Understand the Basics of Membrane Filtration

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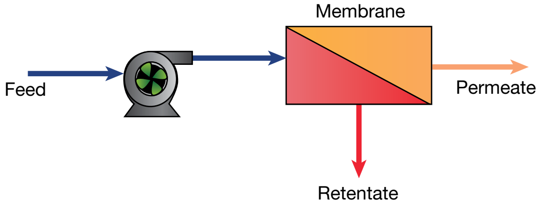
Membrane filtration is an integral part of many industrial processes, as it is often more environmentally sustainable and cost-effective than other separation technologies.

Separation processes account for 40% to 70% of capital and operating costs in the chemicals industry *(1)*. Membrane-based separation technologies have a broad range of applications, including process water treatment, wastewater treatment and reuse, metal and catalyst recovery, solvent recovery, gas separation, and concentration of heat-sensitive biological macromolecules and proteins, among others *(2, 3)*.

This article compares some of the liquid-phase membrane technologies commonly used in the chemical process industries (CPI), and presents examples of membrane use in seawater and brackish water desalination, production of high-purity industrial process water, and protein separation.

Membrane terminology

A membrane is a semipermeable, or selectively permeable, barrier that allows some molecules or ions to cross it while hindering the passage of others. In membrane separation, a portion of fluid known as permeate (or filtrate) passes through the membrane, while other constituents are rejected by the membrane and retained in the retentate (or concentrate) stream (Figure 1).



▲ **Figure 1.** In a membrane separation process, the permeate passes through the membrane while the retentate is rejected.

The transport of materials across a membrane requires a driving force. A chemical potential gradient provides the driving force for material transport from one side of a membrane to the other. The chemical potential gradient can come from a pressure difference, concentration difference, or temperature difference (Table 1). Material transport through ion exchange membranes by means of an electric potential via electrodialysis is also an important membrane separation technology but is outside the scope of this article *(4)*.

Synthetic membranes can be classified as microporous membranes or nonporous (dense) membranes according to

Table 1. The chemical potential gradient, or driving force, in membrane separation processes can arise from a pressure, concentration, or temperature difference.

Driving Force	Membrane Process
Pressure Difference	Reverse Osmosis, Nanofiltration, Ultrafiltration, Microfiltration
Concentration Difference	Pervaporation (PV)
Temperature Difference	Membrane Distillation (MD)

Table 2. Microporous and nonporous (dense) membranes employ different mechanisms of separation.

Morphology	Separation Mechanism	Membrane Process
Microporous	Size Exclusion	Ultrafiltration, Microfiltration
Nonporous (dense)	Solution-Diffusion	Reverse Osmosis, Nanofiltration, Pervaporation, Gas Separation

their structure and mechanism of separation (Table 2). Membrane separation can be further classified in terms of the size range of the permeating species.

Dead-end versus crossflow filtration. Membrane filtration can be accomplished in either dead-end flow mode or crossflow mode. In dead-end filtration, the feed stream moves perpendicular to the membrane surface, and it passes through the membrane as filtrate (Figure 2a). Particulates and aggregates rejected by the membrane form a filter cake, which reduces filtrate flux and increases feed pressure over time.

In crossflow — or tangential flow — filtration, the feed stream moves parallel to the membrane surface, and some portion of the feed stream passes through the membrane as permeate while the remainder of the feed stream becomes retentate for further processing or recirculation back to the feed (Figure 2b). The tangential (parallel) feed stream continuously sweeps across the membrane surface, which prevents the buildup of particulates and aggregates and maintains a more steady permeate flux and low transmembrane pressure.

Most large-scale industrial filtration processes operate in crossflow filtration mode.

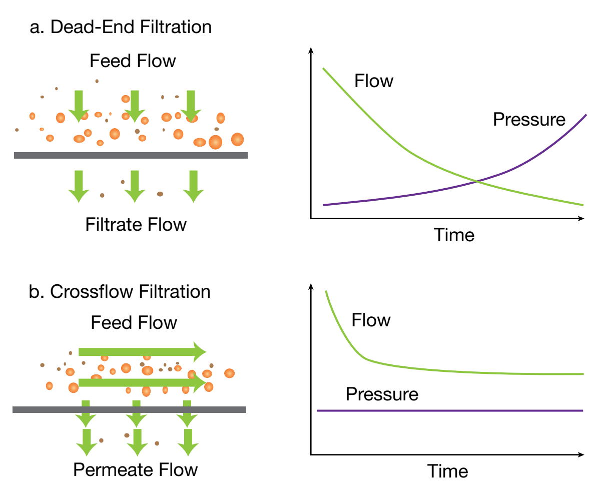
Pressure-driven membrane separation

The most widely used membrane separation technologies are pressure-driven processes — reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). Figure 3 and Table 3 compare the characteristics of these processes, and Table 4 lists some common applications.

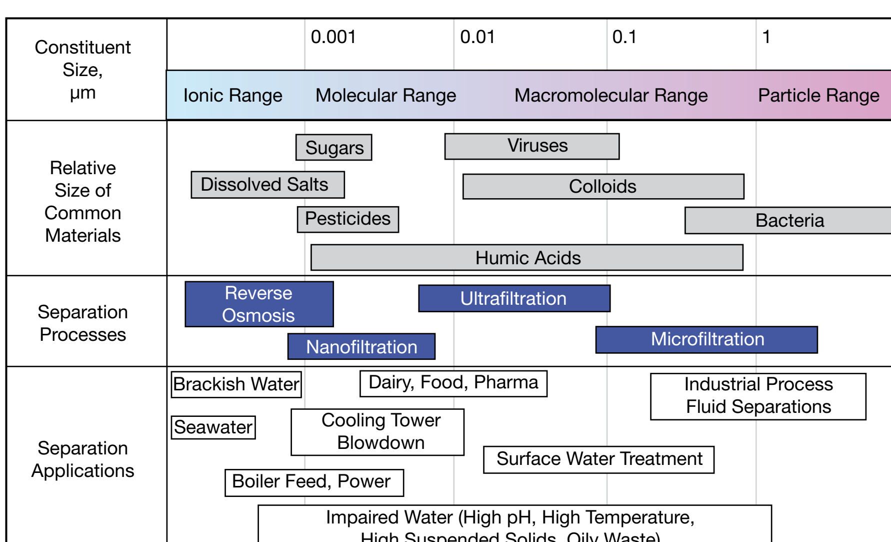
Reverse osmosis. RO employs the tightest membranes for liquid separation. Dissolved salts, inorganic solutes, and organic solutes with a molecular weight greater than approximately 100 Dalton (Da) are rejected by RO membranes; water is able to pass through RO membranes. Rejection of dissolved salts such as sodium chloride by RO membranes is typically 95–99.8%. The operating pressures of RO processes are typically in the range of 100–1,000 psi. Examples of RO membrane applications include brackish water and seawater desalination and the production of high-purity process water for industrial applications.

Nanofiltration. NF removes multivalent ions and small molecules in the nanometer range (*e.g.,* sulfate ions, sugars). NF membranes can fractionate small compounds, such as salts and small organic molecules, and are commonly used to permeate monovalent ions while retaining divalent ions. In NF processes, salts with divalent anions (*e.g.,* sulfate) have rejection rates in the range of 90% to more than 99%, while salts with monovalent anions (*e.g.,* sodium chloride) have rejection rates of 20–80%. Solvent-resistant NF membranes are also used to separate organic compounds in an organic solvent. The operating pressures of NF processes are typically in the range of 50–225 psi.

Both RO and NF membrane processes are governed by the solution-diffusion transport mechanism, where the permeating species first dissolve into a membrane and then diffuse through it. Because of the nonporous nature of these membranes, RO and NF membranes are operated at signifi-



▲ **Figure 2.** In dead-end filtration, the process stream flows through the membrane, whereas in crossflow filtration, the flow is parallel (tangential) to the membrane surface.



▶ **Figure 3.** The spectrum of pressure-driven membrane separation processes as a function of constituent size.

Table 3. Characteristics of commercial pressure-driven membranes *(7)*.				
	Reverse Osmosis	**Nanofiltration**	**Ultrafiltration**	**Microfiltration**
Membrane	Asymmetric, Thin-Film Composite	Asymmetric, Thin-Film Composite	Asymmetric	Symmetric, Asymmetric
Pore Size	Nonporous	Nonporous	0.002–0.1 μm	0.1–10 μm
Total Thickness	150 mm	150–250 mm	150–250 mm	10–150 mm
Thin Film	1 mm or less	1 mm or less	—	—
Rejected Components	HMWC, LMWC, Sodium Chloride, Glucose, Amino Acid	HMWC, Mono-, Di-, and Oligosaccharaides, Multivalent Ions	Macromolecules, Proteins, Virus, Polysaccharides	Particles, Clay, Bacteria
Membrane Material(s)	Polymeric (thin-film composite and integrally skinned)	Polymeric (thin-film composite and integrally skinned)	Polymeric, Ceramic	Polymeric, Ceramic
Membrane Module	Spiral-Wound, Plate-and-Frame	Spiral-Wound, Plate-and-Frame	Spiral-Wound, Hollow-Fiber, Plate-and-Frame	Hollow Fiber
Operating Pressure	5–84 bar (100–1,000 psi)	3.5–16 bar (50–225 psi)	1–7 bar (15–100 psi)	0.7–3.5 bar (10–50 psi)

HMWC: high-molecular-weight components (*e.g.,* protein molecules). LMWC: low-molecular-weight components (*e.g.,* NaCl).

Table 4. Membrane separation is used in a wide range of commercial applications *(7)*.			
	Feed	**Permeate**	**Concentrate**
Reverse Osmosis	Water	Low-salinity water	Salty water
	Whey	Low-BOD permeate	Whey concentrate
	Dyeing effluent	Clean water	BOD, salt, chemicals, waste products
Nanofiltration	Water	Softened water	Waste product
	Antibiotics	Salty waste product	Desalted, concentrated antibiotics
	Whey	Salty wastewater	Desalted whey concentrate
	Dyeing effluent	Clean, salty water	BOD/COD, color
Ultrafiltration	Water	Clarified water	Waste product
	Oil emulsion	Oil-free water (≤10 ppm)	Highly concentrated oil emulsion
	Enzymes	Waste product	High-value product
	Washing effluent	Clarified water	Dirty water (waste product)
	Bio-gas waste	Clarified liquid for discharge	Microbes to be recycled
	Milk	Lactose solution	Protein concentrate for cheese production
	Antibiotics	Clarified fermentation broth	Waste product
	Carrageenan	Waste product	Concentrated carrageenan
Microfiltration	Water	Clarified water	Waste product
	Fruit juice	Clear juice	Waste product (suspended solids, micro-organisms, and undesirable proteins)
	Wine	Clear wine	Waste product (fine fruit particles, spent yeast, bacteria, soil, debris, and fining agents)
	Therapeutic proteins	High-value product	Waste product
	Amino acid	Clarified fermentation broth	Waste product

Biological oxygen demand (BOD): a measure of the amount of oxygen that is consumed by bacteria during the decomposition of organic matter. Chemical oxygen demand (COD): a measure of the amount of oxygen that is consumed in the chemical decomposition of organic matter and oxidation of inorganic matter. Both BOD and COD are standard methods for indirect measurement of the amount of contaminants (that can be oxidized biologically or chemically) in a wastewater sample.

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cantly higher pressures than the more-porous UF and MF membranes.

Ultrafiltration. UF membranes are commonly used to retain relatively large dissolved materials (*e.g.,* proteins, starches) and suspended solids (*e.g.,* colloids, viruses) while allowing salts and smaller dissolved organic compounds to permeate. UF membranes are typically classified by their ability to retain components of specific sizes dissolved in a solution. This is referred to as the molecular weight cut-off (MWCO), which is defined as the smallest molecular weight at which at least 90% of the solute is retained by the membrane. UF membranes generally have MWCO values between 1,000 and 300,000 Da and pore diameters in the range of ≤10 nm to 0.1 μm *(5, 6)*. UF membrane processes are widely used in biopharmaceutical protein separation, virus clarification, and whey protein concentration and isolation in the dairy industry. UF processes typically operate at pressures ranging from 15 to 100 psi.

Microfiltration. MF is a process by which suspended solids and large colloids are rejected, while dissolved solids and macromolecules pass through the membrane. MF membranes are suitable for the removal of total suspended solids (TSS), flocculated materials, and bacteria. Many membrane manufacturers rate their MF membranes according to nominal pore sizes, which are in the range of approximately 0.1–10 μm. MF processes operate at very low pressure, typically 10 psi or less.

Most microporous membranes tend to have highly nonuniform pores with a broad pore size distribution. Thus, MWCO and nominal pore size are only guidelines for membrane selection. Other important factors for choosing membranes include molecular shape, electrical charge, sample composition and concentration, and operating conditions. Therefore, it is important to perform pilot experiments with real feed streams to verify membrane performance.

Table 5. Commonly used polymers for membrane separation processes.

Polymer	Membrane Type
Polyamide	RO, NF, UF, MF
Cellulose acetate (CA)	RO, UF, MF
Polysulfone (PS)	UF, MF
Polyether sulfone (PES)	NF, UF, MF
Polyvinylidene fluoride (PVDF)	UF, MF
Polyimide (PI)	NF
Polyetherimide (PEI)	UF, MF, GS
Polyethylene (PE)	UF, MF
Polypropylene (PP)	UF, MF
Polyacrylonitrile (PAN)	UF, MF, PV
Polyethylene terephthalate (PET)	MF
Polydimethylsiloxane (PDMS)	NF, PV, GS

GS: gas separation. PV: pervaporation.

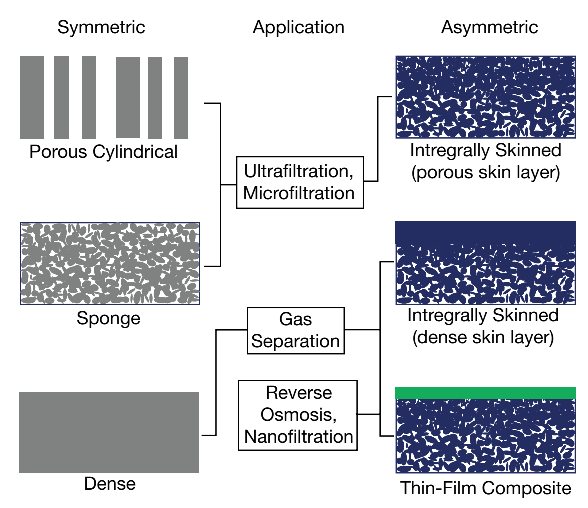
Membrane materials, structure, and morphology

Synthetic membranes are fabricated from a variety of materials, including both organic and inorganic materials such as metals, polymers, and ceramics. Ceramic and metal membranes can be employed in separations where aggressive media (*e.g.,* acids, strong solvents) are present. They also have excellent thermal stability, which makes them suitable for high-temperature operations *(7, 8)*.

Polymeric membranes dominate the market because they are less expensive and more versatile than inorganic membranes. They are typically formed by coating a thin polymer layer on a porous backing or support to create a combination that provides high permeability, selectivity, mechanical strength, and chemical stability. Table 5 provides a list of the most commonly used polymers for commercial membranes. Desired membrane properties include high porosity (MF/UF), narrow pore size distribution (MF/UF), sharp MWCO (UF), high mechanical strength and flexibility, high pH and chemical stability, desired surface properties (*e.g.,* surface charge and hydrophilicity/hydrophobicity balance), low fouling tendency, and low cost.

Membranes can be classified according to structure, morphology, and application. The principal structures and morphologies of commercial pressure-driven membranes are shown in Figure 4.

Symmetric membranes. Only a few commercially available membranes are symmetric throughout their thickness.



▲ **Figure 4.** Membrane structures may be symmetric or asymmetric. Membrane morphologies include porous cylindrical, sponge, and dense (symmetric); and integrally skinned and thin-film composite (asymmetric) *(10)*.

Expanded polytetrafluoroethylene (ePTFE), polyethylene (PE), and polypropylene (PP) are examples of microporous symmetric membranes.

Asymmetric membranes. Most commercially available membranes are asymmetric. An asymmetric membrane has either a thin microporous or dense permselective layer supported by a more-open porous substrate. The skin layer and its substrate may be formed in a single operation (*e.g.,* integrally skinned) or separate steps.

Composite membranes, a subset of asymmetric membranes, are comprised of a permselective skin layer and a microporous support layer made from different polymers. The skin layer determines the membrane separation performance while the open support layer provides mechanical support.

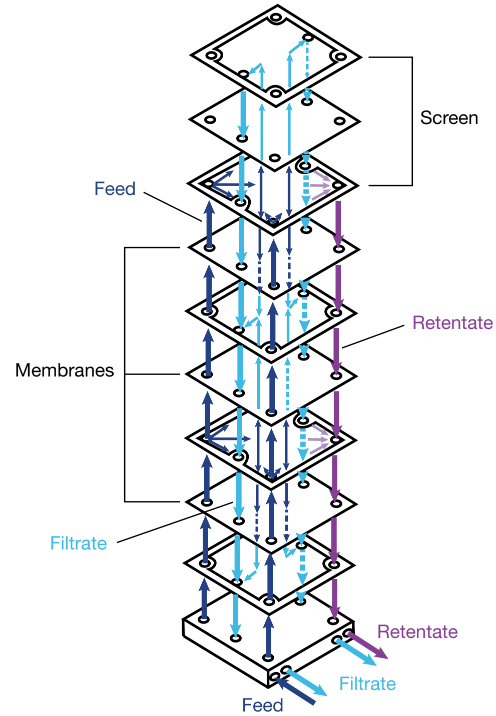
A cellulose acetate RO membrane is an example of an integrally skinned asymmetric membrane where both the dense permselective layer and microporous support layer are formed of cellulose acetate in a single-phase inversion operation *(5, 7)*. A polyamide RO membrane is an example of a thin-film composite membrane where a thin (100–200 nm) crosslinked polyamide permselective skin layer is formed on a microporous polysulfone UF support *(5, 9)*. The vast majority of commercial RO and NF processes use composite membranes because they allow high water fluxes.

Membrane format and module design

Membrane filtration employs several different membrane formats (*e.g.,* flat sheets and hollow fibers) and a wide variety of module designs (*e.g.,* cassette, cartridge, and spiral-wound). Membrane format and module design are closely related. For example, flat-sheet membranes are suitable for cassette and spiral-wound modules, whereas hollow-fiber membranes are ideal for cartridge modules. Each module design has specific hydrodynamics and is suitable for certain commercial applications based on factors such as process flux, rejection, specific surface area, and operating costs. Table 6 compares the cassette, cartridge, and spiral-wound module designs *(6, 9, 13)*, and the following paragraphs discuss these crossflow modules in more detail. Additional discussion on these modules can be found in Refs. 10–13.

Cassette modules. Membrane cassettes, which are used for MF and UF, have a complex plate-and-frame assembly of flat sheets of membranes, gaskets, spacers, and flow manifolds (Figure 5). The membrane performs the actual filtration and the gaskets provide a tight seal to separate the feed, permeate, and retentate streams. The presence of the spacers introduces turbulence in the feed stream, which would otherwise be laminar flow due to long (6–60 cm) and narrow flow channels. The flow turbulence promotes local mixing and effective mass transport, which disrupts concentration polarization (*i.e.,* formation of a gel layer) and improves process flux. However, membrane cassettes with spacers are prone to particulate plugging and are difficult to clean.

Cartridge modules. Membrane cartridges for MF, UF, or



▲ **Figure 5.** Membrane cassettes have a complex plate-and-frame assembly of flat sheets of membranes, gaskets, spacers, and flow manifolds *(11).*

Table 6. Crossflow filtration module configurations include flat-sheet cassettes, hollow-fiber cartridges, and spiral-wound modules.

	Flat-Sheet Cassette	Hollow-Fiber Cartridge	Spiral-Wound Module
Flow Channel	Narrow (0.03–0.5 cm)	Narrow (0.02–0.25 cm)	Narrow (0.03–0.1 cm)
Crossflow Velocity	2–3 m/s	0.5–2.5 m/s	0.5–1.5 m/s
Reynolds Number	>10,000	500–3,000	500–1,000
Packing Density	Low (300 m^2/m^3)	High (1,200 m^2/m^3)	High (600 m^2/m^3)
Energy Cost	Moderate	Low	Low
Ease of Cleaning	Good	Fair	Poor to Fair
Holdup Volume	Moderate	Low	Low
Particulate Plugging	Moderate	Fair	Very High

NF are produced by potting a large number of hollow-fiber membranes in a cylindrical housing with permeate ports and end caps (Figure 6). Since hollow-fiber membranes are self-supporting, the cartridge has very high packing density, and therefore has a high surface-area-to-volume ratio. For example, a cartridge with a 3-in.-dia. housing could contain more than 3,000 hollow fibers. Such a cartridge also has very little dead volume, making it ideal for product recovery. The fibers (or lumens) in a hollow-fiber membrane typically have a small diameter (0.2–2 mm) and a length between 10 and 60 cm, which creates laminar flow during the filtration process. It is possible (but not typical) to promote flow disturbance to improve local mixing for effective mass transport inside the lumen. Cartridges have flexible surface areas; the surface area can be changed by varying the fiber length and the number of fibers. Hollow-fiber cartridges can be operated either with feed flow through the lumen (inside the hollow fiber) and permeate collection from the shell (inside-out), or with feed flow from the shellside and permeate collection from the lumen (outside-in). Inside-out filtration is preferred based on fluid hydrodynamics, while outside-in filtration is used when back flushing is needed to clean the membrane.

Spiral-wound modules. Spiral-wound membrane modules are used predominantly for RO. They are composed of a multilayer assembly of flat sheet membranes and spacer screens, and are constructed by rolling the assembly around a perforated tube and sealing the membrane/spacer layers on three sides (Figure 7). Spiral-wound modules may have additional reinforcement (*e.g.,* they can be wrapped with fiberglass) to ensure safety during high-pressure filtration. The spacer screens are thin, usually between 0.3 and 1.0 mm, to ensure high packing density. Most industrial RO systems are large-scale continuous operations involving many RO modules connected in parallel.

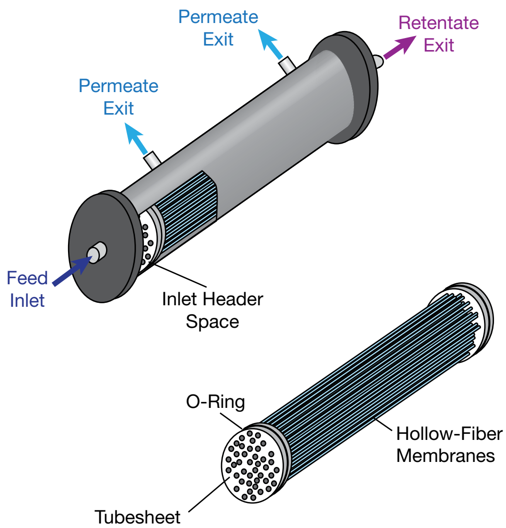
Common membrane applications

Seawater desalination by reverse osmosis. In regions with limited freshwater resources, membrane desalination has increasingly become a cost-effective option to turn seawater into potable and process water for residential, commercial, and industrial use. Impurities that need to be removed from seawater include salts, organic substances, algae, bacteria, and suspended particles.

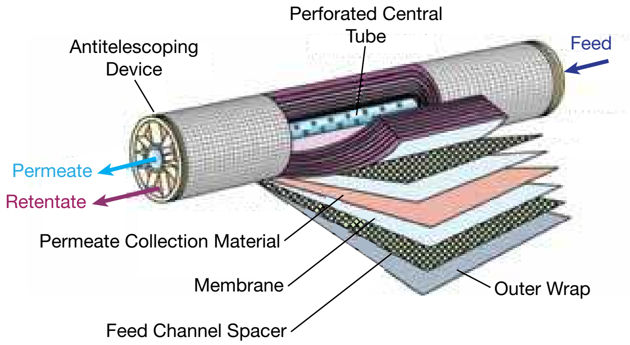
Figure 8 shows a typical RO membrane seawater-desalination process. A pretreatment system comprised of flocculation, sedimentation, and media filtration cleans up the seawater by removing TSS and dissolved organic carbon (DOC) prior to RO membrane desalination. The RO desalination unit removes total dissolved solids (TDS) and salts (*e.g.,* NaCl, $MgSO_4$). The RO-purified water then goes through post-treatment steps, including pH adjustment, remineralization, and disinfection, to meet potable water standards before it is used by industrial, commercial, or residential customers.

Industrial water treatment. High-purity water is required for boiler feedwater and cooling tower water, as well as for process water in the electronic, medical, and pharmaceutical industries, among others. Impurities in process water can jeopardize critical and expensive equipment as well as the operational efficiency of an entire plant. For example, total organic carbon (TOC) in make-up water breaks down to lower-molecular-weight, corrosive organic acids at the high temperatures and pressures experienced in steam generators in power plants.

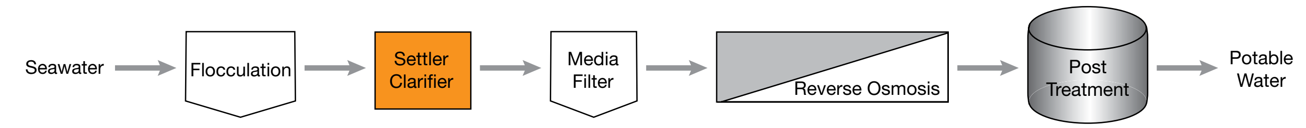
Figure 9a shows an example of a conventional boiler



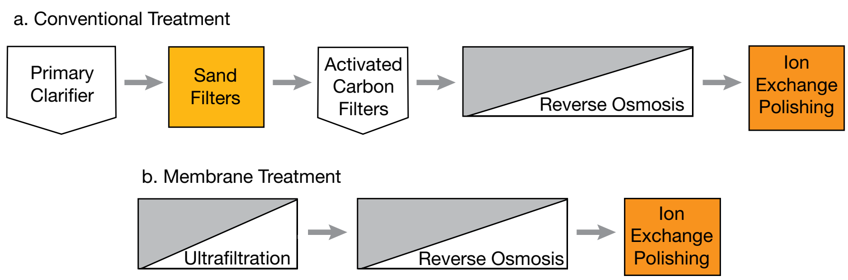
▲ **Figure 6.** Membrane cartridges contain a large number of hollow fibers in a cylindrical housing with permeate ports and end caps *(12).*



▲ **Figure 7.** Spiral-wound membrane modules are constructed by rolling a multilayer assembly of flat-sheet membranes and spacer screens around a perforated tube and sealing the membrane/spacer layers on three sides.



▲ **Figure 8.** Reverse osmosis is a common seawater desalination technology.



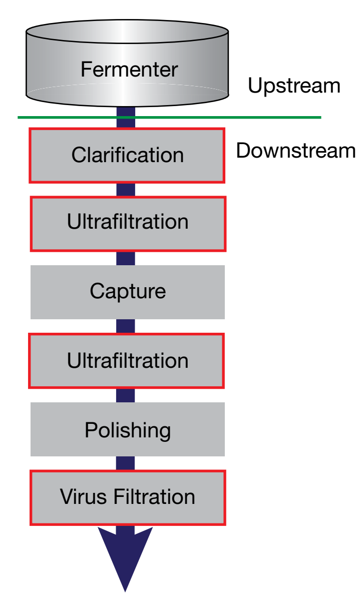
▲ **Figure 9.** Conventional boiler feedwater treatment (a) involves more steps than the hollow-fiber UF and RO water treatment process (b).

water treatment process that includes clarification and sand filtration to remove TSS, carbon adsorption to remove TOC, RO membrane filtration to remove TDS, and ion exchange to remove any remaining contaminants. In Figure 9b, a simplified UF and RO membrane process treats the boiler water. A hollow-fiber UF pretreatment step reduces the concentrations of suspended solids and organics, and is followed by an RO membrane filtration step. After a final ion exchange polishing step, the purified water is suitable for use as boiler feedwater. The integrated UF/RO membrane process is a compact design that can minimize land costs, construction costs, and operating costs.

Biopharmaceutical manufacturing. Biopharmaceutical processing includes upstream (cell culturing in a bioreactor or fermenter) and downstream (recovery, purification, and concentration of biological products) operations, as shown in Figure 10. After upstream processing, the desired product is typically in a complex mixture of unwanted cellular debris and remnants of the cell culture medium, and it is necessary to both concentrate the product and remove the impurities, while maintaining the potency of the delicate therapeutic product. The impurities that need to be removed vary widely in their physicochemical properties, and include host-derived impurities (*e.g.,* host proteins, DNA), product-related substances (*e.g.,* degraded, misfolded, cleaved, or oxidized product), and process-related impurities (*e.g.,* dye chromatography ligands, acetonitrile), as well as any adventitious agents (*e.g.,* bacteria, mycoplasmas, viruses) that may be present. Membranes are very attractive in downstream processing for purification, sterile filtration, concentration, and final formulation *(14, 15)*.

Sterile microfiltration has widespread use in bioprocessing, for streams ranging from cell cultures to buffers to final products. Microfiltration membranes typically have pore size ratings of 0.45 µm, 0.2 µm, and 0.1 µm, with the larger pore sizes providing higher flux rates or requiring a smaller membrane area. The performance of a sterile filter is rated by its log reduction value (LRV), which is defined as the logarithm of the ratio of bacteria concentration in the feed to the bacteria concentration in the filtrate ($LRV = \log[C_{feed}/C_{filtrate}]$). An LRV greater than 10^7 is usually required to ensure sterility. There is a strong correlation between membrane pore size and LRV — the smaller the pore size, the higher the LRV. Membranes are commonly used in a pleated format in dead-end filtration mode to maximize membrane capacity.

Ultrafiltration is often used for intermediate buffer exchange and final product concentration. These membranes typically have pore sizes in the range of 1 kDa to 300 kDa. Ultrafiltration membranes are highly asymmetric; they have tight surfaces with small pores to provide the separation capability, and large pores through the rest of the membrane thickness to maximize flux. Crossflow filtration with flat-sheet cassettes dominates this application, although hollow-fiber cartridges are sometimes used. Membrane performance is typically characterized by the product retention coefficient, which is defined as one minus the ratio of product concentration in the filtrate to product concentration in the feed ($1 - C_{filtrate}/C_{feed}$). Low process flux and membrane area are the tradeoffs for high retention — to achieve high flux, a



▶ **Figure 10.** A typical bioprocess consists of an upstream fermenter followed by multiple downstream separation steps. Membrane processes may be used for the operations outlined in red — clarification (often a combination of centrifugation and microfiltration), ultrafiltration, and virus filtration.

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large membrane is necessary, which reduces retention.

Virus filtration is a special case of ultrafiltration, where the goal is to remove any viral contaminants from the final products. Although virus filtration operates in the ultrafiltration range based on membrane pore size, it has special requirements for pore size distribution. A virus filtration membrane must have a narrow pore size distribution for maximum virus removal and minimum product loss — this is challenging due to the small difference between the product size and the size of viruses. Another unique characteristic of virus filtration is that, unlike most UF processes, it is typically operated in dead-end filtration mode to maximize membrane capacity.

Final thoughts

Membrane technology is an established part of many industrial separation processes. Membrane processes typically do not involve phase changes or chemical additives, and are often more environmentally sustainable and have lower energy costs than other separation technologies, such as distillation and crystallization. They are modular, easy to scale up, and simple in concept and operation.

In the design of an effective membrane separation process, the first steps are to determine the separation goal (*e.g.,* clarification, concentration, fractionation, and/or purification) and to characterize the composition of the feed streams (*e.g.,* nature and loading of suspended solids, and molecular composition and concentration of the dissolved species). Next, work closely with membrane suppliers to select the appropriate membrane type (RO, NF, UF, or MF), membrane format (flat-sheet or hollow-fiber), and module design (cassette, cartridge, or spiral wound) for the specific application to achieve the highest yield of the desired product(s). Ensure the chemical compatibility between the feed liquid and membrane, and assess the membrane-fouling propensity. The chemical and thermal stability and fouling resistance are especially important for membranes deployed in more-challenging separation applications and in harsh environments (*e.g.,* oily water, nonaqueous organic solvents, high temperature, and extreme pH).

In addition, it is important to perform pilot experiments with real feed streams and the selected membrane material and module design to establish the optimum operating parameters (*e.g.,* dead-end or crossflow filtration, batch or continuous operation, membrane flux, and pressure drop) and to ensure process reproducibility with the desired product quality. Pilot studies also help quantify the degree of membrane fouling, effectiveness of a membrane cleaning regimen, and membrane lifetime under repeated cycles of usage and cleaning. Finally, it is important to perform engineering and economic analyses to determine the capital investment and operating costs. CEP

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