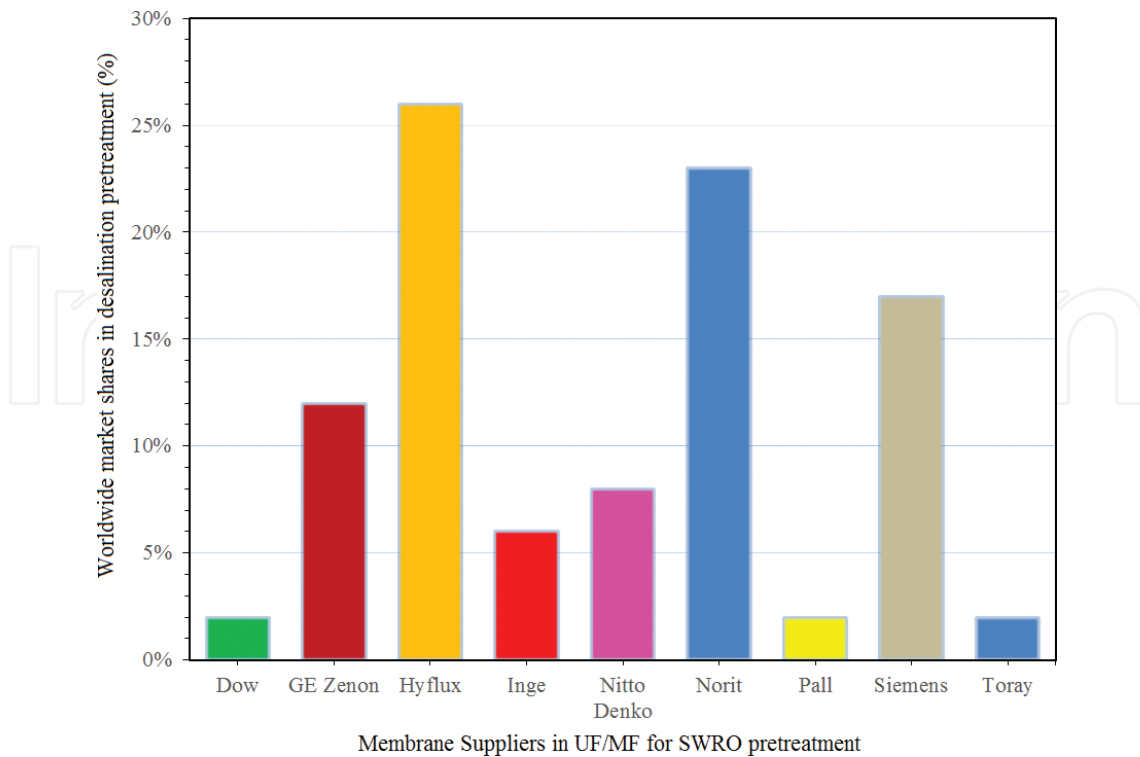


Figure 12. Top seller of UF/MF membrane configuration [17, 63].

American Membrane Corporation (AMC) was incorporated in Michigan USA in 2001 and established its first subsidiary in China in 2002. AMC has launched the Accupor membrane which is a highly microporous membrane composed of modified hydrophilic PES that is a

Manufacturer	Brand	Material & module	MWCO (kDa)	Flux ($L \cdot m^{-2} \cdot h^{-1}$)	Application
Applied Membranes (USA)	M-U4040	PES (SW)	10	4.5–18.2 at 3.2 bar	Pharmaceutical & food
	MU2540	PAN (SW)	20	50 at 3.5 bar	Wastewater
DOW/FLMTEC	SFP & SFD	PVDF, (HF)	0.03 μm	40–90 at 2.5 bar	RO feed water & Wastewater
AMC (USA/China)	AC 120R01	PES (HF)	15	112 at 4.1 bar	Pharmaceutical & food
AsahiKasei, JP	AP	PAN (HF)	69	16	Pharmaceutical & food
KOCH, USA	HFK	PES,	5–10	24–53 at 3–4 bar	Wastewater
	HF8H7235PMPW	PSF	100	32 at 3 bar	PVC separation
Luxx Ultratech, USA	L series	PES, PSF, PVDF (tubular)	5	27–45	Food & Wastewater
PCI, USA	CA, ES, PU, FP, AN, FP	CA, PES, PSF, PVDF, PAN (Tubular)	2–200	NP	MBR, wastewater, Pharmaceutical & food

Manufacturer	Brand	Material & module	MWCO (kDa)	Flux (L.m ⁻¹ .h ⁻¹)	Application
Millipore, USA	Biomex & Amicon	CA& PES	5–10	35–97.2 at 1 bar	Protein purification
membrane element	M-series	PAN (HF)	0.03–1 μm	4.5–18.2 at 9.3 bar	Oil water separation
Nitto Denko, JP	Hydracap	PES (HF)	150	51–128 at 3 bar	Wastewater
PALL, USA	BTS	PES (Cassette)	0.5–10	187.2 at 3 bar	Pharmaceutical & food
Polymem	polymem	PSF (HF)	6	313.2 at bar	Protein purification
Synder, Canada	PES 100	PES (SW)	70	51 at 3 bar	Gelatin separation
Trisep, Canada	UE10	PES (SW)	10	2.1 at 2–3 bar	Dairy and Food
Toray, Switzerland	HFU, HFS, HSU	PVDF (HF)	150–200	2.6–8 at 3 bar	RO feed water & Wastewater

Note: Polyethersulfone (PES), polysulfone (PSF), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), cellulose acetate (CA), spiral wound (SW), hollow fiber (HF), Japan (JP), note provided (NP).

Table 4. Commercially available membranes for ultrafiltration.

tough, durable, and temperature-resistant aromatic polymer. This membrane is specifically designed for biological, analytical, electronic, pharmaceutical, beverage, and sterilizing filtration applications [17, 63]. Nitto Denko and Asahi Kasei commercialized Hydracap (hydrophilic PES), UF AP series (Hydrophilic PAN), low-pressure UF hollow fiber membranes for wastewater, pharmaceutical, and food industry. Recently, KOCH has supplied a series of UF HFK-131/138 (PES) and HF8H-72-PMPW (PSF) spiral wound and hollow fiber membranes for wastewater treatment [17, 52, 63]. PALL has introduced BTS highly asymmetric membranes; these membranes are cast from PES and PSF by a unique process exclusive to another supplier. The “cut off” layer in the BTS membranes is only about 10 μm thick, vs. traditional membranes with cut-off layers of about 100–125 μm thickness. This difference in thickness gives the BTS highly asymmetric membrane significantly higher flow with much lower pressure drop for pharmaceutical purposes. Besides that Polymer has also launched a very high-performance asymmetric PSF hollow fiber membrane with uppermost permeation rate at very low pressure for Protein Purification.

3. Conclusion

During 50 years, UF/MF membrane technology has experienced a quick growth as it relates to most applications such as pharmaceutical, food, and beverage industries. Also, theoretically, it has been proven that UF/MF is the best post-treatment process (upstream) for RO, eliminating from the feed water nearly all of the possible constituents liable of desalinating membranes fouling. The 30 years of commercialization have viewed new materials of UF/MF membranes

employed at ever lower pressures (1–2 bar) and with remarkable performance. However, UF/MF technology still has some limits, and yet membrane fouling is a destructive obstacle for UF/MF membranes. Material customization and membrane configuration (modules) for selective application and molecular transport modeling are efficient tools to minimize the fouling phenomenon, which is used in the advancement of membrane technology. Also, UF/MF system design continues to progress, and current movements in MF and UF in certain are a feedback to industry pressures for a basic MF/UF system design that holds a diversity (not clear) of membrane components and system configurations. Consequently, the remarkable UF/MF market growth leads to continuously increasing demand particularly in feed water treatment for SWD and wastewater treatment process and without doubt, UF is recently becoming a reasonable feed water system for RO in an extensive field of raw water quality.

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Appendix

See Appendix Table.

Technical words	Abbreviations	Chemical compounds and polymers	Abbreviations
Sea water desalination	SWD	Calcium carbonate	CaCO ₃
Spiral wound reverse osmosis	SWRO	Zinc selenide	ZnSe
Multi-stage flash	MSF	Polyethylene oxide	PEO
Multi-effect distillation	MED	Polyamide	PA
Electrodialysis	ED	Polyurethanes	PU
Reverse osmosis	RO	Polyethylene terephthalate	PET
Nanofiltration	NF	Polycarbonate	PC
Ultrafiltration/ Microfiltration	UF/MF	Polysulfone	PSU or PSF
Thin film composite layer	TFC	Polyethersulfone	PES
Ultra thin film	UTF	Polyvinylidene fluoride	PVDF
Pore size distributions	PSD	Polyimide	PI

Technical words	Abbreviations	Chemical compounds and polymers	Abbreviations
Molecular weight	MW	Aliphatic polyamide (Nylon)	PA6 and PA66
Molecular weight cut-off	MWCO	Aromatic polyamide	Ar.PA
Fourier transform infrared	FTIR	Polyethylenimine (PEI) or polyaziridine	PEI
Equilibrium water content	EWC	Polyether ether ketone	PEEK
attenuated total reflection	ATR	Polyacrylonitrile	PAN
Atomic force microscope	AFM	Cellulose acetate	CA
Scan electron microscopy	SEM	Cellulose triacetate	CTA
Energy-dispersive X-ray	EDX	Trimethyl polysulfone	TM-PSF
Field emission scanning electron microscopic	FE-SEM	Sulfonated polysulfone	SPSF
transmission electron microscope	TEM	Sulfonated polyethersulfone	SPES
Kilo Dalton	KDA	N-Methyl-2-pyrrolidone	NMP
Ultraviolet	UV	Dimethylacetamide	DMAc
Silt density index	SDI	Dimethylformamide	DMF
Carbon oxygen demand	COD	Dimethyl sulfoxide	DMSO
Biological oxygen demand	BOD	Bovine serum albumin	BSA
Annual growth rate	CAGR	Polyethylene glycol	PEG
Hollow fiber	HF	Polyvinylpyrrolidone	PVP

Equations

Mean pore radius	\bar{r}	pure water viscosity	J_{μ}
Membrane thickness	Δx or Δa	Hydraulic pressure	H_p
Membrane porosity	ε	Water permeation	J_p
Transmembrane pressure	TMP (ΔP)	Tortuosity	τ
Water content	W_c	Pore volume	P_v
Pore size distributions	PSD	Mean roughness	Ra
Root mean square of data	Rz	Highest peaks	Ry
Difference between the highest and lowest points	Z	Wet membranes	M_{wet}
Dry membranes	M_{dry}	Empty volume	V_e
Dry volume	V_d	Wet volume	V_w
Membrane density	ρ_m	Density of base polymer	ρ_p
Pure liquid	P_l	Wet membranes	M_{wet}

Technical words	Abbreviations	Chemical compounds and polymers	Abbreviations
Membrane hydrodynamic resistance	R_m	Applied pressure	π_m
Osmotic pressure	π_b	Permeate weight	ΔW_p
An interval of time	Δt		
Membrane active surface area	A	Density of permeate	ρ
Solute concentration in the flux	C_p	Solute concentration in the feed	C_f
Solute concentration at membrane surface	C_s or C_m	True rejection	R_t
Hydrodynamic resistance	Rb_1	Solute diameter	D_s
Geometric mean diameter	μ	Solute rejection	R_i
Geometric standard deviation	σ_g	Intercept	A
Slope	B	Boundary layer resistance	BLR

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