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Water Treatment: Are Membranes the Panacea?

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Abstract

Alongside the rising global water demand, continued stress on current water supplies has sparked interest in using nontraditional source waters for energy, agriculture, industry, and domestic needs. Membrane technologies have emerged as one of the most promising approaches to achieve water security, but implementation of membrane processes for increasingly complex waters remains a challenge. The technical feasibility of membrane processes replacing conventional treatment of alternative water supplies (e.g., wastewater, seawater, and produced water) is considered in the context of typical and emerging water quality goals. This review considers the effectiveness of current technologies (both conventional and membrane based), as well as the potential for recent advancements in membrane research to achieve these water quality goals. We envision the future of water treatment to integrate advanced membranes (e.g., mixed-matrix membranes, block copolymers) into smart treatment trains that achieve several goals, including fit-for-purpose water generation, resource recovery, and energy conservation.

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1. INTRODUCTION

TDS: total dissolved solids

PW: produced water

Lack of reliable access to clean water poses an immediate threat to millions of people and has been identified as one of the top 10 problems facing humanity in the next 50 years (1). Unfortunately, the vast majority of water on Earth is unsuitable for human consumption or many other beneficial uses (e.g., agricultural, energy-extraction, and industrial applications) owing to a lack of cost-effective technologies for removing undesirable solutes (e.g., ions, organics, particles, and pathogens). One example of the complexity of water purification is presented in **Table 1**, which shows the wide variability in ion concentrations in potential water sources. For reference, potable drinking water typically has ion concentrations below 500 mg/L, measured as total dissolved solids (TDS). Seawater contains approximately 70 times the salt concentration of potable water, and inland groundwater sources are often brackish (2,000 to 10,000 mg/L TDS) (2). Municipal wastewater contains low TDS, but it must be treated extensively to remove organics, pathogens, and trace contaminants of concern. Nevertheless, water reuse and the concept of “one water,” in which all effluent discharges are considered a potential source for another downstream use, are taking hold (3). Produced water (PW) is defined as the water that exists in the subsurface and is brought to the surface during oil and gas production (4). During early periods of production, PW often includes chemicals that were injected to enhance oil and gas production; this water is often referred to as flowback water (5). PW is among the largest man-made wastewater streams (6), but more than 90% of PW is reinjected into the subsurface, in part because it is often highly impaired (7, 8). PW treatment must consider a plethora of contaminants, including dispersed oils, soluble organics, inorganic ions, and bacteria (8). A primary component of PW treatment is organic separations (e.g., oil/water) via membranes, hydrocyclones, and flotation techniques, as the complex organics present in PW can be detrimental to the environment and hydraulic fracturing processes; however, treatment technologies differ according to water composition and end-use requirements, and even with advanced equipment, PW treatment is never 100% efficient (8). Reuse of PW and other lower-quality wastewaters for energy-related (e.g., hydraulic fracturing or thermoelectric power station cooling) or other alternative uses could expand the availability of potable water. Additionally, wastewater can be a potentially valuable source of nutrients and metals (e.g., nitrogen and phosphorus from municipal wastewater, lithium from PW) if cost-effective extraction technologies are developed (9).

Water purification requires effective removal of organics, salts, bacteria, and targeted solutes, such as fertilizers, antibiotics, metals, personal care products, pharmaceuticals, and other

Table 1 Exemplary major ion concentrations (mg/L) of potential source waters (8, 10–15)

Constituent	River water (world average)	Groundwater			Brackish groundwater (Cameron County, TX)	Seawater	Municipal wastewater effluent		Produced water	
		Limestone	Volcanic	Metamorphic						
Na ⁺	7.1	26.9	36.8	2,700	931	10,800	50	400	23,000	57,300
Mg ²⁺	3.6	55.0	12.0	161	81.4	1,310	10	50	530	4,300
Ca ²⁺	14.4	144	6.4	4,540	153	410	25	100	2,530	25,800
K ⁺	1.2	2.0	3.1	32.0	15.6	399	10	30	130	3,100
Cl ⁻	8.2	52.9	17.0	12,600	1,110	19,500	50	500	46,100	141,000
SO ₄ ²⁻	11.5	60.5	15.4	1.0	991	2,830	-	-	210	1,170
HCO ₃ ⁻	53.1	622	76.9	54.9	338	150	-	-	77	560
TDS (mg/L)	99.1	964	168	20,100	3,645	35,300	200	1,300	72,600	233,000
Ionic strength (M)	0.0020	0.019	0.003	0.48	0.07	0.70	0.01	0.03	1.33	4.95

carcinogenic, neurotoxic, and endocrine-disrupting compounds (16). Variability in source water composition and next or end use requires reevaluation of traditional water treatment goals and processes; consideration of alternative treatment and treatment train strategies; and development of new feasible, economically sound, and resilient technologies. The goal of this article is to review current treatment goals and strategies and evaluate the potential of membranes to address current and future water purification needs.

1.1. Water Treatment

Water treatment typically means removing objectionable solutes, but it may also include adding desirable solutes. In ultrapure water production for semiconductor or pharmaceutical production, essentially any solute in the water is objectionable, whereas for uses such as crop irrigation, some solutes are desirable (e.g., nutrients, low levels of boron and selenium). Technologies for solute removal from water typically exploit differences in the physical and chemical properties of solutes and water. Solid and gaseous solutes can be readily removed, but water-soluble solutes often require a chemical transformation for their removal. Soluble metals, for example, are often precipitated and physically separated, whereas many organics and nitrogenous constituents are biologically transformed into dissolved gases (carbon dioxide, methane, nitrogen) for removal. Other soluble solutes are removed via sorption (e.g., adsorption, ion exchange) or are transformed to acceptable forms via changes in oxidation state or other chemical properties. Membrane processes [e.g., pressure-driven membrane processes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) and electric potential-driven processes such as electrodialysis (ED)], which do not rely on phase changes or chemical transformations, are also used to purify water (2). Although much is known about both the traditional and developing processes, integration of these processes is critical for obtaining a desired water quality from a particular source water (**Figure 1**). This article focuses on the current and future roles of membranes in water treatment and considers under what circumstances the desired removal is better accomplished by modern membranes than traditional processes. The potential for membrane treatment for different water quality goals is presented in **Table 2**.

1.2. Membrane Treatment

Membranes implemented in water treatment processes today are typically polymers exhibiting various degrees of porosity to permit solute removal from water at scales ranging from angstroms to microns (**Figure 2**). Conventional treatment processes also have the ability to treat solutes in a similar size range. Polymers with permanent pores (e.g., MF and UF) separate solutes from water primarily via size exclusion; the transport mechanism is pore flow, typically described using porous media fluid flow models (e.g., Hagen–Poiseuille; **Figure 2**) (17, 18). In UF and MF, membrane pore size and pore size distribution, solute/membrane electrostatic/chemical interactions, solute size/shape, solute concentration, and osmotic pressure can influence solute and water transport rates. Water and solute transport in nonporous or dense polymers (e.g., RO or ED membranes) is described by the solution-diffusion mechanism (**Figure 2**). Molecules sorb from a feed solution into the polymer, diffuse through the polymer, and desorb into a downstream (i.e., permeate) phase (17). Applying the appropriate transport mechanism links observed transport to intrinsic material properties (i.e., permeability and selectivity). In solution-diffusion membranes, permeability and selectivity are strongly influenced by solute properties (e.g., size, charge, hydration), interactions (e.g., electrostatics and chemical/physical affinity) at the membrane–solution interface and within the membrane, and polymer properties (e.g., fixed charge density, polymer chain mobility, free volume) (19). Performance is measured as flux and solute rejection, which depend on permeability and selectivity as well as operating parameters (e.g., pressure, solute

MF: microfiltration

UF: ultrafiltration

NF: nanofiltration

RO: reverse osmosis

ED: electrodialysis

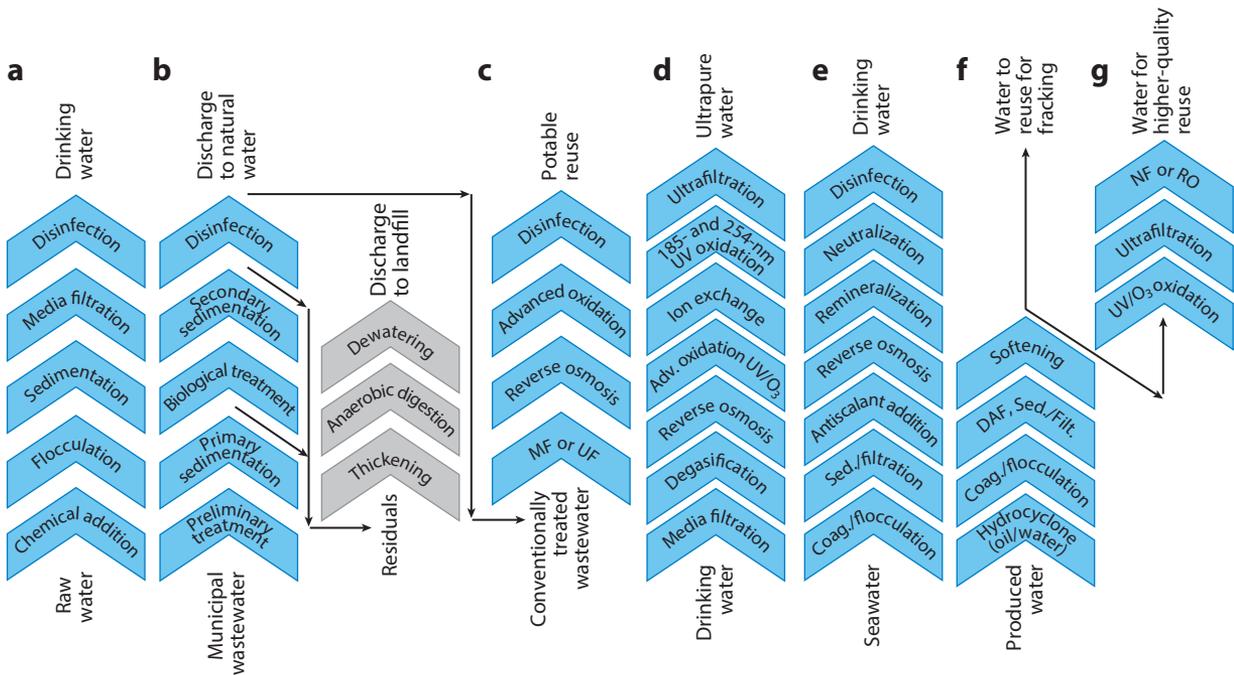


Figure 1

Integrated treatment processes for achieving desired water quality objectives from source waters (a–g). Abbreviations: Coag., coagulation; DAF, dissolved air flotation; Filt., filtration; MF, microfiltration; NF, nanofiltration; RO, reverse osmosis; Sed., sedimentation; UF, ultrafiltration; UV, ultraviolet.

concentration, and osmotic pressure) (2). In both porous and nonporous membranes, feed-side fluid mechanics (e.g., concentration polarization) can also influence flux and rejection (2, 18).

MF and UF are typically used to sieve larger particles such as microorganisms, viruses, and macromolecules that are larger than the nominal pore size (i.e., ~0.1–10 μm for MF and 2–100 nm for UF) (2). RO membranes are nonporous (i.e., dense) and can reject even small molecules, such as ions and some organics. RO, commonly used to desalinate seawater and brackish water, requires application of a hydrostatic feed pressure greater than the feed solution osmotic pressure. NF membranes exhibit behavior between that of porous and dense membranes, allowing passage of monovalent ions while still rejecting dissolved organic matter and divalent ions (2, 20). Key NF applications have been for water softening (removal of Ca^{+2} and Mg^{+2}) and removal of natural organic matter (NOM) (2, 16). NF requires lower pressure than RO membranes (e.g., from 0.34 to 1.4 MPa for NF versus ~5.5 MPa for seawater RO) (2).

Several other membrane technologies are under development but are not widely used today. For example, membrane distillation (MD) uses heat to drive water evaporation from aqueous solutions and permeation of the vapor through hydrophobic, microporous membranes. Although MD is more energy intensive than ED or RO, it can treat high-salinity feed waters ($\text{TDS} \gg 35,000 \text{ mg/L}$) (21, 22). In forward osmosis (FO), water flux is driven by an osmotic pressure gradient across a membrane to extract water from a contaminated feed solution into a highly concentrated draw solution. Typically, FO processes separate the permeated water and draw solute (e.g., ammonium bicarbonate) via a low-temperature thermal separation (23). A common feature of draw solutes is a phase change from an aqueous solute to a gas, solid, or immiscible liquid at a moderate temperature so that low-quality heat sources may be used (23, 24).

NOM: natural organic matter

MD: membrane distillation

FO: forward osmosis

Table 2 Potential membrane alternatives for traditional treatment goals

Conventional (non-membrane) process	Goal	Membrane alternative
Sedimentation	Removal of particles with settling velocity $\gtrsim 1$ m/h	MF
Granular media filtration	Removal of most particles $\gtrsim 1$ μm and some removal of smaller particles	UF
Flocculation	Agglomeration of many small particles into far fewer large particles	None
Precipitation of calcium as calcium carbonate and magnesium as magnesium hydroxide	Hardness removal	NF, ED
Enhanced coagulation	Removal of hydrophobic NOM	NF
Activated carbon adsorption	Removal of natural and synthetic organics	RO
Activated sludge sedimentation	Conversion of biodegradable organics to CO_2 and microorganisms	Membrane (i.e., UF or MF) bioreactors (MBRs)
Gas stripping	Removal of volatile organics	Membrane stripping
Gas absorption	Addition of desirable dissolved gas (e.g., O_2 , CO_2 , Cl_2)	Membrane diffusers
Conventional chemical oxidation	Oxidation of reduced inorganics and some organics	None, though RO would remove many solutes of interest
Disinfection	Inactivation of pathogenic organisms	None, though UF removes most pathogens of interest and is more effective than chemical disinfection for <i>Cryptosporidium</i> and <i>Giardia</i>
Precipitation	Conversion of metal constituents into particles for subsequent removal by various solid/liquid separation processes	None, though RO removes most constituents without requiring chemical conversion
Ion exchange	Ion removal (specific or nonspecific)	ED or RO
Nitrification	Conversion of ammonia to nitrate	None, though RO could remove ammonia
Denitrification	Conversion of nitrate to N_2	Anaerobic MBRs

Abbreviations: ED, electrodialysis; MF, microfiltration; NF, nanofiltration; NOM, natural organic matter; RO, reverse osmosis; UF, ultrafiltration.

FO has been investigated for seawater desalination, zero-liquid discharge, and power generation via controlled mixing of fresh and saline water across a membrane, but these processes have generally not been economically viable (25, 26). Rather, FO may offer advantages in dewatering concentrated feed solutions, such as highly saline feed water (e.g., PW and RO brine) that would otherwise be treatable only via thermal processes (27).

Whereas many of the membrane processes described above remove solutes from water by selectively permeating water and rejecting the solutes, ED uses dense ion-exchange membranes with an electric potential driving force to selectively permeate ions from saline water (2, 28). The most common application of ED is potable water production from brackish water sources. ED is cost competitive with RO at salinity levels from $\sim 1,000$ to $5,000$ mg/L TDS and is used mainly in small- to medium-sized plants (100 m^3/day to near $20,000$ m^3/day) (29). ED can also be used as a pre- or posttreatment process for other membrane processes, including NF and RO, primarily, to improve water recovery (30) or recover valuable resources (31, 32). **Table 3** highlights the synthetic membranes that are currently applied for water treatment and provides representative

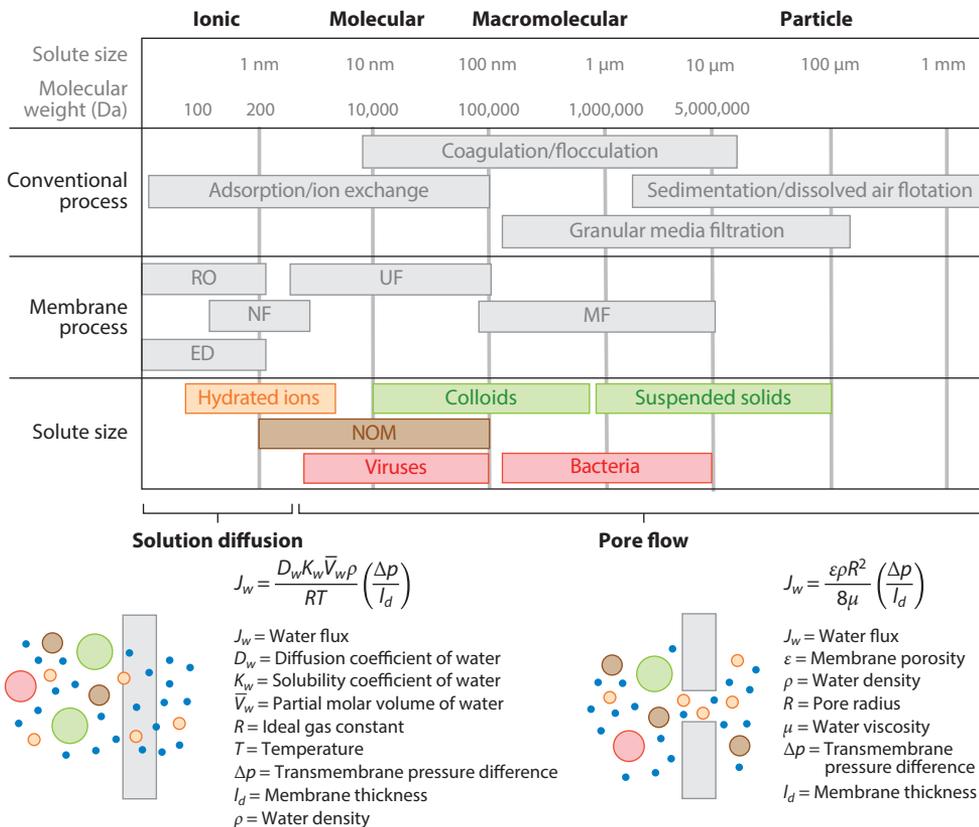


Figure 2

Comparison of several conventional and membrane processes for water purification and subsequent mechanisms of water transport through membranes based on solute size and molecular weight (2, 16). Abbreviations: ED, electro dialysis; MF, microfiltration; NF, nanofiltration; NOM, natural organic matter; RO, reverse osmosis; UF, ultrafiltration.

examples of water permeance (i.e., water flux normalized by pressure driving force) and polymeric materials for each process.

Expansion of membrane use to wider ranges of treatment objectives for increasingly complex, nontraditional water sources may benefit from recent advances and potential developments in materials science and integrated process design strategies. Subsequent sections highlight different treatment goals for impaired water, conventional membrane methods to achieve these goals, and novel approaches under investigation.

2. PARTICLE REMOVAL

2.1. Current Treatment

Conventionally, turbidity and particle removal has been accomplished by coagulation/flocculation followed by solid/liquid separation (sedimentation and granular media filtration). Coagulation involves chemical addition to destabilize particles, making them susceptible to rapid flocculation (agglomeration), changing the particle size distribution from a large number of small particles to a far smaller number of large particles (16). Large particles are settled or filtered from the

Table 3 Water treatment membrane processes and their functionality (2, 16, 33–37, 156, 157)

Membrane process	Solutes rejected	Driving force	Approximate water permeance	Solutes permeated	Exemplary membrane materials
Microfiltration	Large particles (e.g., bacteria, silica)	Pressure gradient, 0.05–0.10 MPa	20–10,000 L/m ² -h-bar	Water, dissolved solids, and solutes smaller than membrane pore size	PES, PSF, PVDF
Ultrafiltration	Small particles and macromolecules (e.g., colloids, proteins)	Pressure gradient, 0.05–0.50 MPa	10–2,000 L/m ² -h-bar	Water, dissolved solids, and solutes smaller than membrane pore size	PES, PSF, PVDF
Nanofiltration	Divalent ions and organics	Pressure gradient, 0.50–1.00 MPa	5–15 L/m ² -h-bar	Water and monovalent ions	PA/PSF composite
Electrodialysis	Co-ions	Electric potential gradient	0.001–0.02 L/m ² -h-bar	Counterions	Ion-exchange polymers
Reverse osmosis	Salt	Pressure gradient, 1.00–6.00 MPa	0.1–10 L/m ² -h-bar	Water and small neutral molecules	CA, PA/PSF composite
Forward osmosis	Salt	Osmotic pressure gradient	1–10 L/m ² -h-bar	Water and small neutral molecules	CA, PA/PSF composite, PES
Membrane distillation	All nonvolatile solutes	Pressure gradient due to applied thermal energy	200 L/m ² -h-bar	Water vapor and volatile solutes	PTFE, PVDF

Abbreviations: CA, cellulose acetate; PA, polyamide; PES, polyethersulfone; PSF, polysulfone; PTFE, polytetrafluoroethylene; PVDF, poly(vinylidene difluoride).

solution relatively easily. The most common coagulants, salts of aluminum or iron, are added at a combination of dose and pH to precipitate aluminum or iron hydroxide. Whereas coagulation and flocculation have historically been employed for turbidity removal only, these processes can effectively treat complex water streams containing NOM, particles, and a range of inorganic substances (16). The conventional solid/liquid separation following coagulation and flocculation is sedimentation and granular media filtration; if particle loads are low, sedimentation is omitted. Pore spaces in granular media filters are much larger than the target particles to be removed, so removal occurs via particle attachment either to the media itself or to previously captured particles (16). Consequently, granular media filtration may fail if the surface chemistry is not correct; the 1993 Milwaukee *Cryptosporidium* outbreak, which sickened ~400,000 people, was caused by inadequate filtration at a Milwaukee drinking water treatment plant.

Although the above discussion focuses on drinking water treatment from surface water, particle removal is central to many of the treatment trains depicted in **Figure 1**. In traditional municipal wastewater treatment, the most common biological treatment is the activated sludge process, which uses a suspension of microorganisms and is followed by a solid/liquid separation process (e.g., sedimentation) (16). Seawater often contains substantial particle concentrations, so the treatment train for seawater desalination starts with the same processes commonly used for treatment of river water to make drinking water. PW contains relatively high TDS, total suspended solids,

and turbidity levels, so particle removal is essential for reusing such water for fracking or higher-quality uses such as agriculture (8). Oil particles are first removed by oil/water separators (e.g., gravity separators, hydrocyclones) followed by conventional particle removal processes (e.g., sedimentation or flotation and granular media filtration). Of increasing concern are the manufactured nanoparticles and microplastics present in many water sources; these particles tend to be more stable than those of natural origin and require higher chemical dosages (or other conditions, such as lower pH) for effective coagulation/flocculation (38).

2.2. Membrane Processes

Membrane filtration for particle removal was originally used as a stand-alone process; however, high feed turbidities led to challenges (e.g., colloidal fouling, higher loading rate, and frequent backwashing), underscoring the importance of pretreatment (39). Membrane filtration pretreatment is now common and can involve conventional treatment methods (e.g., coagulation, pre-oxidation, or lime softening), microstraining, or pH adjustment (16). The Milwaukee outbreak, coupled with tightening drinking water regulations and declining membrane filter costs, provided a strong impetus for drinking water treatment plants to adopt MF or UF rather than granular media filtration as the final solid/liquid separation process (40). Following successful operation of the first large-scale membrane filtration facility in 1994 in Saratoga, California, the number of MF/UF plants has increased rapidly. In general, for drinking water UF/MF systems exceeding 20 million gallons per day (mgd) capacity, capital costs range from \$26.5/m³/day to \$40/m³/day (2004 USD) and operational costs are in the range of \$0.01–0.05/m³ of product water (2004 USD); a large fraction of the operating costs is due to membrane cleaning/replacement and energy costs (41). Membrane bioreactors (MBRs) have replaced conventional activated sludge-sedimentation processes in many wastewater treatment systems owing to their smaller footprint and higher effluent quality (i.e., more complete solid/liquid separation) (2, 16, 42). MBR plants can typically be constructed for the same capital cost as a conventional wastewater treatment plant [e.g., the capital costs for a 20 megaliters/day (MLD) capacity MBR plant are in the range of \$0.35–0.68 million (2015 USD) per MLD] (43). MBR operating costs have decreased in recent years and depend on flux and the age of the membranes; a 2017 review (43) estimated typical MBR operating costs to be between \$0.14/m³ and \$0.26/m³. MBRs have eliminated the need for granular media filtration during tertiary treatment of municipal wastewater. If wastewater treatment effluent is to be further treated to produce potable water, UF is almost always used either in a wastewater plant or as an early step in an advanced treatment plant to avoid particle contamination of RO units. Furthermore, the high particle concentration in most PWs usually means that conventional processes such as sedimentation or flotation are used for removal, yet MF and UF have the advantage of being more easily skid-mounted and are able to be moved easily from one site to another as wells are taken out of service.

Current research in the area of particle removal by membrane technologies has focused on membrane materials and pretreatment technologies that can be implemented to reduce membrane fouling. These topics are discussed in Section 6.

3. MICROBIAL CONTAMINANTS

3.1. Current Treatment

Important microbial contaminants include bacteria (<1–10 μm in size) (e.g., *Escherichia coli*, enterococci species, *Clostridium*, and of emerging concern, *Legionella pneumophila*), viruses (4–100 nm)

that consist of RNA or DNA wrapped in a protein coat [e.g., Caliciviridae (noroviruses), Picornaviridae (enteroviruses), and Reoviridae (rotaviruses)], and protozoa. Protozoa (*Giardia*, *Cryptosporidium*, and the less common *Naegleria fowleri*) are particularly challenging to disinfection processes because they vary in size and go through a life cycle from trophozoites (active forms) to 3–14- μm cysts (dormant forms) that can survive extreme conditions (44).

Typical untreated municipal wastewater concentrations of bacteria are 10^{10} colony-forming units/mL, 10^6 viruses/L, and 10^{10} protozoa/L (44); these values are variable and depend on the enumeration method. Conventional wastewater treatment (i.e., activated sludge) can achieve as much as 3 \log_{10} (i.e., 1,000 \times) reduction values (LRV) of bacteria, 2.5 LRV of viruses, and 2 LRV of protozoa (44). Although conventional chlorination can achieve 6 LRV of both bacteria and viruses, it is not effective against most protozoa (44). The US Environmental Protection Agency (USEPA) mandates removal of protozoa from drinking water (3 LRV of *Giardia* and 2 LRV of *Cryptosporidium*) (45). Credits are given for the types of filtration methods used based on the removal efficiencies: 2.5 log credits for *Giardia* are given with conventional filtration, whereas more advanced filtration methods (UF, NF, or RO) give >3 log credits for *Giardia* (45). Along with the limitations of chlorination to remove protozoa, residual chlorination for posttreatment microbial control can yield carcinogenic disinfection by-products (DBPs) through reactions with NOM (46) (see Section 4).

Microorganism removal is essential for water reuse (44, 47). California and a National Water Research Institute expert group set regulations for direct potable reuse that include 12 LRV of enteric viruses, 10 LRV of enteric protozoa, and 9 LRV of total coliforms with raw wastewater as the basis (44). PW can have unique bacterial communities (e.g., sulfate-reducing bacteria), so removal of bacteria becomes critical before PW is disposed of or reused owing to environmental concerns and other challenges, such as reservoir souring during well injection (48, 49).

3.2. Membrane Processes

Membranes readily remove microbes by size exclusion and charge repulsion of large, often negatively charged species. Membrane-based microbe removal began in the pharmaceutical and microelectronics industries; 200-nm (nominal pore size) MF membranes can remove nearly all bacteria (18, 50). Additionally, MF and UF use in beverage and food industries is widespread; MF is used for clarification (removal of yeast and bacteria) in wine and beer purification, and UF is used in production of cheese and fruit juices to concentrate whey proteins and sterilize, respectively (51). Membranes are also critical in the purification of biotechnology products, as they can achieve sterile filtration, protein concentration and purification, and virus removal (18, 52).

Increasing use of membranes for drinking water treatment is due, in part, to their better microbe removal relative to granular media filtration. Similarly, MBRs have better microbial removal from wastewater than conventional processes (53, 54). In a pilot study comparing MBRs to a conventional activated sludge process, MBRs achieved >1 LRV—higher removal of fecal coliforms and coliphages (55). MBRs have also been found to remove antibiotic-resistant bacteria and antibiotic-resistance genes up to 7.1 LRV (56).

Effective pathogen removal is generally based on multiple-barrier treatment trains that include secondary wastewater treatment, MF, RO, and advanced oxidation processes (AOPs); such processes can produce a variety of fit-for-purpose water products. For example, the Edward C. Little Water Recycling Facility in Los Angeles produces five different types of water for various applications (e.g., cooling towers, industrial boilers, landscape irrigation, and groundwater recharge) (57). However, membranes used for microbial decontamination are limited by biofouling, as discussed in Section 6. Additionally, degradation of polymeric membranes by membrane-cleaning chemicals

LRV: \log_{10} reduction value

USEPA:
US Environmental Protection Agency

DBP: disinfection by-product

AOP: advanced oxidation process

(e.g., chlorine) decreases membrane lifetime (58). Disinfection followed by dechlorination is used to address this challenge, but novel membranes may provide more robust solutions.

MMM: mixed-matrix membrane

UV: ultraviolet

GO: graphene oxide

TOC: total organic carbon

BOD: biochemical oxygen demand

COD: chemical oxygen demand

VOC: volatile organic compound

THM: trihalomethane

HAA: haloacetic acid

3.3. Novel Membranes

Development of novel antimicrobial membranes relies on bacterial-inactivation mechanisms, such as collapsing proton motive force, electrostatic interaction, and oxidative stress (59), which are impacted by membrane/contaminant properties and operating conditions (59). Mixed-matrix membranes (MMMs) may address limitations of current membranes for pathogen removal by combining the abilities of different materials (e.g., inorganic biocides, metal-based nanoparticles, and carbon-based nanomaterials) for specific purposes, one primary purpose being biofouling control (60, 61). Incorporating ultraviolet (UV)-responsive materials (e.g., TiO₂, ZnO, and quantum dots) into membranes can create photocatalytic membranes that inactivate pathogens and prevent biofouling, while also providing high reductions in antibiotic-resistant bacteria (62, 63). Moreover, MMMs containing carbon nanotubes, graphene oxide (GO), and TiO₂ have shown improved chlorine resistance (64). Despite these advantages, challenges remain with incorporating antimicrobial and chlorine-resistant materials into membranes, including release of nanomaterials, limited lifetime of antibiofouling functionalities, and membrane scale-up (61).

4. ORGANIC CONTAMINANTS

4.1. Current Treatment

Organic compound removal from water focuses on three main targets: (a) removal of total organic content, often quantified by surrogate parameters [e.g., total organic carbon (TOC), biochemical oxygen demand (BOD), and chemical oxygen demand (COD)]; (b) removal of specific contaminants of concern [e.g., volatile organic compounds (VOCs), semivolatile organic compounds, insoluble oils, pharmaceuticals, pesticides, and industrial solutes]; and (c) removal of naturally occurring organic contaminants (e.g., NOM, proteins, carbohydrates). Removal of NOM is especially important during drinking water treatment, as disinfectants react with NOM to form DBPs, some of which are toxic and carcinogenic (65). In drinking water, the USEPA limits levels of trihalomethanes (THMs) and haloacetic acids (HAAs), but more than 600 DBPs have been identified, and although many of these unregulated DBPs appear at lower concentrations than THMs and HAAs, they have greater genotoxicity than regulated ones (66). Additionally, the presence of inorganics such as bromide and iodide in source waters can trigger formation of more toxic DBPs (67).

Reduction of TOC, BOD, and COD is accomplished via several biological and physicochemical processes. Biological treatment is typically employed for municipal wastewater sources via activated sludge processes (16). Alternative biological treatment methods, such as fixed-bed biofilm reactors (i.e., biofilters) for drinking water treatment, can provide enhanced organic removal (68). Physicochemical processes, such as solid/liquid separation, adsorption, and chemical oxidation, have been explored to address TOC and COD removal in both industrial and drinking water processes. Conventional strategies for removing droplets of insoluble oil from water include gravity [e.g., gravity settlers, API (American Petroleum Institute) separators, and plate coalescers] and centrifugal separations (i.e., centrifuges, hydrocyclones). Dispersed oils and emulsions are treated using induced air flotation or dissolved air flotation coupled with chemical treatment. However, these technologies are not efficient for treatment of stable emulsions or solutions with fine droplets or low oil concentrations (69). Consequently, oxidation by either traditional or advanced processes has also been explored for degrading organic compounds to minimize waste generation.

Removal of regulated dissolved organic compounds from potable water sources and wastewater has been dominated by physical separation processes like adsorption and air stripping. Emerging organic contaminants, such as pharmaceuticals and personal care products (PPCPs), pesticides, and industrial chemicals, are a growing area of concern. Polyfluorinated compounds (PFCs) (e.g., perfluorooctanoic acid) have gained widespread attention owing to persistence, bioaccumulation, and toxicity in the environment; research efforts in electrochemistry, AOPs, and adsorbent-based technologies are prolific (70, 71). Whereas all of the pollutants in the USEPA's list of 129 priority pollutants established in 1977 are considered at least moderately hydrophobic, many of the emerging contaminants of concern are polar and contain acidic/basic functional groups, thereby challenging conventional treatment processes. With the exception of activated carbon, conventional physiochemical processes like coagulation generally exhibit marginal removal of many emerging contaminants (72), and biodegradation varies significantly (0% to 100%). Source water composition and operating parameters also significantly affect degradation of organics (73). Consequently, individual wastewater treatment plants must customize treatment based on specific organic contaminants of concern in the water and are unlikely to adopt treatment processes for those that are unregulated.

Strategies to reduce chlorinated DBP levels in drinking water include switching from chlorination to other disinfection methods, removing DBPs after formation, and removing NOM. Replacing chlorine with chloramines can reduce THM and HAA formation, but chloramines can increase the formation of nitrosamines, toxic, unregulated DBPs that can cause leaching of lead pipes (46). DBPs can be removed from water by air stripping using countercurrent packed columns, diffused and sprayed aeration, and hollow fiber membranes, but these methods apply only to volatile DBPs. Current water treatment processes for NOM removal include enhanced coagulation, AOPs, adsorption, ion exchange, and membrane technologies. Enhanced coagulation is a US regulatory requirement for conventional water treatment plants to remove NOM (74), but the maximum removal goal is only 50% TOC reduction (75). Typically, TOC remaining in the treated water is associated with lower-molecular mass, non-humic materials (76). Moreover, when treatment plants add higher coagulant doses to remove TOC, the amount of process residuals (sludges) generated increases, which increases treatment costs (77). Removal efficiencies for AOPs range between 40% and 90% (78) but depend on NOM characteristics and source water composition. Granular activated carbon and powdered activated carbon adsorb NOM to some degree, but performance varies widely over time (79), and NOM interferes with adsorptive removal of other solutes through either competition for sites or pore blocking (80). NOM is negatively charged in natural waters, so anion-exchange resins can remove NOM from natural water (81), especially for lower-molecular weight, charged hydrophobic and transphilic DBP precursors (82).

PPCP: pharmaceutical and personal care product

PFC: polyfluorinated compound

4.2. Membrane Processes

TOC or COD removal using membranes has been explored in both industrial and drinking water treatment. Appropriate membrane technology selection relies on required removal levels and end use (**Figure 1**), which limits establishment of universal treatment schemas. Depending on feed composition and conditions, MF, UF, and NF/RO can remove 60%, 90%, and >90% of COD, respectively (83). MBRs remove COD in both municipal wastewaters and high-salinity industrial wastewaters (84), including PW (85). Owing to its complexity, PW treatment traditionally involves a combination of physical and chemical treatment processes to remove dissolved and dispersed oil compounds, solids, dissolved gases, and production chemicals.

MF and UF membranes remove turbidity, oil, grease, and some organic compounds and are generally combined with conventional pretreatment processes like coagulation to mitigate fouling.

Table 4 A comparison of the removal of several classes of emerging contaminants between conventional and membrane processes (data obtained from 70, 92–94)

Group	Classification	Conventional treatment							Membrane processes		
		AC	BAC	O ₃ /AOP	UV	Cl ₂ /ClO ₂	EO	C/F	RO	NF	UF
EDCs	Pesticides	✓	✓	✓	✓	✓	✓		✓	✓	
	Industrial chemicals	✓	✓	✓	✓		✓		✓	✓	
	PFCs	✓					✓		✓	✓	
	Steroids	✓	✓	✓	✓	✓	✓		✓	✓	
PhACs	Antibiotics	✓	✓	✓	✓	✓	✓		✓	✓	
	Antidepressants	✓	✓	✓	✓		✓		✓	✓	
	Anti-inflammatories	✓	✓	✓	✓		✓		✓	✓	
	Lipid regulators	✓	✓	✓	✓		✓		✓	✓	
	Psychiatric control	✓	✓	✓	✓		✓		✓	✓	
PCPs	Synthetic scents	✓	✓	✓	✓		✓		✓	✓	
	Sunscreens	✓	✓	✓	✓				✓	✓	
	Antimicrobials	✓	✓	✓	✓		✓		✓	✓	
	Surfactants/detergents	✓	✓	✓	✓		✓		✓	✓	

✓ = Excellent (>90%); ✓ = Good (70–90%); blank cells, <70%.

Abbreviations: AC, activated carbon; AOP, advanced oxidation process; BAC, biologically activated carbon; C/F, coagulation/flocculation; EDCs, endocrine disrupting compounds; EO, electrochemical oxidation; NF, nanofiltration; PCPs, personal care products; PFCs, polyfluorinated compounds; PhACs, pharmaceuticals; RO, reverse osmosis; UF, ultrafiltration; UV, ultraviolet.

Hydrophilic MF, UF, and NF membranes for oil/water separation are typically operated such that water permeates the membrane while oil is retained (69). Microporous hydrophobic hollow-fiber membrane contactors that minimize the viscous fouling layer, which forms when oils accumulate at the membrane surface, can efficiently recover submicron lipids from microalgae slurries (86) and oil from oil/water/surfactant mixtures (87).

NF and RO membranes can remove some organics in PW for either reinjection or beneficial reuse. Removal of such organics has also stimulated development of unconventional membrane processes, including osmotically driven (e.g., FO) and thermally driven (e.g., MD and pervaporation) approaches (88). Similar to PPCP removal, MBRs can achieve higher levels of organic contaminant removal than conventional activated sludge systems; however, high-salinity PW can negatively influence biological treatment systems, resulting in decreased COD removal (89). Ultimately, the use of membranes for PW treatment will likely require integrated membrane processes with feed pretreatment (**Figure 1f**) or effluent posttreatment to meet water treatment requirements and mitigate fouling (90).

Trace contaminant removal (e.g., of PPCPs) varies with membrane type, contaminant physicochemical properties, and operating conditions (91); specifically, low-molecular weight organics exhibit poor removal using current membrane technologies (70). **Table 4** presents a scope of the processes that have been considered for the removal of several classes of emerging contaminants by conventional and membrane processes, with reported removals from various studies (70, 92–94). By-products of emerging contaminants, such as pesticide transformation products, often evade removal by conventional NF membranes owing to their size and require RO membranes to achieve adequate removal (95). Complete removal of trace organic compounds often requires dual-membrane processes or integration of conventional treatment with membranes (96). MBR-based

processes have improved removal of PPCPs relative to conventional activated sludge treatment (96, 97). For volatile components, membrane air stripping using microporous hollow-fiber membranes for VOC removal has been proposed as an alternative to packed tower aeration owing to the high surface area-to-volume ratio, independence of liquid and gas flow rates, and modularity of membranes (98).

UF pore sizes are similar to the size of higher-molecular weight organics, which enables UF to remove some NOM, proteins, and polysaccharides (99). Moreover, NOM removal efficiency via NF and RO can exceed 90% (99). Membrane-based NOM removal occurs via several mechanisms, including size exclusion, charge repulsion, and hydrophobic interactions and depends on membrane materials, operating conditions, and NOM properties, such as hydrophobicity, size, and charge (100, 101). However, membrane fouling remains a major challenge, especially in hard waters. Thus, research has focused on pretreatment via lime softening, ion exchange, and hybrid membrane processes to remove Ca^{2+} and Mg^{2+} (e.g., NF-NF, ED-NF) (102, 103). Membrane fouling by NOM can also be reduced by decreasing the concentration of O-C-O and C-O-C functional groups in the NOM using UV/persulfate pretreatment (104).

4.3. Novel Membranes

Continued investigation of novel membrane materials and integration of membranes with conventional and advanced treatment processes are required to enhance organics removal and address fouling and permeability/selectivity challenges. NF has been explored for organic solvent separations (e.g., ethanol, hexane, toluene), and more recently, integrated processes have improved these separations for recalcitrant waters, such as the use of an integrated NF-MBR system to not only separate but ultimately degrade pharmaceuticals into nontoxic products (105). Full degradation of these solutes is desirable, as the sludge and residuals associated with rejecting these contaminants during conventional membrane processes require advancements in the area of concentrate management. Wang et al. (106) have shown a novel, hollow-fiber NF membrane to remove PFCs from water sources. The use of adsorptive membranes has also shown promise for several classes of organic solutes, including PFCs (70). Meanwhile, nanocomposite membranes can also exhibit fouling resistance (107, 108), and application of novel coatings has reduced fouling in MBRs while maintaining high COD removal efficiency (84). Membrane fouling is discussed in more detail in Section 6.

5. INORGANIC CONTAMINANTS

5.1. Current Treatment

Inorganic solutes of interest include salts (e.g., NaCl, MgCl_2), heavy metals (e.g., lead, chromium), metalloids (arsenic, boron), common radionuclides (uranium, radium), and nutrients (nitrogen, phosphorus) (**Figure 3**). Recently, rare earth metals have also gained significance as emerging contaminants (109). Two important surrogates that quantify inorganic content of water are TDS (TDS also includes dissolved organic content) and hardness. TDS is operationally defined via filtration of water using a specified pore size (typically 0.45 μm) prior to evaporation of the water. The USEPA secondary (not federally enforceable) standard for drinking water, 500 mg/L TDS, is similar to that of many fresh waters, but it presents technical and economic challenges for high-TDS water sources (**Table 1**). Hardness measures multivalent cation concentration in water; values above 120 mg/L CaCO_3 affect detergency and contribute to scaling in water distribution systems, boilers, and industrial equipment. Moreover, water that is too soft (<50 mg/L as CaCO_3) can be corrosive and deleteriously affect soil structure and permeability. Thus, water reuse for agriculture must consider water hardness (or more specifically, what is termed the

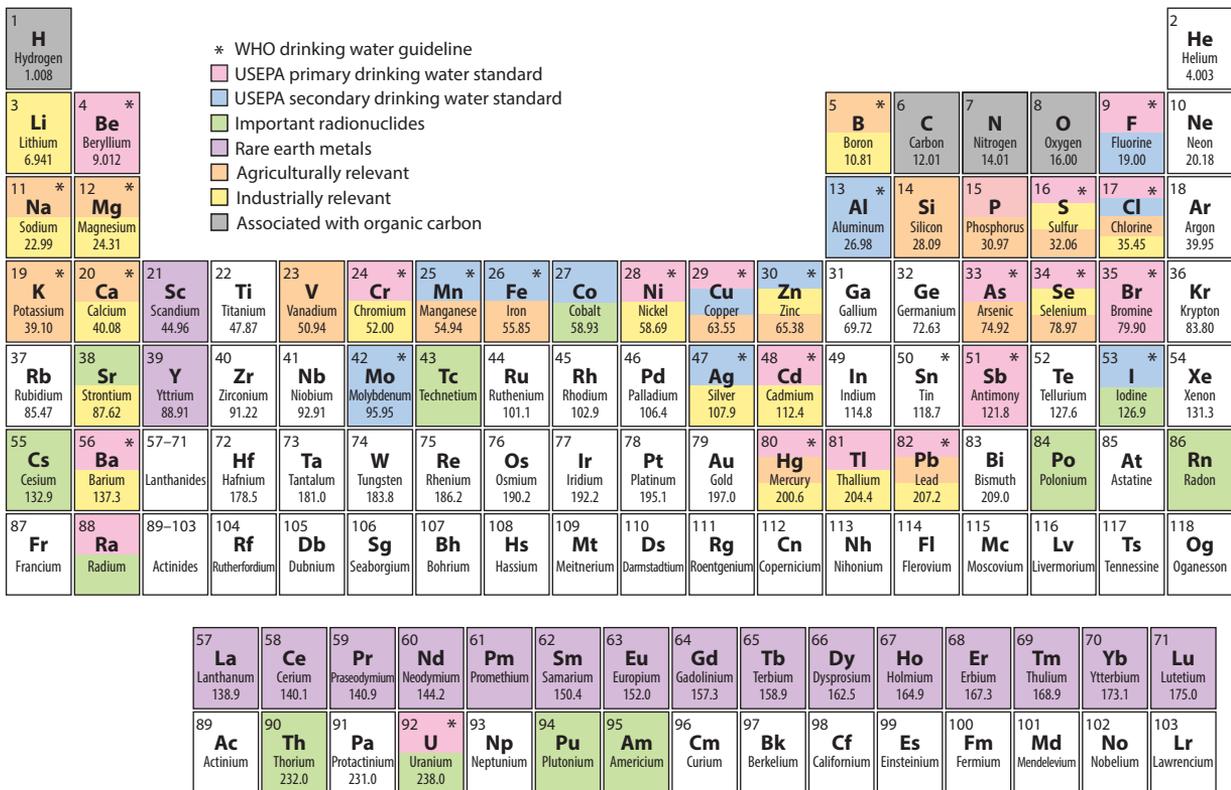


Figure 3

A periodic table showing the importance of different elements in the context of various water uses. Abbreviations: USEPA, US Environmental Protection Agency; WHO, World Health Organization.

sodium adsorption ratio). Finally, while many elements and radionuclides identified in **Figure 3** are known for their potential human health or ecological effects at the parts per billion level and below, speciation can have a significant impact on exposure routes, relative toxicity, and mobility. Because there is no ultimate destruction of an element, treatment process selection must consider the efficacy of treatment of varying oxidation states of an element and the sorptivity and solubility of different aqueous complexes of metals in source and effluent waters.

Conventional TDS removal processes are often membrane based (e.g., RO and ED for water desalination), whereas hardness removal typically relies on inorganic salt precipitation via lime softening. Ion exchange and NF membrane softening are also viable options for hardness reduction, depending on source water quality, system size, and water quality objectives. Both TDS and hardness can be removed via RO, but starting TDS levels greater than ~35,000 mg/L present economic challenges (110). Thermal processes, including MD, are promising for high-TDS PW, as MD is not significantly influenced by feed salinity (111). Integrated treatment systems (e.g., hybrid membrane/thermal systems) can yield higher water recovery during PW treatment than the use of segregated processes (110).

Typical processes for nutrient, trace inorganic, and radionuclide removal include biological treatment, chemical oxidation, precipitation, coagulation/flocculation, biocatalytic processes, adsorption/ion exchange, and membrane separation (112). Many conventional treatment plants meet primary water quality standards for trace contaminants and radionuclides without advanced

treatment processes. For example, enhanced coagulation processes employing alum or iron precipitative coagulation/flocculation can often meet drinking water maximum contaminant levels for Cr(VI), As(V), fluoride, and several radionuclides (113, 114). However, for some solutes (e.g., N, Se, As, Sr, Cs), chemical or biological redox processes may be needed prior to separation, as oxidation states dictate adsorption of contaminants (114, 115).

5.2. Membrane Processes

Membrane-based RO reduces TDS levels during seawater and brackish water desalination and offers substantial energy consumption reductions compared with thermal technologies owing to the absence of phase changes (2, 116). Typically, seawater desalination by RO costs approximately US \$2.00/m³ of product water, with capital costs accounting for approximately 60% of these total costs (per a 2015 report) (117). ED can reduce TDS in lower-salinity brackish waters but is only partially effective for high-salinity desalination owing to high energy consumption. Often, the concentrate from seawater desalination is discharged into the ocean, which can impact a range of marine habitats and organisms. Interestingly, a recent study showed a 279% increase in the abundance of reef fish around a seawater brine discharge outlet, suggesting that changes in water chemistry near discharge outlets can influence the structure of marine communities (118). Concentrate can also be disposed of via other methods, including deep well injection, or it can be further treated for reuse. High costs associated with concentrate disposal are among the key limiting factors to the widespread use of inland desalination (119). In contrast, MD can contribute to zero liquid discharge in oil and gas industries through hybrid technologies (120). For example, hybrid electrocoagulation-MD provides stable water fluxes with minimal fouling by high-salinity PW (TDS up to 265,000 mg/L) (121). Extraction and reuse of saline water from deep geologic formations during CO₂ sequestration reduces subsurface overpressurization, which prevents earthquakes and provides irrigation water; this multifaceted approach provides significant cost reductions compared with conventional desalination processes because energy is obtained from excess pressure at the wellhead (122). The implementation of NF as a pretreatment to RO has been considered a breakthrough in desalination (123). NF membranes are used to treat several types of waters, removing turbidity, microorganisms, hardness, and some dissolved salts at significantly lower operating pressures than RO, enabling NF membranes to reduce water hardness yet not overdemineralize drinking water (unlike RO).

RO has demonstrated enhanced radionuclide removal over conventional processes (124). A recent pilot study (125) assessed the ability of RO to treat synthetic natural waters based on the composition of groundwater at the Chernobyl nuclear site and of seawater at the Fukushima nuclear site. Cs and Sr rejection were >90% for both waters, proving that RO is a viable choice for radionuclide treatment (125). Furthermore, shock ED has recently been shown to provide continuous separation of radionuclides in synthetic by-product water from nuclear processes (126).

A current challenge for membranes is neutral and low-molecular weight solute removal, as electrostatic repulsion and size exclusion mechanisms are weak for these solutes. For example, in natural waters, removal of As(III), a toxic metalloid with a pK_a of 9.1 and Stokes radius of 0.24 nm (127), varies from 25% to 75% depending on operating conditions (128). Therefore, pH adjustments and oxidation of As(III) to As(V), which is charged at neutral pH and has a slightly larger Stokes radius (0.26 nm) (127), are the prevalent strategies to improve arsenic rejection (128). Boron is another small, neutral solute of concern, as it is present in seawater at an average concentration of 5 mg/L (119) and is toxic to certain plant species (129). In water, boron is present as boric acid [Stokes radius of 0.16 nm and pK_a of 9.2 in freshwater, 8.6 in saltwater (130)] and tends to diffuse rapidly through RO membranes via hydrogen bonding between the hydroxyl groups in boric acid and bound water in the membrane (131). Conventional seawater and brackish water

RO membranes exhibit varying levels of single-pass boron rejection, which depend on factors such as solution pH and membrane choice (119). Consequently, desalination plants often deploy multistage RO to reduce boron concentrations to desired levels; maximum boron concentrations in the range of 0.5–1.0 mg/L are common for irrigation of several sensitive crops. At the Ashkelon plant in Israel, the boron polishing system has been estimated to account for 10% of the overall energy cost (132). Therefore, improving boron rejection will significantly benefit overall water purification membrane performance.

5.3. Novel Membranes

Recent advances have focused on several of the existing membrane science challenges, including the permeability/selectivity trade-off, selective transport between ions of the same valence, and rejection of small and neutral solutes. In conventional membranes, increases in permeability typically come with a loss of selectivity (133). Considerable research is aimed at adding highly selective fillers [e.g., carbon nanotubes, polymer grafted nanoparticles, metal organic frameworks (MOFs), and aquaporins] into polymeric membranes to form MMMs (60). These fillers enhance selectivity and permeability for certain solutes through control of cavity size and specific interactions. By combining selective fillers with polymeric materials, MMMs may achieve high selectivity, high permeability, and scalability. Polymeric membranes filled with carbon nanotubes were reported to provide water flow three orders of magnitude higher than expectations based on continuum hydrodynamic models (134). Similarly, di-block copolymer membranes with aquaporins are reported to have 800 times the permeability per unit driving force of commercial desalination membranes (135).

Conventional membranes have limited selectivity among ions such as Li^+ , Na^+ , K^+ , and Rb^+ because transport occurs in hydrated domains of the polymer, so the relative order of permeation follows hydrated radii (e.g., Li^+/Na^+ selectivity ~ 0.7 – 1.0 and Li^+/Rb^+ selectivity ~ 0.6 – 0.8) (136). Ionic/molecular sieves having narrow pore size distributions on the angstrom scale, such as MOFs, are promising for highly selective ion separations. Recently, a zeolitic imidazole framework (ZIF-8), with a pore window size of 3.4 \AA , exhibited unusual alkali metal ion discrimination: Li^+/Na^+ selectivity of 1.4 and Li^+/Rb^+ selectivity of 4.6 (136). Addressing these challenging separations by developing MMMs incorporating similar MOFs is an area of continued investigation.

Several approaches have been proposed to enhance small and neutral solute rejection in polymer membranes. Ali et al. (137) reported the use of defect-free, highly selective, highly crosslinked, interfacially polymerized membranes to enhance selectivity of membranes for boron removal. Hybrid membrane systems may also incorporate chemical conversions; for example, electrically conducting RO membranes have been proposed for enhanced boron rejection via electrochemical pH modification to convert boric acid to borate at the membrane interface (138). Whereas these approaches theoretically enhance the rejection of many small and neutral solutes, other approaches to remove boron have focused on polyol functionalities to selectively complex boron from aqueous solutions. Kamcev et al. (139) designed porous aromatic frameworks as rapid adsorbents for boric acid, and technologies similar to this advanced material may be integrated into future MMMs. Adsorbent-based membranes are promising for future membrane design, as enhanced boron removal has been reported by polyol-functionalized polymeric membranes (140), as well as heavy-metal capture by other adsorbent-based membranes (141), owing to reductions in mass transfer limitations relative to conventional adsorbent resins. However, adsorbent-based membranes can have limited binding capacities and affinities (141); thus, more research and development are necessary for commercialization.

Integrated systems incorporating conventional processes (e.g., adsorption, chemical conversions) into advanced membrane materials and hybrid processes are an evolving area of research

for removal of inorganic solutes that are traditionally challenging to remove. Thus, as materials science and process design advance, membranes will have an increasingly important role in removal of inorganic contaminants from water.

6. CHALLENGES AND OPPORTUNITIES

6.1. Membrane Fouling

A major recurring challenge to using membranes for the applications discussed above is fouling, in which solutes in the water to be filtered adhere to the surface of the membrane (external fouling) or in the interior of the pores of porous membranes (internal fouling), thereby increasing the mass transfer resistance to water permeation (142). Conventional approaches to limit/reverse membrane fouling include introduction of fluid instabilities at the membrane surface (e.g., air sparging of UF membranes) and chemical (e.g., acid, base, or chlorine) membrane-cleaning steps, all of which increase energy use or operational costs while potentially degrading the membrane and lowering permeate quality (143–145). Cleaning protocols, such as backflushing, cleaning in place, air scouring, and ex situ cleaning procedures, vary based on membrane and foulant type and in frequency, occurring as often as every several hours/days for UF membranes treating flowback water (146) and twice a year for RO membranes (2). MBR fouling by wastewaters can require very frequent in situ cleaning (i.e., on the timescale of minutes to hours) and occasional (i.e., every 1–3 years) ex situ cleaning due to the complex nature of wastewater foulants (147).

The most common categories of membrane foulants are (a) organic compounds, such as colloidal particles in MBRs, that aggregate and can form a cake layer on membrane surfaces (145–149); (b) inorganic compounds (e.g., calcium sulfate, calcium carbonate, calcium phosphate, and silica) that are concentrated at membrane surfaces beyond their saturation limit, so they precipitate on the membrane surface (i.e., membrane scaling) (145, 149, 150); and (c) biological growth on membrane surfaces (i.e., biofouling), where microorganisms proliferate, metabolize, and produce extracellular polymeric substances that provide an anchored network to support biofilm growth on the membrane surface (145, 149, 151). Organic fouling can be exacerbated by divalent cations (e.g., bridging of NOM molecules by Ca^{2+} to form supramolecular species that adhere to membrane surfaces) (102). Emulsified oil droplets in PW can form gel-like cake layers on membrane surfaces (148).

Combining membranes with other technologies in hybrid processes to selectively remove/transform foulants is being explored to mitigate fouling. Use of conventional coagulation/flocculation/sedimentation upstream from membranes has been considered (16). Membrane fouling can be reduced through selective removal of target solutes at different stages of treatment; one example is the ED-NF system presented in Section 4 (103), which removes Ca^{2+} and other multivalent cations via ED prior to removing NOM through NF/RO.

Surface modification of membranes is another approach to mitigate fouling (142). Fouling-resistant membrane surfaces are generally hydrophilic, smooth, and either neutral or negatively charged, as hydrophobic, rough, or positively charged surfaces enhance fouling potential (152). Incorporation of hydrophilic functionalities [e.g., poly(ethylene glycol) and polydopamine] onto membrane surfaces promotes the formation of hydration layers that limit the solute–membrane interactions that drive adsorption/fouling (142). Polydopamine modification is widely studied, as this approach can be applied to virtually any membrane surface and creates a thin hydrophilic layer that reduces fouling (142). Other approaches include MMMs composed of zwitterion polymers, silica nanoparticles, GO, and carbon nanotubes (142, 153, 154). Molecular-level understanding of the interactions between water, membrane surfaces, and foulants that promote or resist fouling is at an extremely rudimentary level. Future experimental studies characterizing *operando* membrane

surface structure, water structure and dynamics near membrane surfaces, and the impact of foulant solutes on membrane surface structure, water structure, and dynamics near membranes would, if combined synergistically with modeling/simulation studies, provide a much clearer understanding of the basic science behind fouling. This understanding would, in turn, stimulate insights regarding polymer and surface coating synthesis strategies to minimize fouling.

6.2. Selectivity Versus Permeability

Conventional nonporous polymer membranes invariably exhibit a trade-off between permeability and selectivity that results in a trade-off between flux and rejection (155, 156). Porous (e.g., UF) membranes also show such trade-offs (157). Much of the materials science research in membranes is aimed at making materials with better combinations of permeability and selectivity. For example, recent efforts to prepare novel porous membranes that are both highly permeable and selective have focused on so-called isoporous membranes to overcome the broad pore size distribution typical in conventional membranes (158, 159). A relatively few large pores in such membranes substantially reduce selectivity (and rejection), whereas most of the permeability (and flux) is contributed by the much larger number of smaller pores in the membrane. By narrowing the pore size distribution in such materials and tuning the pore size to a value just below that which will reject the solute(s) of interest, combinations of flux and rejection that are more favorable than those of conventional membranes may be achieved. However, owing to synthetic limitations, isoporous membranes today are made from a very limited set of polymers, and their ability to be scaled to the large surface area needed for practical applications has not been demonstrated. Nevertheless, developing better fundamental understanding of mechanisms to control and tailor pore size in porous membranes is an area of considerable interest. In nonporous (e.g., RO) membranes, attempts to achieve better combinations of permeability and, particularly, selectivity have typically focused on adding chemical functionality or additives that increase the selectivity for a particular solute over others in an aqueous mixture, such as insertion of aquaporins into the walls of desalination membranes (135, 160). In a recent study, artificial water channels based on aquaporins have been shown to exceed the current upper bound of the permeability/selectivity trade-off for desalination membranes by a factor of 10^4 (161). Although such membranes show interesting performance, studies of such membranes operating on real water streams and at typical operating conditions (e.g., applied hydraulic pressure) and studies of the impact of membrane-cleaning chemistry on their performance are not available. Fundamental studies of structure/property/processing/performance relations in novel materials, to better understand the molecular parameters controlling water and solute transport in membranes, are urgently needed.

6.3. Reactive Membranes

Incorporating reactive species in membranes to provide an additional pathway for solute degradation has been considered for a variety of separations. For example, incorporation of Pd/Cu-based heterogeneous catalyst particles into a polymer membrane was used to reduce nitrate to N_2 in water (162). However, the reaction requires a continuous supply of H_2 to perform the nitrate reduction. Photocatalytic membrane reactors have been prepared to, for example, degrade organics in wastewater. In one study, polyacrylonitrile UF membranes were prepared with TiO_2 added to the membrane casting formulation. Upon exposing the membranes to UV irradiation, 4-chlorophenol in water was degraded. This study was extended to degradation of a range of organic components from an adhesive manufacturing facility (163). Such membrane systems require significant energy input to support the UV degradation, and the membrane materials must be chosen carefully to avoid degradation. In another application, dissolved oxygen removal from ultrapure

water was accomplished via catalytic reduction involving a porous polypropylene hollow-fiber membrane, the surface of which had been coated with Pd (164). Generally, such reactive membranes could potentially degrade toxic organics into innocuous forms and transform inorganics to be more easily treatable. However, the economics of such membranes, based on precious metal catalysts, must be carefully considered when assessing their practicality. To date, many promising reactive membrane approaches have been proposed; however, none is in widespread use.

6.4. Integrated Membrane Processes

The previous sections highlight the potential for meeting water quality goals using integrated treatment systems that combine multiple membrane processes (e.g., ED/NF, NF/NF, NF/RO) or conventional and membrane-based processes (e.g., coagulation/filtration/RO). Combined integrated treatment processes such as MBRs can provide high-quality effluent with shorter residence times, smaller footprints, lower residual volumes, and simultaneous removal of multiple contaminants (e.g., BOD, ammonia, nitrate) (165). Sequentially integrated processes can remove interfering solutes from downstream processes (e.g., ED-NF) or alter the reactivity of a solute to facilitate downstream treatment [e.g., chemical oxidation of As(III) prior to NF]. Consideration of such integrated systems must include technical, economic, and life-cycle assessments to evaluate competitiveness for particular water qualities, quantities, and end uses.

A treatment train for a particular water source must optimize a series of treatment processes to meet all water quality objectives. To respond to the increased variability in source water quality imposed by water scarcity, extreme weather events, and industries with temporally variable water quality (e.g., PW), it would be ideal to consider water treatment as a series of plug-and-play technologies. Most treatment plants lack this flexibility and reflect compromises in the combination of processes that meet minimum water quality standards. For example, whereas membrane treatment is better than enhanced coagulation for removing NOM, coagulation is more appropriate for turbidity removal. Thus, the development of treatment strategies and technoeconomic evaluations of alternative systems must evaluate potential treatment trains using a holistic approach that addresses variable water quality, multiple end uses, and multiple treatment objectives. By integrating water treatment technologies (both conventional and membrane based) to achieve different goals, this “one water” approach (2) will create a more resilient and extensive portfolio of global water supplies (Figure 4).

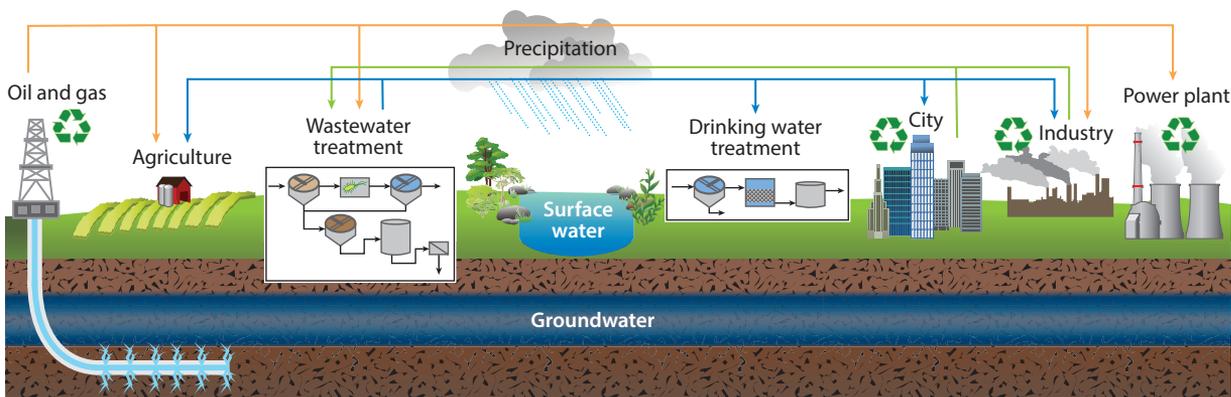


Figure 4

Opportunities for water reuse exist across (*arrows*) and within (*recycling symbols*) sectors (adapted with permission from Reference 166).

7. CONCLUSIONS

Harnessing nontraditional sources of water that are often highly impaired and complex (e.g., PW, treated wastewater) is crucial to sustain humanity. Membrane processes have several advantages compared with conventional strategies, such as their modularity, small footprint, and resiliency to temporal variations. Membranes exhibiting different pore sizes and different transport mechanisms offer strategies for addressing several classes of contaminants (e.g., particles, microbes, organics, inorganics). However, current membranes were not designed (and are unsuitable) for applications such as purification of PW and face several challenges that can be addressed only via application of fundamental theory and chemistry to design advanced membrane systems. Greater basic science understanding will enable (a) rational tailoring of fouling-resistant membrane surfaces; (b) synthesis of dense membranes with desired functionality to selectively and rapidly permeate or react with specific solutes; and (c) precise tuning of pore size and pore size distribution in UF and MF membranes to prepare highly permeable, selective porous membranes. Such materials could be used to separate water from aqueous mixtures and recover resources from complex water streams (e.g., Li^+ from PW). However, the variability in source water quality and end use suggests that membranes on their own are not a panacea for water treatment. Rather, the integration and coupling of novel membranes with conventional treatment processes offers a potential solution to meet challenges associated with lower-quality water sources, temporal variation of water quality, and resource recovery. Additionally, membranes can have niche applications in scenarios with specific water quality goals, and the identification of these scenarios in terms of water source, system size, and location is essential for the future adoption of membrane technologies in water treatment. The continued development and incorporation of membranes in integrated technologies to treat recalcitrant waters will enhance our abilities to meet the increasing global water demand.

DISCLOSURE STATEMENT

B.D.F. has a financial interest in Energy Exploration Technologies, Inc. (Energy-X), which is seeking to commercialize membrane technology for resource recovery from wastewater, and in NALA Systems, Inc., which is seeking to commercialize new membrane materials for desalination.

AUTHOR CONTRIBUTION STATEMENT

L.E.K. and B.D.F. conceived the idea for the review, and together with M.R.L. and R.S. drafted the manuscript. Each of the remaining authors contributed to individual sections of the paper by researching the literature and cowriting their respective sections: K.K.R. and D.F.L. assisted with the introduction; S.Y. and D.F.L. wrote the particles section; L.S.R. wrote the microbial section; S.H.B., C.M.C., S.K., and C.P.O. assisted with the organic section; A.G.D., L.K.N., S.M.N., and A.P. assisted with the inorganic section; and R.J.D. and K.K. assisted with the challenges and opportunities section.

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