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Materials and membrane technologies for water and energy sustainability



Ngoc Lieu Le, Suzana P. Nunes*

King Abdullah University of Science and Technology, Biological and Environmental Science and Engineering Division, 23955-6900 Thuwal, Saudi Arabia

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ABSTRACT

Water and energy have always been crucial for the world's social and economic growth. Their supply and use must be sustainable. This review discusses opportunities for membrane technologies in water and energy sustainability by analyzing their potential applications and current status; providing emerging technologies and scrutinizing research and development challenges for membrane materials in this field.

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* Corresponding author.

E-mail address: suzana.nunes@kaust.edu.sa (S.P. Nunes).

1. Introduction

Water and energy are fundamental resources used for economic, social and cultural development. These resources have been long presupposed as abundant. With the increase of population and the developments brought by the industrial revolution, their demand increased and scarcity is now an undeniable result.

Fig. 1 illustrates the total global stock of water for human use [1]. From the global water reserve, only 2.5% is fresh water and the rest is saline. From the 2.5% the largest part is frozen in polar regions and 30% are also in remote aquifers of difficult access. As a result only 0.007% of the total global water is directly accessible for use. Unfortunately part of this water is polluted by industrial plants, mining, oil or gas exploration, fertilizer and pesticide residue used in agriculture. In addition, the uneven distribution of water over the globe causes even more severe water scarcity in some regions. Desalination and water reclamation are of paramount importance in water security, where desalination happens to be one of the main life supports in many arid regions.

The current global energy problem originates not only from limited fossil energy supplies, but also its environmental impacts for its entire energy lifecycle, from mining and processing to emissions, waste disposal and recycling. The indicators of energy sustainability include its price, environmental impacts and greenhouse gas emissions, availability of renewable energy sources, land requirements, water consumption and social impacts [2]. One solution to achieve energy sustainability is to develop sustainable technologies to gradually replace non-renewable fossil fuels. These include energy conversion from renewable and/or natural resources (e.g. biomass, wind, solar and water) into usable energy (e.g. electricity) and energy storage systems for long-term or remote usage.

Membrane technologies play a significant role in water and energy sustainability. Some of them are already applied in industries at scale. Examples include desalination by reverse osmosis (RO), wastewater treatment by membrane reactors (MBR), lithium-ion batteries and membrane-based fuel cells. Besides addressing water and energy scarcity, membrane technologies meet sustainability criteria in terms of environmental impacts, land usage, ease of use, flexibility and adaptability. On the other hand, they still need to be improved in terms of cost and affordability, energy consumption and expertise. To achieve these improvements, advances in membrane materials are needed. This article aims to analyze opportunities for membrane technologies and the revolution and advancement of membrane materials to tackle water and energy sustainability. This review may provide membrane researchers with greater clarity in membrane criteria targets, provide industrial end-users with emerging membrane technologies and reinforce the engagement between research and application aspects.

2. Membrane technology in water sustainability

2.1. Desalination

Desalination plays an important role in water sustainability for many countries around the world, particularly in the Middle East. For instance the water supply for domestic and industrial use in Qatar and Kuwait is 100% provided by desalination [3]. Desaldata [4] reported that 63.7% of the total capacity of global desalted water is produced by membrane processes, validating the importance of membrane technologies in this application. Regarding water sources for desalination, seawater contributes for 58.9%, brackish groundwater 21.2%, surface water and wastewater for the remaining of 19.9% [4]. Application of membrane desalination to produce drinking water from seawater has been comprehensively reviewed [5–15]. Therefore, in this review, we focus on desalination for other applications. Examples are desalination of produced water, desalted water for agriculture, desalination in mining, and removal/recovery of heavy metals and rare earth elements (REEs) from saline wastewater.

2.1.1. Produced water

Produced water is the largest waste generated in oil and gas industries. The global amount of wastewater co-produced in oil and gas exploration is about 210 million barrels/day, three times higher than the produced oil [16]. Its production increases in an attempt to exhaustively recover oil from matured fields with significant environmental consequences. Produced water management is one of the most challenging issues facing the oil and gas industries and protecting human health and the environment. Treatment of produced water for reuse and recycling is an effective option for its handling, which has the potential to be a harmless and valuable product rather than a waste for disposal.

Produced water is difficult to treat because of its complicated physicochemical composition, which may change over the lifetime and well-to-well. Produced water consists of dissolved and suspended organics and solids. Membrane technology plays an increasingly important role in produced water treatment to remove all above components. Depending on the reuse purpose of produced water, the quality of reused water may vary and the applied membrane techniques may be different. External reuse applications, other than for reinjection, require much higher water quality. Microfiltration (MF) and ultrafiltration (UF) standalone processes or their hybrid integration have been efficiently used to separate suspended particles, macromolecules and oil as a pretreatment step while the combination of ultra-low-pressure nanofiltration (NF) and reverse osmosis (RO) has been applied to treat produced water for higher water quality standards which are potable and for irrigation [17–29]. However, in this review, we focus more on

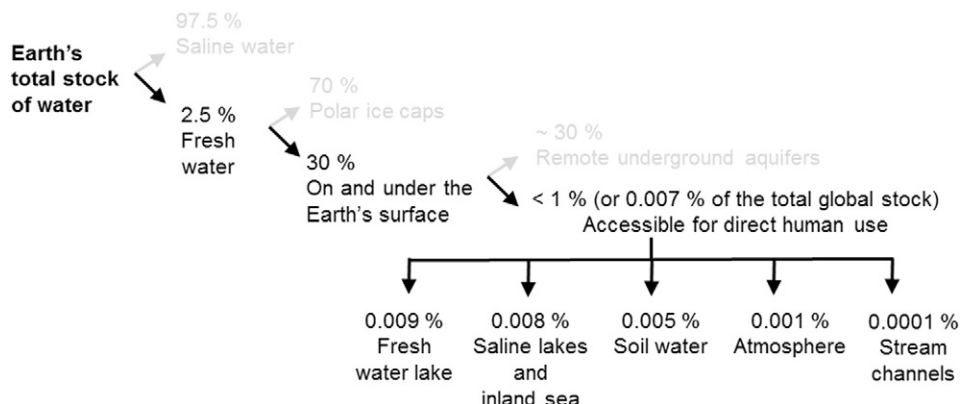


Fig. 1. The total global stock of fresh water for human use.

advanced membrane technologies for high-salinity produced water sources, such as produced water from shale gas wells [30,31], where the concentration of total dissolved solids (TDS) varies from 8000 to 360,000 mg/L [32]. The high value of TDS concentration restricts the choices of appropriate desalination technologies. RO, which is commercially employed to desalinate seawater (TDS \approx 35,000 mg/L), is not a good choice because of its high hydraulic pressure (high energy) required to overcome the osmotic pressure of high-salinity produced water, making the process unfeasible. This hydraulic pressure may exceed the allowable pressure of the membrane modules and other process equipment, making impractical this application.

On the other hand, emerging technologies such as membrane distillation (MD) and forward osmosis (FO), can be potentially used to treat high-salinity water with low energy consumption. In addition, as compared to RO, both MD and FO are expected to have lower fouling propensity due to the absence of an applied hydraulic pressure. MD is a membrane-base desalination technology which utilizes low-grade heat to drive separation. In MD, a hydrophobic and microporous membrane is employed to separate the aqueous feed stream and the permeate. The transport of liquid feed water across the membrane pores is hindered by the hydrophobic nature of the membrane. The vapor pressure difference, provided by temperature differences in both sides of the membrane, drives the transport of water vapor through the pores to the permeate side. Different configurations to promote the vapor pressure gradient in MD, such as direct contact, air gap, sweeping gas, and vacuum, have been proposed [33–37]. The process has the advantage of energy efficiency because it requires only minor auxiliary energy to circulate the solutions. However, the complexity in produced water composition is challenging for MD, where small organic components and dissolved gases could pass through the membranes with water and contaminate the permeate stream; or certain feed compounds such as alcohols and surfactants could reduce the feed surface tension and cause membrane wetting, which enables the feed solution to penetrate the pores and compromise the permeate quality. Therefore, to address the produced water quality, pretreatment to remove these above components or post-treatment to remove permeated volatile compounds and gases may be required [35,38]. In addition, periodic membrane cleaning could be essential to preserve the MD productivity [35,38].

In the FO process the water transport is driven by an osmotic pressure difference between the feed solution and a concentrated draw solution, which has higher osmotic pressure than the feed. The water flow across the membrane dilutes the draw solution and lowers the osmotic pressure gradient. Consequently, a supplemental draw solution regeneration step is essential to recover the draw solute and collect the produced water [39,40]. Draw solution selection is crucial for FO, especially for desalination of high-salinity water, because it must provide a higher osmotic pressure than the feed and should be easily recyclable. Draw solutes generating insufficiently high osmotic pressures such as magnetic nanoparticles [41], stimuli-responsive hydrogels [42] and polyelectrolytes [43], are normally not satisfactory for FO desalination of high-salinity produced water. Although dissolved salts can provide high osmotic pressures, the need of RO for their regeneration makes them inapplicable for produced water treatment [44–46]. Thermolytic salts, which can vaporize via a change in solution temperature, may be the most suitable draw solute candidate for this application. Thermal energy such as distillation can be utilized for its regeneration. Among thermolytic salts, ammonia–carbon dioxide is the most popular thermolytic draw solute studied for FO [47–49]. It was first discovered as a draw solution for water desalination in 1964 by Neff [50]. Its solution can produce osmotic pressures greater than 200 atm and can be regenerated at 60 °C [49]. Besides ammonia–carbon dioxide, other thermolytic draw solute such as trimethylamine–carbon dioxide [51] or switchable polarity solvents [52,53] may also be promising for the FO desalination of produced water. However, they are still at early stages of investigation and the presence of ammonia even in low concentration can be a problem for some applications.

2.1.2. Desalinated water for agriculture

In the past, direct sources of fresh water were cheap, not justifying the use of more costly desalinated water in agriculture [54]. However, desalinated water is becoming more competitive because its cost is decreasing, while the costs of surface water and groundwater are elevating. It is now clear that the use of groundwater is not sustainable and new regulations are expected to mitigate their use compared to desalinated water. In spite of this evolution, the cost of desalinated water is still too high for its full usage in irrigation. However, it might be affordable for intensive horticulture with high-value crops such as vegetables and flowers grown in greenhouse or coastal areas (where safe disposal of brines is easier than in inland areas) [54,55]. Moreover, the high quality of desalinated water can cause less negative impact on soils and crops as compared to the direct use of brackish water [56]. Other advantages of desalinated water for agricultural use are additional and sustainable water resource not depending on the weather (especially important for drought countries), enhancement in productivity and quality of agriculture products, less water consumption and recovery of salty soils [56,57]. Furthermore drinking water quality is not needed for agriculture. Partial desalination could be enough in many cases, particularly by choosing salt-resistant crops [58].

According to Desaldata [59], there is an increasing use of desalinated water in agriculture around the world. Spain contributes to the highest proportion of desalinated water use in agriculture, where the current desalination capacity is 1.4 million m³/day and 22% is utilized for agriculture. Most of Spanish desalination plants for agriculture employ brackish water as the feed and are located in coastal areas or within 60 km of the sea. The next country applying high percentage of desalinated water for agriculture is Kuwait (13%). Saudi Arabia, despite its highest production of desalinated water in the world, uses only 0.5% of its desalination capacity for agriculture. Other countries such as Chile, China and Australia are also evaluating the feasibility of desalination technologies to support agricultural water supply.

For agricultural uses, RO is the preferred desalination technology because of its maturity and its reduced cost [57] compared to thermal desalination. Both sea and brackish water are used as the feed. Seawater has salinity of 35,000 mg/L equivalent with the osmotic pressure of 2800 kPa while brackish water has low salinity of 1600 mg/L equivalent with the osmotic pressure of 140 kPa [57]. Such data imply a significantly higher hydraulic pressure and hence higher energy consumption required for RO when applying seawater as the water resource. RO desalinated water has reduced amount of calcium and other essential minerals, as well as a slightly acid pH, which could damage soil structure [56]. Consequently, this water requires a re-mineralization step to adjust the mineral ratios. However, the cost of this post-treatment is virtually negligible as compared to the desalination cost [56]. The use of nanofiltration for partial desalination is also under consideration with the advantage of lower hydraulic pressure, delivering water with higher mineral content than RO. Another concern of desalinated water for agriculture is its boron concentration because boron is toxic to different crops even with its low content of 0.3–4 mg/L [60] and it has high permeability across membranes [56]. To reduce boron content to an acceptable value, additional treatments such as the use of ion exchange resin might be required [56], which increases the capital cost and operational expense of the desalination plants. In addition, disposal of the RO retentate stream is challenging for inland desalination plants, which adds a supplemental cost to water product.

2.1.3. Desalination in mining

Water plays an important role in the mining industry. It is used for flotation, heap leaching of copper or gold ores, dust suppression, equipment cooling, slurry transport and human needs at mine sites [61]. There are two main water concerns in mining. Firstly, mining requires a sustainable supply of water because mines are often located in remote and arid areas [61]. Secondly, the contamination of the spent mine

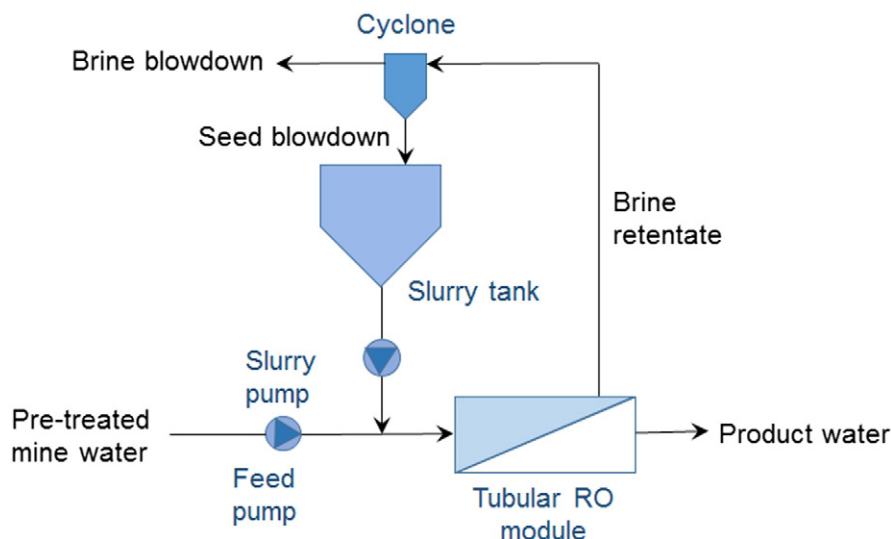


Fig. 2. The schematic representation of the SPARRO pilot plant.

water with explosive residues, salts, and acids requires treatment before it can be recycled or disposed [62].

The main water resource for remote and arid mines is groundwater and seawater, both of which have high salinity [61]. The salinity of groundwater in mine sites may exceed 100,000 ppm TDS or even higher, such as the mines in Western Australia [61]. These water resources alone or blended with mine water runoff from stockpile, waste or mine dewatering can be directly used for some processing steps in mining such as copper leaching, flotation or cooling [63–66]. However, to alleviate negative impacts on local aquifers, protect the health of miners and to minimize corrosion of underground equipment in underground mines, desalinated water produced from seawater and groundwater are preferred [67,68]. RO is the key desalination technology used to treat groundwater in many mines to provide potable and fresh water [61].

On the other hand, spent mine water also requires the desalination process before recirculation or prior to discharge. Mine waters are classified into two groups, according to their tendency to form calcium sulfate [62]. The conventional membrane-based desalination processes such as tubular reverse osmosis (TRO) and electrodialysis reversal (EDR) have been demonstrated for their technical viability in desalinating non-scaling mine water in the early 90's decade [62,69]. TRO uses a tubular membrane module. This is the only practical mode for desalination of feed solutions with high suspended solids concentrations, such as mine water [69]. EDR is the desalination membrane process where an electric current is used to migrate dissolved salt ions through an electrodialysis stack consisting of alternating layers of cationic and anionic ion exchange membranes. The advantages of EDR over RO are its lower sensitivity to effluent temperature or pH and lower capital cost [70]. An EDR pilot plant at Beatrix gold mine in South Africa achieved 80% salt recovery and recycled 84% water [71].

Table 1
Prices of some metals and rare earth oxides [77,78].

Metal	Price ^a (US\$/kg)	Rare earth oxides	Prices (US\$/kg) ^b	
			2011	2015
Sodium	0.13	Lanthanum oxide	20.1	0.6
Magnesium	2.80	Cerium oxide	50.0	1.4
Potassium	0.15	Neodymium oxide	11.6	10.0
Rubidium	79,700	Terbium oxide	48.2	0.9
Caesium	63,000	Dysprosium oxide	4.7	0.5
Germanium	1700	Yttrium oxide	1.8	0.1

^a Estimated selling price in 2005 if extracted from RO brine.

^b Source: Arafura Resources Limited (2011 and 2015).

Recently, advanced membrane technology such as vacuum membrane distillation has been studied for mine water desalination [72], using a hollow-fiber membrane to remove up to 99.9% of TDS from Appin (New South Wales) mine water. However, its long-term operation has been not investigated.

For scaling mine water, modified RO processes including seeded RO (SRO) and the slurry precipitation and recycle reverse osmosis (SPARRO) technology have been proposed [62,68,73,74]. In SRO, calcium sulfate is removed prior to membrane treatment to reducing the scaling. This CaSO_4 removal involves a suspension of seed crystals added into the feed via recycling of waste slurry. Although SRO provided high salt rejection and water recovery, its high energy consumption and poor control of CaSO_4 seeds constrained its development. Based on SRO mechanism, SPARRO was developed and patented by the Chamber of Mines Research Organization (COMRO) from 1989 to 1993 [74]. The schematic representation of the SPARRO pilot plant is shown in Fig. 2 and its operational principle can be found elsewhere [74]. It is capable to produce a high quality produced water at water recovery of around 95%. However, the fouling of quartzitic suspended materials declines the flux. The capital cost for a 4 ml/day SPARRO plant was US\$ 1 million, with an estimated operating cost of US\$ 0.09/m³ of produced water.

2.1.4. Removal/recovery of heavy metals and rare earth elements (REEs)

Removal/recovery of heavy metals and REEs from wastewaters contribute to water sustainability in two ways. First, removal of toxic metals makes wastewater safe for disposal or reuse [75]. Second, recovery of expensive metals and especially REEs can save the cost of wastewater treatment through metal reuse or sale [76]. Table 1 lists the prices of some heavy metals and REE oxides [77,78]. REE prices have strongly oscillated in the last decade, depending on demand mining restrictions. In wastewater, the metals exist in their ions and dissolved salt form. Conventional treatment technologies for such salts include chemical precipitation, coagulation, flocculation, floatation, ion exchange, adsorption and electrochemical processes [79]. Compared to these

Table 2
MBR applications in domestic and municipal wastewater treatment.

Country	Size of operation	Membrane configuration	Ref.
Japan	Full-scale ~ 125 m ³ /day	Plate and frame external	[114]
USA	Full-scale 9000 m ³ /day	Hollow fiber submerged	[113]
The Netherlands	Pilot-scale 360–840 m ³ /day	Tubular external	[112]
France	Pilot-scale 2.4–4.8 m ³ /day	Tubular external	[111]
Korea	Pilot-scale 48 m ³ /day	Cartridge-disc external	[110]
Germany	Pilot-scale 6–9 m ³ /day	Hollow fiber submerged	[109]

conventional technologies, membrane processes such as ultrafiltration, nanofiltration and reverse osmosis have proven their competitiveness in removal/recovery of metals from wastewater because of their low energy requirement, small volume of retentate, high selectivity, possibility of achieving zero discharge, continuous operation and minimal labor requirement [80–82].

Ultrafiltration (UF) uses a permeable membrane to separate macromolecules based on its pore size (5–20 nm) and their molecular weight (1000–100,000 Da) at low transmembrane pressures. Since the pore size of UF membranes is much larger than that of dissolved metal ions in its hydrated ion form or low molecular weight complexes, the metal ions have to bind with large molecules of surfactants [83–85] or complex with water-soluble polymers [86–90] to increase their size before the treatment. The former succeeded to remove 99% of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) from synthetic wastewater while the latter was able to remove 100% Ni(II), 94% Cu(II) and 100% Cr(III). Although their recovery is high, a post treatment is essential to recover metal ions and reuse surfactants and water-soluble polymers.

Reverse osmosis (RO) has also commonly been studied for metal recovery. It provided high recovery of > 99% for Cu(II), Ni(II), Zn(II) and As(V) [91–94]. However, it has yet to be widely applied, mainly because of its high-pressure operation, tendency for fouling and high energy consumption. Nanofiltration (NF) is the intermediate membrane process between UF and RO. Its pore size is equivalent with the molecular weight of 200–1000 Da and it operates at pressures of 150–500 psi (10–34 bar) (lower than that of RO). It allows partial permeation of monovalent salts such as sodium chloride but rejects bivalent salts. Since all heavy metals or REEs are bivalent or higher, NF is an effective process to remove/recover them. NF is now a promising technology to reject heavy metal ions such as nickel [95], chromium [96,97], cadmium [98], lead [99], copper [100,101] and arsenic [102,103] from wastewater. It has benefits from high efficiency of metal removal, ease of operation, reliability and comparatively low energy consumption as compared to RO [104]. Membranes with capacity to better separate specific metals and salts would be an important achievement.

2.2. Wastewater reclamation and reuse

2.2.1. Municipal wastewater

Municipal wastewater refers to sewage, the main wastewater produced in human daily life's activities, including kitchen sink, shower, laundry, etc., and flush toilets sewage. Most municipal wastewater

contain biodegradable compounds and limited chemicals, which can be treated using activated sludge systems. Membrane bioreactors (MBR) integrate either a microfiltration (MF) or UF membrane into conventional activated sludge (CAS) reactor to perform the sludge separation. The MBR process has been introduced in 1960s and enabled to remove high amount of BOD (biochemical oxygen demand), TOC (total organic compound) and completely eliminate TSS (total suspended solid) [105]. Compared to CAS, its product effluent has auxiliary advantage of low turbidity and SDI value (silt density index, an index to characterize the fouling potential of suspended solids on membrane surfaces), which makes it available as the feed water to an RO system. Lozier et al. [106] reported moderate success of a pilot-scale study using MBR effluent as feed water for RO. MBR is advancing rapidly both in R&D and commercial application on around the world. An example of successful MBR plants was commissioned by The Public Utilities Board (PUB) of Singapore in December 2006 [107], which provides valuable information on design and operation of the MBR systems under tropical environment. The plant consumed an energy of about 0.55 kWh/m³ and needed no intensive chemical cleaning since the start-up for about 7 months. Currently, over 1500 MBRs are in operation around the world in Japan, Europe and North America [108]. Table 2 summarizes their configuration and size of operation [109–114].

Since 2011, Cranfield University (UK) has been developing waterless hygienic toilet (the Nano Membrane Toilet, NMT), supported by Bill & Melinda Gates Foundation for the Water, Sanitation & Hygiene program [115,116]. This NMT design is an innovative sanitation solution which can turn human waste into pathogen-free water and encapsulated briquettes for irrigation and fertilizer, respectively. It works without external energy or water. Fig. 3 shows its schematic representation. In this toilet, membrane technology plays a key role. A bundle of hollow-fiber membranes is used to separate loosely bound water (mostly from urine) through the mechanism of membrane distillation, where water penetrates through the membrane in the vapor state. A sweep gas is pumped through the permeate side of the membrane to produce the vapor pressure difference between the feed and permeate to drive the water transport [116]. The nanostructure of the fibers rejects pathogens. Nano-coated beads are subsequently used as a “condenser” to recover the permeate water with the efficiency of 90%. Since the condensed water has certain amount of volatile organic compounds (VOCs), it cannot be stored. Instead, it must be used in the home daily for washing or irrigation. More details on its operation can be found elsewhere [115]. A prototype for it is expected to be ready for field testing in January 2016.

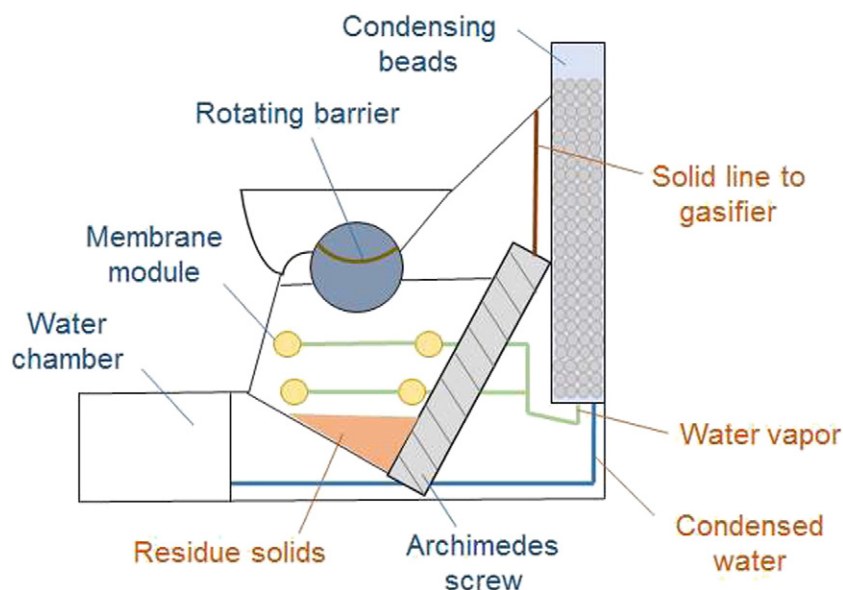


Fig. 3. The schematic representation of the Nano Membrane Toilet.

Table 3
MBR applications in industrial wastewater treatment.

Source	Country	Size of operation	Efficiency	Ref.
Wool scouring	Japan	Pilot-scale ~ 10 m ³ /d	TOD removal > 89%	[117]
Pulp mill	Japan	Pilot-scale ~ 10 m ³ /d	TOC removal > 85%	[118]
Automotive industry	USA	Full-scale 113 m ³ /d	COD removal > 94%	[119]
Metal transforming	Canada	Pilot-scale 0.2 m ³ /d	COD removal > 90%	[120]
Cosmetic industry	France	Full-scale	COD removal > 98%	[114]
Maize/egg processing	South Africa	Full-scale 500 m ³ /d	COD removal > 97%	[121]

2.2.2. Industrial wastewater

Industrial wastewater originates from many sources, including the iron and steel, mining food, pulp and paper, textile, pharmaceuticals chemical industries. Most industrial wastewater can be efficiently treated by MBR (Table 3) [114,117–121], which is similar for municipal wastewater treatment. However, along with the rapid development of industrialization and urbanization or due to the particularity of some industries, many industrial wastewater and municipal wastewater sources contain toxic chemicals such as heavy metals and trace organic contaminants (TrOCs). These cannot be removed easily by conventional water treatment technologies or MBR alone. Removal/recovery of heavy metals from wastewater was reviewed in the Section 2.1.4, hence we will review membrane-based technologies for TrOC removal in this section.

TrOCs are a diverse group of compounds including persistent organic compounds (POPs), pesticides, pharmaceutically active compounds (PhACs) and endocrine disrupting chemicals (EDCs) [122]. TrOC concentration ranges from 100 ng/L to 100 µg/L in raw wastewater. Even if their content in wastewater is very small, many are biologically active and can cause acute and chronic toxicity to aquatic organisms and possible harmful effects on human health. Intensive membrane-based technologies have been studied to remove TrOCs, such as MBR, single membrane processes (NF, RO, FO), dual membrane processes (UF + RO, FO + RO) and hybrid processes (MBR or BR (bioreactor) + NF, RO, FO, MD) [123].

All the standalone processes have certain inherent advantages and disadvantages and their commercial application of TrOC removal is yet to be developed. Previous studies reported from virtually complete removal for some TrOCs to almost no removal for some others by MBR [123]. Their removal mechanism is governed by the adsorption of the TrOCs on the sludge retained by a membrane and subsequent degradation by the biomass in the reactor. As a result, the TrOC removal efficiency depends on their intrinsic biodegradability and other physicochemical properties affecting their biosorption on the sludge such as hydrophobic interaction, molecular weight, functional groups and electron withdrawing/donating groups [124–128]. Operating conditions (temperature [129–131], pH [132–135], hydraulic retention time [136], sludge retention time [137–139], dissolved oxygen concentration [140–143]) also have various effects depending on the physicochemical properties

of TrOCs. For single membrane separation processes (NF, RO, FO) [144–160], the separation is accomplished by size exclusion, charge repulsion, or sorption diffusion mechanism [122]. Removal efficiency of >90% can be achieved but it also largely depends on physicochemical properties of TrOCs. In addition, TrOCs cannot be degraded in these processes, only concentrated and hence further treatment is required to recover or neutralize them. Some dual membrane processes have also studied for TrOCs removal, where one membrane process is supplemental to the other. For example, UF was used to reduce the foulant concentration for the RO process [161] or RO was employed to recover water from the diluted draw solution of the FO process [162–164].

The complete removal of a broad range of TrOCs by a single process is however hardly feasible. Therefore integrated/hybrid processes including MBR and other membrane separation technologies are under consideration to efficiently remove TrOCs [152,165–172]. For example, the combination of MBR with NF or RO can improve the removal of both hydrophobic and hydrophilic TrOCs. The hydrophobic compounds, which may absorb and subsequently pass through NF or RO membranes, can be first retained into the MBR sludge. The hydrophilic compounds, which have less interaction with the sludge, can be efficiently removed by the following NR or RO. In addition, MBR can retain bulk organic or colloidal compounds to reduce the fouling issue for the NR and RO. Nguyen et al. [170] reported that this model can remove 90% to 100% of 22 diverse TrOCs from the synthetic wastewater. Similarly, Sahar et al. [171] achieved >99% removal efficiency of 11 TrOCs from wastewater by a MBR–RO system.

The integration of MBR with FO in an osmotic membrane bioreactor has been demonstrated with promising results [39,162,173–178]. Fig. 4 illustrates this hybrid process, which takes the advantages of both technologies. It has low fouling propensities, inheriting from the osmotic-pressure-difference-driven nature of FO instead of hydraulic pressure. In addition, the FO process can keep small and persistent TrOCs in the reactor, increasing their retention time and hence improving their biodegradation. Alturki et al. [174] reported that this combination obtained high removal efficiency of 25 out of 50 TrOCs while Lay et al. [178] found that it efficiently removed four pharmaceuticals to produce excellent water quality. However, the build-up of salinity in the reactor as the result of the FO operation may be toxic to the bioreactor and reduce

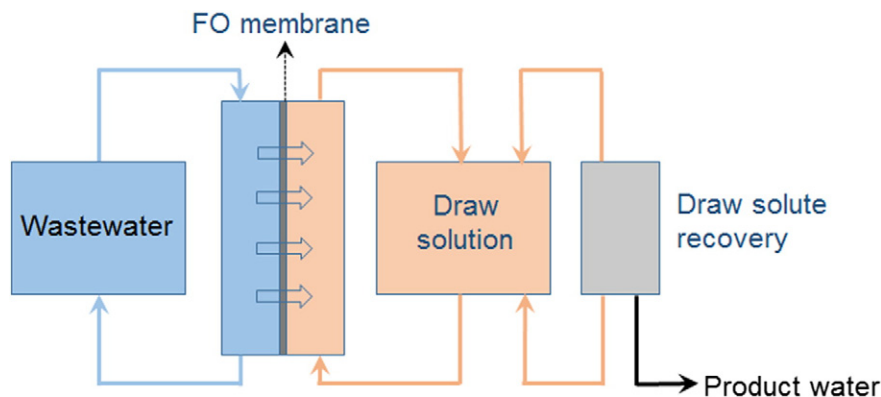


Fig. 4. FO set-up for water/wastewater treatment.

Table 4
Examples of MF and UF membrane types and configurations used in MBR systems.

Types	Configuration	Supplier	Pore size	Wastewater	Ref.
MF ceramic	Tubular	Adams hydraulics	0.2 μm	Food waste	[191]
MF ceramic	Tubular	Kerasep	0.1 μm	Municipal	[192]
MF ceramic	Tubular	–	0.2 μm	Municipal	[193]
MF alumina	Tubular	SCT	0.2 μm	Municipal	[194]
UF	Plate and frame	DDS Lab	20 kDa	Alcohol distillery	[195]
UF Zircon	Tubular	SCT	0.05 μm	Municipal	[194]
UF	Tubular	Zenon environmental	75 kDa	Sanitary and industrial	[196]
UF	Tubular	–	15 kDa	Synthetic (fuel oil)	[197]

its effectiveness in degrading TrOCs. In addition, FO-related challenges such as water recovery from the draw solution, draw solution regeneration and reverse solute leakage need to be targeted.

More recently, Phattaranawik et al. [179] integrated an MD unit into a bioreactor. The bioreactor can first digest the organic matters such as carbohydrates or proteins before they may wet the MD membrane pores and deteriorate its performance [180]. On the other hand, the need to operate MD at 30–80 °C suggests the use of thermophilic microorganisms for the bioreactor may lead to an enhanced biodegradation of organics [181]. Even the salinity was still built up in the reactor, Wijekoon et al. [182,183] found that the high overall removal of >95% can be achieved for all 25 studied TrOCs.

2.3. Membrane materials for water sustainability and their challenges

2.3.1. Microfiltration (MF) and ultrafiltration (UF)

In MBR, several types of membranes are used based on the size of contaminants, such as MF for suspended particles (100–1000 nm), UF for bacteria and virus (5–100 nm) and NF for dissolved particles (1–5 nm). MF and UF are technically popular than NF regarding the fouling and cost factors [184–187]. Both ceramic and polymer materials can be used to fabricate MF and UF membranes. Ceramics have advantages of high chemical stability and mechanical strength, ease of cleaning, long and reliable lifetime [188–190]. However, it is expensive and difficult to fabricate in large scale due to its brittleness [189]. Sealing when integrating in modules can be an issue. Polymeric membranes have therefore dominated the market for decades. Common commercial polymers used for MF and UF membranes are poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF), polyethylene (PE), polypropylene (PP) and polytetrafluorethylene (PTFE). Except for PES, all the mentioned polymers are very hydrophobic. PE, PP and PTFE are insoluble in organic solvents at room temperature, making the manufacture by solution processes difficult. Porous membranes based on PP and PTFE are produced by mechanical stretching of extruded films. Thermal induced phase separation (TIPS) of polymer solutions is commonly used for the manufacture of porous polyolefin membranes. However, the most widely used method for membrane preparation, applied for PES and PVDF membranes, is the non-solvent induced phase separation (NIPS). This involves solution casting and immersion in a coagulating water bath. Asymmetric membranes with gradient pore size are obtained in this case. Table 4 lists examples of MF and UF membrane types and configurations used in MBR systems [191–197].

Fouling is one of the biggest challenges for MF and NF membranes because most of them are hydrophobic. The most commonly used strategy to combat fouling is to make membranes hydrophilic by 1) hydrophilically modifying membrane polymers before fabrication, 2) blending with hydrophilic agents; and 3) grafting or coating hydrophilic polymers on the membrane surface. Although fouling can be minimized, undesirable effects such as narrowing the pore size or even blocking the pores of the MF and UF microporous membrane surfaces [198]. In other cases, the pore size enlarges, reducing the salt rejection [199,200]. In addition, many coating layers have inadequate mechanical and chemical properties and do not sustain long-term operations [198].

Material challenges to prevent fouling will be further discussed in the Section 2.3.6.

2.3.2. Nanofiltration (NF)

Advanced membrane formation technologies have been applied to produce NF membranes with high flux and rejection and low fouling tendency. The basic manufacturing method is NIPS. This produces an integrated porous asymmetric membrane with a selective layer on the top or a non-selective porous structure, which can be used as substrate for multilayered membrane preparation. Typical polymeric materials for this purpose are PES, PVDF and polyacrylonitrile (PAN). The deposition of a selective layer constituted by another polymer, which can be crosslinked or not, can be performed by dip-coating [201,202] or interfacial polymerization [203–216]. Additional surface modification by nanoparticle incorporation [217–226] and grafting polymerization [226–242] can be performed to control selectivity or reduce fouling. Interfacial polymerization technique refers to the polycondensation of water-soluble and organic-soluble monomers on a porous support to produce thin-film composite (TFC) membranes. The technique is simple, easy to apply, and capable of creating a very thin selective layer of <100 nm, mainly based on polyamide. This thin layer determines the overall efficiency of the membranes. Efforts to improve NF performance include influencing the selective layer by changing monomers [207,208, 212,213,216], adding additives into the aqueous or organic solutions [204–206] or modifying the surface of the formed polyamide layer [203,209,210,214,215]. The incorporation of nanoparticles into the selective layer during the polymerization has been studied to form thin-film nanocomposite (TFN) [224]. TFC membranes are considered the benchmark in the field of NF for aqueous separations. On the other hand, grafting polymerization via UV/photo-grafting [243–246], electron beam irradiation [227–229], plasma treatment [230–232] and layer-by-layer (LbL) [226,233–236] technique have been also extensively studied to produce NF membranes with high hydrophilicity and low fouling propensity. These techniques are well developed in the laboratory scale but their application in the large scale is still limited.

Although membranes with high permeance and selectivity to salt are available, membranes with tailored selectivity, able to distinguish solutes of similar size are needed. Furthermore the use of NF membranes is also growing for applications other than water purification. This is the case of chemical and pharmaceutical applications, requiring operation in the presence of organic solvents. For this purpose a new class of resistant porous substrates and selective layers is being developed. Materials under consideration are polyetherketone, crosslinked polyimide and polyazoles [247–251].

2.3.3. Reverse osmosis (RO)

The application of membranes for seawater desalination substantially reduced the cost and increased the availability of drinking water. Late in 1980's, the costs were recorded as about US\$2.10/m³ [252]. Since then, the desalination market has been increasingly expanded with improved technologies to reduce the cost. It was remarked in the last decades that large-scale SWRO plants reached US\$0.5/m³ for water price [253]. This price depends on many parameters such as plant location, feed water quality, plant capacity, local energy and labor costs,

Table 5
Examples of commercial RO membrane modules in seawater desalination.

Brand name	Membrane	Module	Operation condition	Flux (m ³ /day)	Salt rejection (%)	Location	Ref.
DOW FILMTECTM 8-in. SW30HRLE	TFC crosslinked membrane	Spiral wound	32 g/L NaCl, 55 bar, 25 °C, pH 8, 8% recovery	28.0	99.60–99.75	Perth, Australia	[257]
Hydranautics 8-in. SWC4+	TFC crosslinked membrane	Spiral wound	32 g/L NaCl, 55 bar, 25 °C, pH 7, 10% recovery	24.6	99.70–99.80	Lobregat, Spain	[256]
Toray 8-in. TM820C	TFC crosslinked membrane	Spiral wound	32 g/L NaCl, 55 bar, 25 °C, pH 8, 8% recovery	19.7–24.6	99.50–99.75	Singapore	[259]
Toyobo 16-in. HB10255	Asymmetric cellulose tri-acetate	Hollow fiber	35 g/L NaCl, 54 bar, 25 °C, 30% recovery	60.0–67.0	99.40–99.60	Fukuoka, Japan	[258]

political and environmental policies and others. The recent capital costs range between US\$900 and 1200/m³/day for a large scale SWRO desalination plant, and can reach about US\$2500/m³/day for a smaller one [6]. Besides the major costs from capital recovery (41%) and energy consumption (19%), membrane replacement (16%) contributes a significant component of the total water cost [254]. Other cost components are operation and maintenance (14%), chemicals for cleaning (6%) and spares (4%).

Polymeric membranes dominate the market for desalination by RO, because of their low-cost fabrication, ease of handling, and excellent performance in terms of selectivity and permeability. A key breakthrough in RO membrane manufacturing and application in different fields was the NIPS process proposed by Loeb–Sourirajan [255]. This allowed production of asymmetric membranes (1960s), initially based on cellulose derivatives, and the fully crosslinked TFC membranes (1970s to 1980s) prepared by interfacial polymerization. The mostly used TFC membranes are constituted by a porous polysulfone substrate and a thin polyamide layer. Thin cellulose acetate hollow fibers and TFC membranes in the spiral module configuration share the market for RO desalination plants. Table 5 provides commercial RO membrane modules in seawater desalination [256–259]. Despite of their success, TFC membranes have a key limitation – the degradation by chlorine, one of the common disinfectants used in wastewater treatment. RO membrane development should focus on chlorine-resistant membranes to eliminate the need of de-chlorination for the RO feed and re-chlorination for the RO permeate, reducing the overall cost of the system [260–263]. In addition, high-boron rejection membranes should be addressed when increasingly stringent water quality standards for which lower boron concentrations are required [264–270]. This will help to reduce the number of RO pass in the RO plants to achieve the required water quality [271,272]. In terms of water permeance and salt selectivity, the current RO membranes are well advanced and successful in large-scale seawater desalination operation. The future RO development should focus on other regulated and emerging trace contaminants such as persistent organic compounds (POPs), pesticides, pharmaceutically active compounds (PhACs) and endocrine disrupting chemicals (EDCs).

The evolutionary development of polymeric RO membranes is mostly mature. Membranes with high salt rejection are available with high water permeance. Even higher permeances would reduce the needed membrane area, but would not considerably save energy for

RO operation [47]. However membranes with higher fouling resistance and higher resistance to chlorine are needed. RO membranes continue to be developed using nanoparticles [206,273–277]. Two major practical challenges need to be overcome before they can move to the next stage of development. The first aspect is cost. The second is the difficulty to scale up. In addition, health and safety aspects particularly in the case of added nanoparticles need to be estimated, especially for drinking water desalination.

There is currently intense interest in biomimetic membranes based on embedded Aquaporin due to the expectation of superior permeability and almost absolute salt rejection [278–280]. However, the fabrication of Aquaporin membranes with high packing density would be hardly feasible at the large scale, being a complex and expensive technique. Moreover, these bio-materials are relatively unstable and hence the durability of the membranes is questionable at least for mass applications like desalination of seawater for drinking purposes.

2.3.4. Forward osmosis (FO)

There are two evolutionary development routes of FO membranes. The first is to modify available commercial NF or RO membranes and the second involves the development of new membranes with specific design for FO applications. Fabrication of FO membranes from existing NF or RO membranes is considered simple, effective to some extent and cost-efficient. Despite the similarity in performance criteria such as high salt retention and high water flux, the difference between NF/RO and FO membranes is the balanced relation between high-pressure tolerance (or mechanical strength) and low internal concentration polarization (ICP) of the support layer. In FO processes, pressure tolerance is not critical (almost no or low hydraulic pressure is applied) while low ICP is important to maintain high water flux and low salt leakage. To achieve it, therefore, the mechanical strength of the membranes is reduced to some extent to increase porosity and reduce tortuosity. For example, when McCutcheon and Elimelech [281] removed the backing fabric support layer (thickness of 80–120 μm) of the commercial RO membranes (overall thickness of 200 μm) and the FO water flux of the modified membranes was improved by a factor of 5. Another difference between RO and FO membranes is the importance of pore wettability. For the FO process, pore wettability must be improved, because the presence of un-wetted pore regions may block the water flux and significantly exacerbate ICP. Coating with a highly hydrophilic polymer like polydopamine (PDA) has been demonstrated as an effective technique

Table 6
Examples of commercial membranes for FO tests.

Material	Type	Supplier	Water permeability × 10 ⁻¹² (m/s·Pa)	Draw solute	Rejection (%)	Ref.
CA-3000	Flat-sheet	Toray	3.75	NaCl	98	[292]
CA	Flat-sheet	HTI	5.69	(NH ₄) ₂ CO ₃	>95	[291]
CTA	Flat-sheet	HTI	7.10	NaCl	>92	[290]
TFC (NF)	TS80	TriSep	20.0	MgSO ₄	100	[290]
TFC (RO)	DS-11-AG	General Electric	11.91	–	99.5	[289]
TFC (RO)	SW30XLE-400i	Dow	3.80	NaCl	–	[288]
TFC (RO)	SWC1	Hydranautics	5.60	–	100	[290]
TFC (RO)	SW30-HR	Dow	4.39	NaCl	98	[287]

to improve wettability, flux, and fouling resistance [282–286]. The water flux can be increased ten folds after PDA coating. Table 6 provides examples of commercial membranes used for FO tests [287–292]. Despite the improvement after modification, the efficiency of the modified FO membranes is still limited and restricted by the inherent properties of their parent NF/RO membranes. Thus, many membrane scientists turn their research scope to develop new FO membranes.

A desirable FO membrane should have (1) highly hydrophilic, greatly porous but adequately strong support layer to minimize ICP effects, and (2) ultrathin defect-free highly selective layer to achieve high water flux, high salt rejection and minimize reverse solute diffusion [293]. These two layers are either integrated by the same materials (asymmetric membranes) or prepared separately from different materials in a thin-film-composite (TFC) membrane structure. The latter has the advantage over the former in its possibility to optimize support and selective layers separately. The development strategy of FO membranes in terms of materials is similar to that of RO membranes. Rather than membrane materials, the development for FO also focuses on membrane morphologies.

The ideal support morphology for FO membranes is still under debate. Some studies reported that the support with straight finger-like macrovoids is more efficient in mitigating ICP effects due to its low pore tortuosity (leading to low structural parameter) that facilitates the transport of both water and salt [294]. On the other hand, finger-like structures were considered not essential by other authors [257] to achieve low overall structural parameter. For example, Li et al. [295] and Widjojo et al. [296] concluded that even though the support exhibits a sponge-like structure, its structural parameter can also be remarkably reduced due to its high hydrophilic characteristics. In addition, the significantly low structural parameter (80–100 μm) can be obtained by using electro-spun fibers as the support [217,297,298]. Although the water flux of the resultant TFC membrane is high, however, the mechanical stability of the thin selective layer deposited directly on the electro-spun nanofiber support is still questionable.

Besides membrane materials, the exploration of suitable draw solute materials is of great importance in FO process. The key criteria of draw solute selection are (1) high osmotic pressure, (2) low reverse diffusion (leakage through the membrane into the feed), (3) easy and economical regeneration, (4) non-toxicity and (5) reasonable price. In addition, the draw solution should not degrade the membranes or cause membrane scaling/fouling. Numerous draw solutes have been proposed, including inorganic [40,290,292,299,300], thermolytic/volatile [49,291,301–305], organic [173,306–308], magnetic and polymer-based solutes [309–313]. Table 7 [40] summarizes their examples, recovery methods and drawbacks, which implies that there has been no perfect draw solutes so far. Different FO objectives and available solute recovery technologies determine different draw solutions.

Table 7

Draw solutes, their recovery methods and drawbacks.

Group	Example	Recovery method	Drawback
Inorganic	Al_2SO_4	Precipitation by doping $\text{Ca}(\text{OH})_2$	Toxic by-products
	MgCl_2	None	Not pure water
Thermolytic/volatile	SO_2	Heating or air stripping	Energy intensive, toxic
	NH_4HCO_3	Moderate heating	High reverse draw solute flux, insufficient removal of ammonia
	Ethanol	Pervaporation-based separations	High reverse draw solute flux and low water flux
Organic	Glucose–Fructose	None	Not pure water
	Sucrose	NF	Relatively low water flux
	Dendrimers	Adjusting pH or UF	Not feasible
	Albumin	Denatured and solidified by heating	Not feasible
	2-Methyl imidazole based solutes	MD	Materials costly
	Fertilizers	None	Only applicable in agriculture
	Organic salts	RO	Low water flux, energy intensive
Magnetic	Magnetic particles	Captured by a canister separator	Poor performance, agglomeration
Polymer-based	Hydrogels	Deswelling of the polymer	Energy intensive, poor water flux
	Fatty acid–polyethylene glycol	Thermal method	Poor water flux
	Polyelectrolytes	UF	Relatively high viscosity
	Hexavalent phosphazene salts	Not studied	Not economical and practical

Table 8

Several commercial membranes studied for MD.

Polymer	Trade name	Company	Mean pore size (μm)
PTFE	TF200	Gelman	0.2
	FGLP14250	Millipore	0.25
	M05E0020	GVS	0.2
	Desal K150	Millipore	0.1
PVDF	Fluropore	Millipore	0.2
	GVHP	Millipore	0.11
	Microza	Ashi Chem	0.2
	M09G0020	GVS	0.2
	Durapore	Millipore	0.2
	GVHP22	Millipore	0.16
PP	Accurel PP	Microdyne	0.22
	Liqui-cel	Celgard	0.04
	MD020TP2 N	Enka	0.2

Despite extensive investigation of FO in the past decade and significant advancement in its understanding, questions and challenges of its energy sufficiency remains. Several recent FO analyses have disproved the common misguided view that FO is a low energy process and a potential alternative of RO in seawater desalination [314–316]. In fact, FO cannot be a single separation process, where water spontaneously permeates through a semi-permeable membrane (i.e. low energy process), but has to be combined with a subsequent separation of the diluted draw solution to recover water (i.e. require further energy). Based on the thermodynamic theories and practical kinetic analyses, the theoretical minimal energy of this hybrid process is unlikely to compete with that of the standalone RO process [315,316]. However, FO is still potentially promising to desalinate the high salinity feed stream with osmotic pressure exceeding the tolerant pressure of RO (as discussed in Section 2.1.1) or treat the waste stream with high fouling tendency (as discussed in Section 2.2.2) [316]. In the former application, the hybrid FO systems employing thermolytic draw solutions may be favorable because only relatively small amount of the thermolytic draw solute (higher vapor pressure than water) must be vaporized as compared to large volume of water having to be recovered in conventional distillation. In addition, the draw solutes with high vapor pressures require less total energy for recovery. Using low-cost thermal energy sources (e.g. solar energy, geothermal energy and industrial waste heat) for draw solution recovery would reduce the energy cost of the whole FO process. In the second application, FO may be advantageous in the integration with MBR because of its low fouling propensity and high reversibility of fouling. Fouling is undesirable because it reduces process performance and increases operation costs. Development of membrane materials with improved fouling properties continue to be active areas of research, which will be discussed in the Section 2.3.6.

Table 9
Category of fouling.

Category	Definition	Foulants
Colloidal fouling	Fouling occurs due to the accumulation of particles on the membrane surface and inside the membrane pores, forming a cake layer.	Suspended solids and particles such as silicate, ferric oxide, iron oxide and aluminum oxide
Inorganic fouling	Fouling occurs through precipitation deposits resulting in bulk and membrane crystallization.	Inorganic salts such as calcium carbonate, calcium sulfate, calcium phosphate and sodium chloride
Organic fouling	Fouling occurs due to adsorption of natural organic compounds on membrane, causing gel formation.	Natural organic matters such as fulvic acid, protein, polysaccharides, and polyacrylic polymer
Biofouling	Fouling occurs when biofilm forms on the membrane.	Aquatic organisms, such as fungi, algae, yeast and bacteria

2.3.5. Membrane distillation (MD)

In general, a MD membrane should (1) exhibit high hydrophobicity to prevent pore wettability on the feed side (membrane liquid entry pressure of water ranges from 48 to 368 kPa for common commercial flat-sheet MD membranes [317]); (2) be thin to achieve high permeation flux (the optimum thickness lies between 30–60 μm [318], but when composite hydrophobic/hydrophilic membranes are used, the hydrophobic layer can be as thin as 5 μm [319]); (3) have reasonably small pore size (in the range of 0.1 to 0.6 μm [320]) to prevent liquid intrusion but not too small to contribute for mass transfer resistance; (4) have high porosity 60–80% [321]) and low tortuosity (a value of 2 has been commonly assumed [322] but 3.9 was also reported [323]) to favor the water vapor transport; (5) have high heat transfer resistance (the thermal conductivity ranges from 0.11 to 0.27 $\text{Wm}^{-1} \text{K}^{-1}$ at 23 °C for three common MD polymers PVDF, PTFE and PP [324]) but low mass transfer resistance (the reported membrane coefficient ranges 3 – 15 $\times 10^{-7} \text{kg/m}^2\text{pa}\cdot\text{s}$ for commercial MD membranes in the direct contact operation mode [36]); (6) have adequate chemical and thermal resistances, strong mechanical properties and long-term stability; and (7) be cheaply available. Early development stages of MD membranes focused on hydrophobic commercial polymers such as PVDF, PTFE and PP, analogously to those used for micro- and ultrafiltration. Some commercial membranes used for MD are listed in Table 8 [325]. The main advantage of these materials is their commercial availability. However, they cannot meet all above requirements of an excellent MD membrane. Hence, research on designing and synthesizing new membrane materials for MD processes is essential to attain a fully commercial status of MD.

Novel MD hydrophobic membranes can be fabricated either by newly synthesized hydrophobic polymers or by surface modification of hydrophilic membranes. An example of the former is synthesis of copolymers between PVDF with hexafluoropropylene (HFP) or tetrafluoroethylene (TFE) [326–330]. Although MD membranes prepared from these materials had lower flux than PVDF membranes due to lower porosity, they exhibited excellent mechanical properties with 100% salt rejection. On the other hand, various surface modifications have been investigated for MD, such as surface segregation [319,331],

impregnation and cross-linking [331], co-extrusion [332], coating [333], grafting [334], and plasma polymerization [335].

A promising MD membrane fabrication is the composite hydrophobic/hydrophilic membranes in the multilayered structure [37,319,335–340]. The advantage of such structure is that high mass transport can be achieved by tailoring the thickness of the hydrophobic layer as thin as possible while low heat transfer and adequate mechanical properties can still be maintained by controlling the thickness of the hydrophilic layer. Other attempts on MD membrane development are use of nanofiber membranes prepared by the electrospinning method to achieve high and controlled void volume [341]; incorporation of carbon nanotubes [342–346] to increase vapor permeation and prevent pore wettability; and adding clay particles to enhance the mechanical strength and long-term stability of the membrane [347]. Finally the synthesis of new hydrophobic polymers and their manufacture into flat-sheet and hollow fiber membranes for MD has been successfully demonstrated [348,349].

2.3.6. Challenges in membrane materials to prevent fouling

Membrane fouling is an important and inevitable challenge in all membrane processes. Lower membrane fouling allows higher water productivity, less cleaning and longer membrane life, and reduced capital and operational costs. Membrane fouling can be categorized by the type of foulant: inorganic (scaling), organic and biofouling. Table 9 provides their definition and common foulants [350,351], being more severe in pressure-driven membrane processes such as RO and NF where high hydraulic pressures are employed.

Classical solutions to membrane fouling are the use of pretreatment technologies, operation optimization and periodic membrane cleaning. Table 10 presents their effects, affecting parameters and challenges [350]. On the other hand, membrane modification is potentially the most sustainable solution to prevent fouling. The characteristics and properties of membranes that affect fouling formation are their chemical structure (functional groups, charge and hydrophilicity) and morphology (pore size, surface roughness or surface pattern). Generally, high hydrophilicity, negative surface charge and low surface roughness are desirable for low fouling propensity.

Table 10
Classical solutions to membrane fouling.

Solution	Methods	Effects	Affecting factors	Challenges
Pre-treatment	Coagulation, precipitation, media filtration, sonication, boiling, membrane filtration, pH changes and chlorination	Alter the physicochemical and/or biological properties of the feed water, and reduce the foulant concentration	Agent, temperature, dosing point, solution and foulant properties, and the characteristics of the membrane	Ineffective pretreatment can lead to high rates of membrane fouling
Operation optimization	Gas bubbling	Increase shear rate at the surface to intermittently remove fouling layers	Size of bubbles, gas flow rate	Mainly effective in addressing external membrane fouling
	Temperature and flow reversal	Inhibit the homogeneous precipitation of salts and disrupt the nucleation of salt crystals	Temperature, flow rate	No in-depth explanation on the nucleation kinetics and scale formation
Chemical cleaning	Rinse with acid or base	Rinsing with acid is particularly effective in removing inorganic scaling while rinsing with base is relatively effective in reducing organic fouling	Type, amount of agents	May cause membrane structural damage

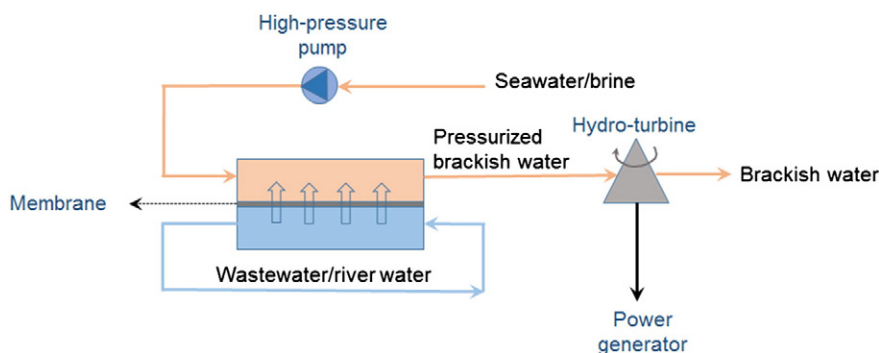


Fig. 5. Idealized continuous PRO system.

To achieve above properties, many membrane modifications have been extensively studied such as surface coating [352–354], surface grafting [355–359], incorporation of hydrophilic monomers/inorganic particles [360–364] and zwitterionic modification [365]. Although membrane modifications can effectively enhance anti-fouling capacity, they often affect flux. In addition, many of them are costly, complicated or only at the laboratory scale. Furthermore most approaches successfully delay the early stages of fouling, but are not able to hinder it in long term. Therefore there is still a need for new membrane materials able to overcome the trade-off between anti-fouling capacity and permeability, as well as advanced methods of membrane modification, which are cost-effective and simple.

3. Membrane technology in energy sustainability

Renewable energy sources are increasingly becoming a greater part of the global energy picture, particularly for power generation. They contributed approximately 58.5% of additions to the world's power generation capacity in 2014 with significant growth in all regions [366]. Membrane technology has a great potential to take advantages of renewables to produce energy. This review covers several examples including conversion of seawater or wastewater into electricity (pressure-retarded osmosis and reverse electrodialysis), energy storage for renewable energy sources such as solar, wind or biofuels (fuel cells and batteries) or direct participation into energy production processes (biofuels). Other applications in natural gas separations, solvent recovery, various refinery and power plant processes (e.g. CO₂ capture) are beyond the scope of this review.

3.1. Salinity-gradient energy

Salinity gradient energy is the power generated by the difference in osmotic pressure between aqueous solutions of different salinities, e.g. fresh and salt water. The chemical potential difference in this case can be equivalent to the power of a 270-m high waterfall to be converted into electrical energy [367–369]. The concept of harvesting such energy was first proposed by Pattle [368], and then reconsidered in 1970s by Loeb [370,371], when the global energy crisis urged the need of exploring new alternative energy sources. Salinity gradient energy is estimated to be the second largest marine energy source with total estimated global power potential of 1650 TWh/y [372,373], equivalent to about half the annual hydropower of 3551 TWh/y [374]. This energy is considered clear and sustainable, with no production of CO₂ or other emissions and no interference with the global climate. Its high potential is supported by the inherent abundance of river and seawater. The two promising technologies of capturing salinity gradient energy are pressure-retarded osmosis (PRO) and reverse electrodialysis (RED). Both of them are membrane-based technologies and they are used in different salinity conditions. PRO is more efficient if using concentrated brines, whereas RED is more favorable with seawater [375].

3.1.1. Pressured-retarded osmosis (PRO)

3.1.1.1. Fundamentals of PRO. The principle of PRO was first reported by Loeb in 1976 [371,376]. However, its research slowed down in the 80s and 90s due to the lack of membranes with the required performance and acceptable cost. Its investigation was resumed in the late 2000s by Skilhagen et al. [377], Gerstandt et al. [378] and Thorsen and Holt [373], bringing the membrane development forward enough to allow the implementation of the technology. With further optimization, Statkraft (Norway) opened the first PRO power plant prototype in 2009 to prove its concept in generating electricity. Fig. 5 depicts an idealized arrangement of a PRO plant. On one side of the membrane seawater or brine is pumped keeping a constant hydraulic pressure. Concurrently, the compartment on the other side of the membrane is fed by fresh or waste water. Water permeates through the membrane from the fresh water to the seawater side, moving a turbine to generate electricity [370,379].

3.1.1.2. PRO membrane development and challenges. A membrane is the important component of a PRO set-up, separating the solutions with different salinity and maintaining the chemical potential difference, which will lead to the electricity generation. The membrane performance in PRO is characterized by the membrane power density, i.e. the power output per area unit, which it would be able to provide. This power density is critical because it directly affects the cost of the generated power. The starting membranes for PRO were practically those used for RO [380–384]. However it has been recognized that concentration polarization [302,304,385] greatly impacts osmotically driven processes. The requirements for PRO membranes are quite different from those for RO. The thick, dense and highly resistant support layer of RO membranes, which is essential to tolerate high pressures, causes severe concentration polarization in PRO [39,292]. Therefore membranes developed exclusively for FO or PRO have a thinner and less dense support layer [385–388].

To achieve high membrane power density, the PRO membrane should have high water flux and pressure tolerance, corresponding to an optimum combination of the membrane properties: A (water permeability), B (salt permeability) and S (structural factor). Most PRO studies have not focused on exploration of new materials but on the discovery of suitable membrane morphology with large A and low B for the active layer and low S for the support.

3.1.1.3. Economical analyses. At the present, it is difficult to obtain a cost estimation for osmotic power due to the lack of their large scale plants to validate current cost assumption. The world's only pilot-scale plant was commissioned by Statkraft in Norway under "The Osmotic Power Project" funded by the European Union [389]. It was reported by Statkraft to have a membrane with the output density of 1 W/m², which is below the target of 5 W/m². This value is estimated a minimum

power density for a PRO business viability [378]. The project was then discontinued in 2014 due to the commercial absence of high-performance and cheap PRO membranes.

Among PRO cost components, according to Loeb's report [390], capital cost contributes a large fraction of more than 60% while operation and maintenance costs would be a small fraction. If the membrane power density is low, a high capital cost is expected because it would require not only a large membrane area to overcome the low power density, but also high membrane installation cost for the large membrane area. A current study reported the range of installed membrane cost for desalination plant from US\$20 to US\$40/m² [391]. If the lowest value is assumed, the capital cost of the 20-MW capacity power plant with the power density of 1 W/m² is estimated US\$20,000/kW [392], which is still above those associated with wind power (US\$1700–US\$2450/kW) [393] and solar (US\$6800–US\$7700/kW) [394]. To compete with solar power, a minimum power density of 5 W/m² and a maximum installed membrane cost of US\$35/m² would be required [392]. Other than wind and solar, the osmotic power seems to be cost-similar or cost-competitive with other ocean energy sources and bio-power sources [392]. However, these cost analyses did not consider the costs related to the intake and outfall systems and pretreatment of feeding streams which depend on plant location and water sources. With inclusion of these cost components, Kleiterp [395] predicted higher capital costs of US\$32,000/kW and US\$29,200/kW for a 25 MW and 200 MW PRO plants, respectively; with an assumed power density of 2.4 W/m². The responsive unit energy costs were estimated \$1.21 kWh⁻¹ and \$1.0 kWh⁻¹ for a 25 MW and 200 MW PRO plants, respectively. These unit costs could potentially reduce to \$0.12 kWh⁻¹ and \$0.07 kWh⁻¹ for a 25 MW and 200 MW PRO plants, respectively if developments in membrane technology achieve increased membrane power density, reduced membrane price and other capital costs. Similarly, Skilhagen [396] predicted the unit energy cost of US\$0.16 kWh⁻¹ for a demonstrated 25 MW osmotic power plant when cost reductions are gained from technology advancement and economical scale-up. This value is higher than the reported value of wind power (US\$0.07 to US\$0.14 kWh⁻¹) [393] but comparable or more economical than that of solar power (US\$0.11 to US\$0.86 kWh⁻¹) [394,397,398].

In summary, membrane elements are the main fraction of the capital cost of an osmotic power plant. Commercially available membranes with high power density and low susceptibility to fouling are required to reduce the capital, operation and maintenance costs. With the expectation that the PRO membranes would be commercialized and their price abruptly reduced in the similar trend observed for RO membranes in last decades, the unit energy cost of PRO could be in the range of US\$0.065–US\$0.13 kWh⁻¹ by 2030 [399]. PRO is a renewable energy source with high environmental advantages. If it receives government subsidy or incentives the cost could drop to US\$0.05–US\$0.06 kWh⁻¹ [400], which is potentially more cost-effective than wind and solar power in the future. Cost is however only one of the aspects to be considered for PRO implementation. This technology depends much more on geographical requirements than most other water-based processes. Special salinity conditions need to be available as prerequisite.

3.1.2. Reverse electrodialysis (RED)

3.1.2.1. Fundamentals of RED. The principle of RED was first applied in the early of 1950s by Pattle [368] and further developed during the late 1970s. RED operates with the reverse principle of electrodialysis (ED), using the similar stack design and membrane. In contrast to ED where a voltage is applied to induce ion flow, in RED electrochemical potential gradient is produced from the concentration difference between the feed streams. A full-scale RED system comprises multiple cell pairs, each of which is composed of dilute (e.g. river water) and concentrated (e.g. seawater) feed channels, and anion/cation exchange membranes disposed alternatively. This membrane stack has electrodes at its two

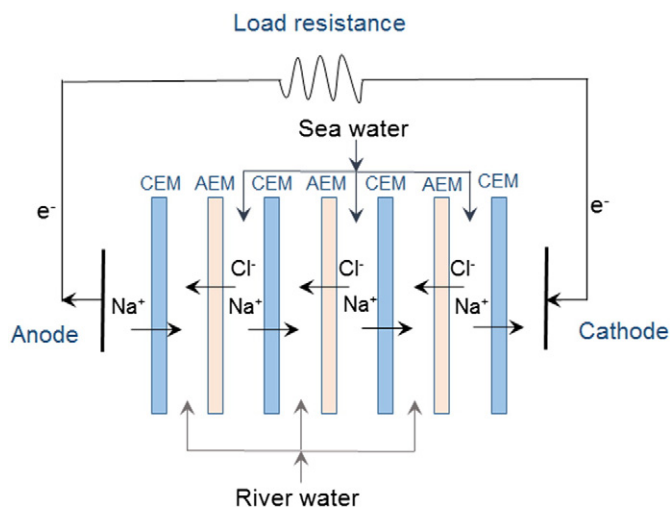


Fig. 6. Schematic drawing of a RED cell.

ends to convert the ionic flow into an electric current through oxidation-reduction reactions (Fig. 6).

Unlike PRO processes that use pressurized water to spin the turbine for electricity production, the RED process can convert ionic flow directly into electricity. The produced power is determined by the electro-chemical potential drop across the membrane and the external load resistance. The potential across the membrane depends on the concentration difference and membrane perm-selectivity.

3.1.2.2. RED membrane development and challenges. Daniilidis et al. [401] emphasized the importance of affordable membrane cost and power performance to the success in RED commercialization. Ion exchange membranes (IEMs) are essential for RED and are currently 2–3 times more expensive than RO membranes [47,369]. Most commercial IEMs are not specifically designed for RED, but for other applications such as ED, diffusion dialysis, electro-deionization and fuel cells [402]. Table 11 presents commercially available IEMs studied for RED [367]. In these studies, rather than the development of membranes, the efforts have been made on system design and operation such as stack, cell configuration, spacers and electrodes. Although some commercial IEMs exhibit properties desirable for RED (e.g. high permeability), they may not meet other RED requirements (e.g. physical and electro-chemical properties). In addition, the high prices of these membranes also disfavor the implementation of power generation by RED.

IEM membranes are known for high thermal, chemical and mechanical stability. However, these properties are not crucial for RED membranes [392,403–405]. Lower stability than that required for fuel cells could be acceptable, especially if it results in lower membrane cost. On the other hand, more critical for RED are the membrane swelling degree,

Table 11
Several commercial IEMs studied for RED.

IEM	Power density (W/m ²)
<i>Anion exchange membrane</i>	
Neosepta AFN	1.23–1.30
Selemon APS	1.23–1.30
Fumasep FAD	1.16–1.24
Neosepta AMX	1.02–1.22
Ralex AMH-PES	0.73–1.12
<i>Cation exchange membrane</i>	
Neosepta CM-1	1.12–1.30
Fumasep FKD	0.99–1.19
Neosepta CMX	1.02–1.30
Ralex CMH-PES	0.73–1.23

ion exchange capacity (IEC) and fixed charge density (FCD), i.e. the ratio of IEC and water uptake. Different from other applications, where swelling is an adverse effect because it might decrease the membrane permselectivity, it can be advantageous for RED to reduce the membrane resistance [406–408]. Good RED membranes should have the ideal balance between high permselectivity and low membrane resistance to optimize its power generation [407].

Easy functionalization is expected to increase IEC and hence permselectivity, whereas easy processability enables possibility of fabricating low-resistant (thin) membranes with adequate mechanical strength. The most considered polymers for RED membranes are polyvinyl alcohol (PVA) [409–416], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [411,416–419] and polyvinylchloride (PVC) [401,420–424]. These materials have advantages of good chemical resistance, good membrane processability and low cost, but the absence of charged groups in their pure chemical structure leads to poor conductivity. Thus, modification of these polymers or membranes is required to produce charged groups. Options include introducing negatively charged sulfonic groups by crosslinking with sulfosuccinic acid (SSA) or functionalizing with sulfonic acid [414,416,417], blending with quaternized cationic polymers [413,422] and incorporating with inorganic particles [409–412,420,423]. Many efforts have also focused on synthesizing new membrane materials for RED membrane. For example, Guler et al. [405] synthesized anion exchange membranes (AEMs) from polyepichlorohydrin (PECH) and 1,4-diazabicyclo-2,2,2-octane (DABCO). The resultant membranes have high IEC, but blending with polyacrylonitrile (PAN) is required to increase mechanical strength. Guler's group [425] also synthesized negatively charged coating layers of 2-acryloylamido-2-methylpropanesulfonic acid (AMPS) and N,N-methylenebis(acrylamide). Although many studies have reported good power density of RED membranes, none of them have been commercialized. Fouling propensity is also critical when using seawater and rivers as feed solutions. However, very few fouling studies have been conducted so far for RED membranes. Thus, optimization of well-balanced permselectivity and membrane resistance and low fouling propensity should be the heart of membrane material development and modification for RED application.

3.1.2.3. Economical analyses. Similar to PRO, the economic analyses of RED are only at the modeling stage because there are no RED plants so far. Membranes are also the major components of the capital, which contributes to about 80% [426] because they are the heart of a RED stack. Membrane related cost parameters such as power density, membrane price, membrane lifetime and its annual loss of power density remain the decisive factors for the unit energy cost while labor and construction costs have small effects [401]. Currently, the maximal power density reported in the literature is about 2.2 W/m² at 35% of energy efficiency when using seawater (~0.5 M NaCl) and river water (~0.01 M NaCl) [427]. A higher power density of 4 W/m² can be obtained if the intermembrane distance is reduced and flow rates increase [427]. Including the power required for pumps, a gross power density of 2.7 W/m² can be theoretically achieved in the near future [401]. The current high membrane prices (~US\$55/m²) for comparably performing

membranes and cheap heterogeneous membranes (<US\$4.4/m²) not associated with a high power density suggest that all of RED applications are not economically viable at the current. However, future membrane advancement in this technology is expected to develop more affordable ion-exchange membranes (<US\$4.4/m²) with the current performance (a power density of 2.7 W/m²). If such condition can be achieved, the levelized cost of energy can be reduced to US\$ 0.17/kWh⁻¹ [401] making RED competitive with conventional and established renewable energy sources. In 2014, a RED pilot plant with a capacity of 50 kW was installed in The Netherlands [428]. Its performance report is expected to offer more relevant data for cost analyses and further development of RED technology.

3.2. Batteries and fuel cells

With unprecedented evolution of clean technologies for electricity generation, energy storage devices are expected to play an important role in electricity networks. Among many energy storage devices, batteries and fuel cells have received great attention because of their high energy density [429]. A common feature is their use of a chemical reaction to produce electricity. Batteries store chemical energy internally. Thus, when this energy is exhausted, the batteries must be recharged. Fuel cells generate electricity through reactants stored externally and hence will live as long as fuel is supplied. Polymer electrolyte membrane fuel cells (PEMFCs) are under consideration for transportation and automotive applications because of their rapid start-up and shutdown, capability of operating even when they have not reached their operating temperature, no thermal shock and no high temperature corrosion [430]. The strongest competitors of fuel cells for transportation are currently batteries. Lithium ion batteries (LIBs) have been widely used also in portable electronic devices such as mobile phones, laptops, and medical microelectronic devices with advantages of long cycle life and low self-discharging [431]. Membranes are critical components both in LIBs and PEMFCs and their performance essentially depends on their chemical composition and morphology. Their primary role is to physically separate the anode and cathode, preventing electrical shorting, while serving as electrolyte reservoir for ionic transport.

3.2.1. Lithium ion batteries (LIBs)

3.2.1.1. Current status. Lithium ion batteries were first introduced in 1991 [432] and since then they have grown into a US\$ 4.64 billion market in 2013 [433] charging portable electric devices such as laptops, cell phones and digital cameras [432]. More recently, their application has been extended to power tools, electric bicycles and hybrid electric vehicles (HEVs) [432,434]. Moreover, LIBs are considered as energy storage for renewable energy sources such as solar or wind. Global sales of such energy storage systems are expected to be approximate US\$ 2 billion in 2015 and to increase to US\$ 6 billion by 2020 [435]. Along with the growth of LIB market, that of their membrane separator is expected to increase. Its market is estimated to exceed US\$ 3 billion by 2020 and its production is estimated to be >1000 billion m² in 2013 [435]. Japan-based Asahi Kasei, USA-based Celgard, South Korea-based SKI and Japan-based Toray Tonen have occupied major market share of battery separators (Table 12).

3.2.1.2. Membrane separator: properties and materials. A typical LIB comprises an anode, a cathode and electrolyte (Fig. 7). During discharging, lithium ions move from the anode to the cathode across the electrolyte to produce the current. During charging period, an external electrical power is applied to drive the current in the reverse direction and make lithium ions re-migrate on the anode. The separator is a must to separate two electrodes to prevent short circuit.

A LIB separator should have (1) chemical and electrochemical stability to prevent degradation and/or loss of mechanical strength during cell reaction or dissolution of electrolyte [436,437], (2) quick wettability for

Table 12
Battery separator market share.

Separator manufacturers	Market share*	Brand name
Asahi	26%	Hipore™
Toray	23%	Setela™
Celgard	19%	Celgard®
SKI	13%	–
UBE	7%	Upore®
Entek	3%	Entek
Sumitomo	1%	Pervio™
Others	8%	–

* Data in 2012.

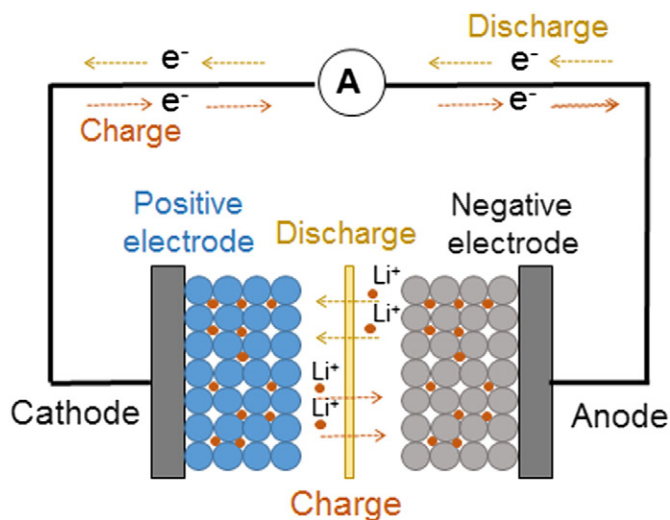


Fig. 7. Schematic drawing of a typical lithium-ion battery.

absorption and retention of the electrolyte to smoothen the lithium ion transport and to facilitate the process of electrolyte filling during the battery assembly [431,436–438], (3) strong mechanical strength to withstand the stress of physical forces or the tension of the winding process during battery assembly [431], (4) strong puncture strength to withstand the penetration of electrolyte [431,437,439], (5) proper thickness to offers both low internal resistance and safety [431,436–438], (6) uniformity of the thickness for stable and long cycle life of the batteries [431], (7) small pore size to restrict the permeation of electrode material particles and dendritic lithium metal [431,437], (8) uniform pore size distribution to avoid performance loss resulted from uneven current distribution [431], (9) appropriate porosity to keep adequate liquid electrolyte inside for sufficient ionic conductivity, low internal resistance, high safety and good shutdown capability [431,437,439], (10) high porosity and low tortuosity [431], (11) high dimensional stability to keep the separators flat and not curled up when immersed into the electrolyte and not shrunk during storage and operation [437], (12) good thermal stability to keep the battery safe during the drying process of battery assembly [431] and (13) shutdown capability when overheating or short circuit occurs [436,437]. Table 13 provides target number for certain properties of LIB membrane separators.

Based on the characteristic requirements of membrane separators, the most commonly used materials for membrane separators are PE and PP or their blends with other polymers such as polystyrene (PS) and poly(ethylene terephthalate) (PET) [431,440–447]. However, their poor thermal stability, low wettability and poor electrolyte retention limit the battery performance. Thus, other polymers such as PVDF [448–455], PAN [456–460], poly(methyl methacrylate) (PMMA) [456, 461–463] have also been used for preparing microporous membranes. Microporous PDVF membranes have good physicochemical and electrochemical stability, high mechanical strength and great wettability. A disadvantage is the potential formation of LiF during operation through reaction between lithium ions and the fluorine atoms in PDVF [452]. Microporous PAN membranes are an alternative, exhibiting good processability, high electrolyte uptake, high thermal and electrochemical

stability with the transport of lithium ions being facilitated by interaction with the C≡N groups. However, PAN membranes face the problem of electrolyte leakage during long-term storage [464]. Like PDVF and PAN, PMMA is also used for fabricating microporous membrane separators because of its high affinity towards electrolytes. PMMA membranes display high conductivity, good thermal and electrochemical stability. However, they have poor mechanical strength due to their amorphous structure [465]. Other problems linked to PDVF and PAN are their high crystallinity, which is one of major obstacle for high ionic conductivity [437,459,461,466,467]. To overcome this problem, many of their copolymers [467–472] and blend polymers [473–487] have been developed for LIB membrane separators.

Optimal mechanical strength, thermal resistance, shutdown capability and electrochemical performance are requirements for a good battery membrane, but this is hard to achieve by using a monolayer. To tackle this issue, multilayer membranes have been proposed [488–495]. Typical examples are multilayer membranes of PE and PP [494,495]. They combine the advantages of PE melting at high temperatures to block the pathway of ions, hence providing safety assurance, and the benefit of strong mechanical properties and dimensional stability of PP for the overall structure. Many patents for bi-layer or tri-layer membranes of PE and PP have been filed [494,495]. Several multilayer membrane separators, such as Celgard® tri-layer separators, have been successfully used in commercial LIBs [431]. However, attempts are still essential to improve them in terms of thickness, wettability and ionic conductivity. Important approaches to simultaneously enhance multi-properties of membrane separators such as physical and chemical properties, thermal stability, wettability and ionic conductivity are grafting [496–499], coating [496,500–506] and filling with nanoparticles [507–523].

All microporous membranes discussed above need to be filled with electrolyte to transport lithium ions. Electrolyte membranes, on the other hand, have inherent ion conductivity property and hence can acts as both separator and electrolyte. In the aspect of materials, these electrolyte membranes are made of similar polymer materials with non-electrolyte membranes, but they are incorporated with ionically conductive components, e.g. lithium salts to form solid polymer electrolytes [524–527] or liquid lithium-based electrolyte such as lithium hexafluorophosphate and lithium polyvinyl alcohol oxalate borate to form gel polymer electrolytes [528–536]. Recently, ion exchange membranes with lithiated perfluorinated sulfonic groups, swollen with organic solvents, have been investigated [537–539], demonstrating high thermal and mechanical stability and good interfacial compatibility with the electrodes. High safety standards have been achieved. In most cases ionic conductivity and mechanical properties still have to be improved.

3.2.2. Polymer electrolyte membrane fuel cells (PEMFCs)

3.2.2.1. Applications and current status. PEMFCs have been applied in three main areas of transportation, portable and stationary power generation. PEMFCs are used in transportation to replace internal-combustion engines (ICEs) because of their potentials of obtaining higher efficiency and lower emission of greenhouse gases [540]. The typical power of transportation including passenger cars, utility vehicles and buses ranges from 20 kW to 250 kW [541]. Many light-weight vehicles using PEMFCs have been developed and demonstrated, such as GM Hydrogen 1, Ford Demo IIa (Focus), DaimlerChrysler NeCar4a, Honda FCX-V3, Toyota FCHV, Nissan XTERRA FCV, VW Bora HyMotion, and Hyundai Santa Fe FCV [540]. Car manufacturers such as Toyota, Honda, Hyundai, Daimler, and General Motors (GM) have announced plans of commercializing their PEMFC vehicles by 2015 [542]. Besides light-weight vehicles, PEMFC buses have been commercialized and their procurement plans have been announced under government funding such as US National Fuel Cell Bus Program and Europe's Fuel Cell and Hydrogen Joint Technology Initiative [543].

Table 13
Target properties of a LIB membrane separator [431].

Characteristic	Target number
Mechanical strength	<2% offset at 6.9 MPa
Puncture strength	>300 g/25.4 μm
Thickness	20–25 μm
Pore size	<1 μm
Porosity	40–60%
Thermal stability	>90 °C

PEMFC's advantages for portable electronic devices are their high energy power capability and short charging time. The global production of portable PEMFC devices grew from approximately 2000 units in 2005 to about 10,000 units in 2009 [544]. The typical power of portable electronic devices ranges from 5 to 50 W, but the power of <5 W for micro power application or 100–500 W has also been considered [541,545]. Besides mobile phones and laptops, portable PEMFCs can also be used for electric toys and utilities such as radio-control cars, boats, robot and emergency lights. Several portal PEMFC companies are CMR, Viaspace, Jadoo, Horizon MTI micro, Neah, Samsung DSI, SFC, Sony and Toshiba [544].

Stationary PEMFC power systems can be used for residential applications, where the waste heat of fuel cells can be used for household usage [546]. Further significant enhancement in fuel cell cost and lifetime is required for this application. However, the cost is already justifiable for applications such as back-up power for banks and telecommunication companies, since an eventual power breakdown [540] would have extremely expensive consequences. Several units like Plug Power GenSys® and Ballard FCgen™ 1020 ACS PEMFC systems have been developed in many locations. Several companies working on the stationary PEMFC application are Alteryg, ClearEdge, Ebara Ballard, Eneos Celltech, Hydrogenics, IdaTech, Matsushita, P21, Plug Power and Toshiba FCP [547].

3.2.2.2. Polymer electrolyte membranes (PEMs). Current research of PEMs has focused on two types of PEMFCs, which are hydrogen/air (H_2/O_2) fuel cells and direct methanol fuel cells (DMFCs). Fig. 8 depicts the schematic drawing of a typical PEM H_2/O_2 fuel cell. The latter is more applicable for portable power applications because its fuel (methanol) is more easily portable. Properties of PEMs determine the efficiency of PEMFCs. Desirable PEMs should have (1) high proton conductivity, (2) low electronic conductivity, (3) low fuel and oxidant permeability (4) adequate electrochemical and chemical stability, (5) high thermal and hydrolytic stability, (6) good dimensional and morphological stability, (7) adequate water transport, (8) high mechanical properties, (9) long lifetime and (10) low cost. Table 14 provides target numbers of certain properties for PEMs. Generally, based on the respective materials, PEMs can be categorized as perfluorinated polymer-based membranes and non-perfluorinated polymer-based membranes. Nafion® membranes (perfluorinated polymer) for DMFCs typically have a price in the range of US\$600–1200/m² depending on the thickness, while the sulfonated poly(ether ether ketone) membranes (sPEEK) have a lower price of US\$375/m² [548].

The perfluorinated polymer Nafion® is currently the benchmark of PEMs in fuel cell industry. This material has high proton conductivity

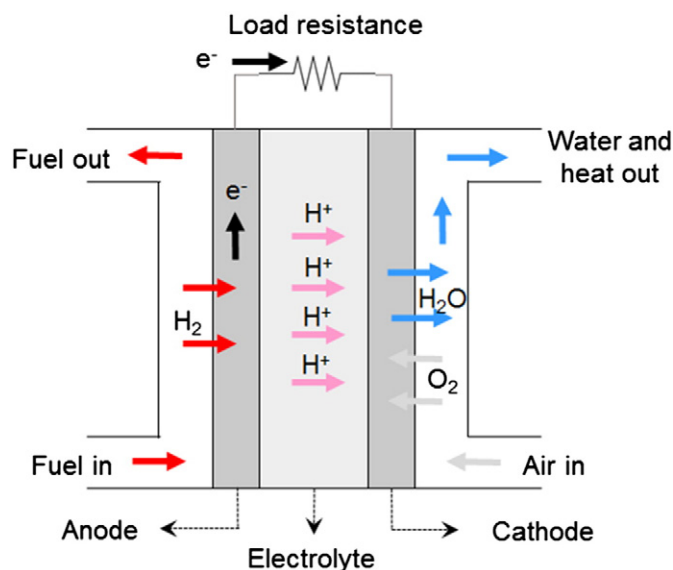


Fig. 8. Schematic drawing of a PEM fuel cell.

Table 14
Target properties of PEMs.

Characteristic	Target numbers
Proton conductivity	>80 mS/cm [570]
Electronic conductivity	negligible or zero [571]
Fuel and oxidant permeability	<10 ⁻⁶ mol min ⁻¹ cm ⁻¹ for methanol [570] <2 mA cm ⁻² for hydrogen/oxygen crossover at 1 atm [572] at >80 °C [573]
Electrochemical and chemical stability	
Long lifetime	>5000 h for transport use [574] >40,000 h for stationary use [574]
Cost	<US\$10/kW [575]

(50–200 mS/cm), moderate water uptake (30–55%), excellent chemical resistance at moderate conditions, and high operation temperature range up to 190 °C [549,550]. However, Nafion still has several serious drawbacks such as (1) polymer chain decomposition by alien cations [551,552], (2) declined conductivity and water uptake if the cell is contaminated with multi-charged ions [553–555], (3) poor chemical and mechanical stabilities at high temperatures [556–559], (4) severe degradation in multiple thermal and hydration/dehydration cycles [560–562], (5) insufficient resistance to methanol permeation when applied for direct alcohol fuel cells [563,564] and (6) high cost due to its complex processability.

To explore cheaper alternatives to Nafion®, many non-perfluorinated polymers have been studied, including polystyrene, sulfonated polyimide, sulfonated aromatic main-chain polymers (e.g. polyphosphazene, poly(arylene ether), polysulfone, poly(sulfone ether), polyphenylsulfone) and natural polymers (e.g. pectin, chitin phosphate, gelatin, agar, alginate acid and uracil) [565–569]. However the requirements of high oxidation stability and high proton conductivity can be hardly achieved at low cost to compete with Nafion® in hydrogen fuel cells at least in temperatures up to 80 °C.

Operation at temperatures higher than 100 °C would be more attractive for different reasons. It provides less catalyst poisoning with CO (impurity in H_2 fuel), faster electrode kinetics and hence higher cell efficiency, and simplified water management due to the absence of biphasic water (vapor and liquid) [572]. Operation above 100 °C is however challenging for Nafion® due to natural dehydration and loss of conductivity. The search for better polymeric materials able to keep high proton conductivity at high temperature and low humidity levels has motivated intense activities in the field. Polybenzimidazole (PBI) is the most investigated polymer for this purpose. Other functionalized polyazoles have been synthesized and investigated in the laboratory [565,566,568,569]. The inspiration of using PBI as PEMs originates from the design of phosphoric acid (H_3PO_4) fuel cells (PAFCs), where phosphoric acid is employed as an ion conductor. In PAFCs, thin silicon carbide ceramic is used as the matrix to carry H_3PO_4 [576,577]. Later on, the polymers with ability of chemical interactions with H_3PO_4 to form acid-base poly salt systems are considered as a new class of proton conducting PEMs. Among many polymers tested for such ability [578–582], PBI is the most promising candidate because of its high mechanical and thermal stabilities [579,583,584]. Several PBI/ H_3PO_4 membranes are commercialized by BASF such as CeltecL, CeltecP, and CeltecV [585]. BASF also reported their long-time stability such as more than 20,000 h for CeltecP1100 and 6000 h for CeltecP2100 for H_2/O_2 fuel cells at 160 °C [586]. However, these data are still lower than the lifetime requirement for commercially viable stationary fuel cells, which should be higher than 40,000 h [572].

3.3. Biofuel production and purification

The use of liquid (mainly bioalcohols and biodiesel) or gaseous (i.e. biogas) fuels produced from biomass for transportation is already an established technology, at least in countries like Brazil and Sweden.

Biofuels have advantages over fossil fuels such as (1) easy availability from common biomass sources, (2) lower carbon dioxide emission, when considering the whole life cycle (3) environmental friendliness, and (4) biodegradability and sustainability [587]. The basic problems of biofuel are large areas needed for feedstock cultivation and competition with food production.

3.3.1. Current status

Although biofuels are growing fast and acquiring global production significance, statistics for 2008 reported that they represented only about 1.5% of the global transport fuel consumption [588]. USA and Brazil are two large bioethanol producers and account for 80% of its global supply with the capacities up to more than 500 million liters per year (2007) [588]. The global bioethanol market is predicted to attain approximately 20% increment from 2015 to 2020 [589]. Bioethanol is the most common alcohol used for internal combustion engines because of its technical and economical suitability [590]. In Brazil bioethanol is used pure (100%) or blended with gasoline in different ratios with comparable performance in cars equipped with “flex” motors [591].

Different from bioethanol, the large biodiesel producers are from Europe, which accounts for 87% of the global supply [588]. Among them, Germany and France are the largest producers. However, the total global production of biodiesel is small compared to that of ethanol, approximately 4.1 Mtoe in 2006. The global biodiesel market is predicted to increase about 35% from 2015 to 2020. Biodiesel can be used as a diesel substitute in the blend with conventional diesel (up to 5%). Higher biodiesel fuel blends are used for fleet vehicles (e.g. trucks and buses).

The global biogas production shows an exceptionally rapid increase from 292 PJ in 2000 to 1.1 EJ in 2011 [592]. In 2011, 90% of global biogas production and consumption is attributed to European Union, China and USA. Two-thirds, one quarter and approximately one-tenth of biogas production in Europe are originated from agricultural factories, waste disposal sites and sewage treatment plants, respectively. Biogas typically comprises approximately 60% methane, 40% carbon dioxide and some trace gases. It can be used for diverse end-use applications such as heating or combined heat and power (CHP) generation. If biogas is purified and upgraded to biomethane, it can be used as natural gas or transportation fuel. Bauer et al. [593] reported that by the end of 2012, there are 221 biogas upgrading plants in the world.

3.3.2. Membrane technology in biofuel production and purification

3.3.2.1. Biodiesel. Biodiesel, which is known as fatty acid methyl ester (FAME), is produced from transesterification of renewable lipid (vegetable oil or animal fat) by methanol. In this process, the membrane plays an important role to remove the byproduct glycerol from the product stream (biodiesel) [594] or to retain the unreacted lipid within the membrane [595]. There are two basic separation principles of membrane-based biodiesel production, based on oil droplet size (or membrane pore size) or perm-selectivity of the membrane.

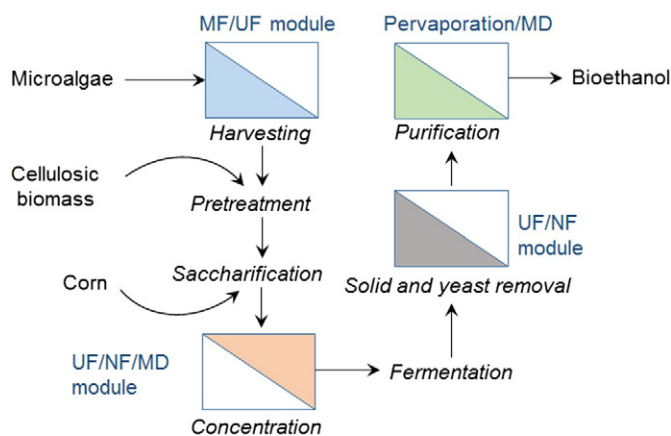


Fig. 9. Application of membrane processes for 3rd – generation bioethanol production.

In the system based on oil droplet size, a microporous membrane, which is typically a ceramic membrane or carbon membrane, is used because its high resistance to degradation and corrosion in the harsh environment of biodiesel production, where acid or base is used as a catalyst [595–597]. Due to the differences in polarity, methanol and lipids are immiscible. Their mixture exists as a two-phase system, where the lipid/oil micelles or droplets are dispersed in the continuous phase of methanol. These droplets have much higher diameter than the product biodiesel, byproduct glycerol, reactant methanol and catalyst (acid or base) and can be filtered by a membrane. Further water-washing is required to purify the biodiesel from other components in the permeate.

In the system based on membrane selectivity, a non-porous dense hydrophilic polymeric membrane (e.g. poly(vinyl alcohol)) is used [594,597,598]. The separation is based on the interaction between the target components and the membrane. Generally, glycerol and methanol have strong interaction with –OH groups of PVA via hydrogen bonding and hence penetrate through the membrane. As the result, they are continuously removed from the mixture during the reaction whereas the unreacted lipid and the product biodiesel, of which chemical structures are different with that of the membrane, are retained in the system. In such separation mechanism, the system can be operated under atmospheric pressure. To restrict the permeation of catalysts through the membrane, activated carbon is used to carry them during the reaction [595]. By this approach, Baroutian et al. [595] reported that the oil to FAME conversion reached 93.5% and high-quality biodiesel can be produced without washing or purification steps.

To combine reaction and separation in a single step, the catalytically active membranes, which are the product of catalyst immobilization into the membrane matrix, have been developed. The acidic catalyst membranes are fabricated by esterifying the –OH groups of PVA with 5-sulphosalicylic acid to achieve sulfonic groups in the polymeric matrix [599] or by blending with poly(styrene sulfonic acid) containing strong acidic groups [600]. In addition, the heterogeneous catalysts, e.g. hydro-talcite $Mg_6Al_2(OH)_{16}(CO_3^{2-}) \cdot 4H_2O$ [601] or amino-functionalized carbon nanotubes (CNTs) [602], can be embedded into the polymeric

Table 15
Bioethanol – definitions and development status.

Generation	Biomass source	Current status	Challenges
1st	Sugar and starch crops	-Technically mature -Commercially available	-The profitability heavily depends on the prices of both fossil oil and the commodity feedstock. -Compete with food prices -The greenhouse gas benefits depend on the feedstock and process used.
2nd	Lignocellulosic biomass such as agricultural wastes (e.g. straw) and energy crops (e.g. Miscanthus, poplar)	-Advanced stage of development and deployment -Demonstration stage	-Cost reduction -Availability of comparatively low-cost and sustainable feedstock
3rd	Algae	-Earlier stage of research and development	-Cost reduction -Technical challenges

matrix to form catalyst membranes by dispersing them in the polymer solution. In the case of CNTs, these particles can also increase the mechanical strength of the membrane when an appropriate content is used. Besides PVA, the polymer polyacrylonitrile (PAN) is also used for biodiesel production. To date, however, only one paper reported its membrane for purifying biodiesel by removing glycerol [603].

Similar to other membrane processes, fouling is one of the major challenges. In biodiesel production, the fouling is caused by the agglomeration of glycerol – which is favored by the presence of excess alcohol, soap (salt of fatty acids) and catalysts – to block the pores of the membrane in the system based on the oil droplet size. However, in the typical biodiesel production, fouling is not serious because the alcohol concentration in the reaction mixture is low. For the system using selective membranes, unfortunately, fouling has been not studied so far. In addition, the mechanical properties and surface morphology of the membranes have not been fully studied. Therefore, these problems should be addressed before applying in practical biodiesel industry.

3.3.2.2. Bioethanol. Among bioalcohols, bioethanol is the most practical because of its high content produced from the fermentation process. Bioethanol can be divided into three generations based on the origin of biomass used as depicted in Table 15 [588]. Higher generation bioethanol requires more steps in its production procedure. An overview of third generation bioethanol production with potential membrane applications is described in Fig. 9 [604], where MF/UF process is applied to harvest microalgae as the biomass/substrate for fermentation, MD/NF/RO process is employed to concentrate the pre-hydrolyzates and remove microorganism-inhibitors before fermentation, UF/NF is used after fermentation to remove some by-products and retain microorganism and MD/pervaporation is integrated to recover and purify the product bioethanol in the final step [604].

Algal biomass harvesting is challenging because of their small size (3–30 μm), similar density to that of water and large volumes of water that must be removed to recover algal cells. Compared to conventional techniques such as coagulation/flocculation, flotation, gravity sedimentation, centrifugation, membrane filtration (MF/UF) is more advantageous in terms of energy consumption, recovery efficiency and non-toxicity. Petrussevi et al. [543] reported a biomass recovery of 70–89% when concentrating algae from large reservoirs by membrane filtration. Although membrane filtration has many advantages over other techniques, membrane fouling – a serious problem – is still under investigation.

Membrane processes can be applied prior to the fermentation process in the production of the 2nd or 3rd generation bioethanol to concentrate sugar concentration (it is low due to different pretreatment processes and hydrolysis efficiency) and to remove fermentation-inhibitors produced during the pretreatment process. The main advantage of membrane processes over conventional techniques (e.g. evaporation, solvent extraction, overliming, activated charcoal adsorption and ion exchange) is the capability of concentrating sugar and removing inhibitors simultaneously [605,606]. Moreover, the capital investment and operation cost of membrane processes are lower than those of the evaporation process [607]. The present membrane processes applied in this aspect include MD, NF and RO, depending on the target inhibitors and sugar concentration. On the other hand, ultrafiltration can be integrated into this stage to recycle valued enzymes (e.g. cellulase) used to hydrolyze the biomass into sugar in the previous step. By this way, economic viability of the enzymatic hydrolysis of biomass is improved.

Subsequent to the fermentation process, a MD/pervaporation (PV) process is integrated to continuously recover bioethanol from the fermentation broth. Generally, the final ethanol concentration of the corn-to-ethanol fermentation (1st generation) is more than 10 wt.% while the microorganisms used for fermentation can tolerate a maximum ethanol concentration of 10 wt.%. Therefore, ethanol must be removed constantly to prevent the activity loss of microorganisms. On the other hand, cellulosic biomass-based fermentation (2nd generation) produces lower ethanol concentrations (<5 wt.%). To save energy and

costs of the refining process, the ethanol should be pre-concentrated. The conventional technique to concentrate fermentation broths is distillation. However, this technique has several main drawbacks [608]: (1) the energy consumption is remarkably higher to concentrate low ethanol concentration than to concentrate high concentration, (2) the mixture of ethanol and water forms an azeotrope at 95.6% ethanol, which cannot be separated by the conventional distillation, and (3) it is technically difficult to integrate the distillation into the fermentation to remove ethanol continuously due to that fact that high-temperature operation of distillation is lethal to microorganisms. Membrane technologies (MD/PV) are therefore more useful to remove ethanol from dilute aqueous fermentation broths. By adding membrane systems to the fermentation, productivity and production rate, as well as the substrate uptake rate can be improved.

Ethanol recovery by MD is based on the higher partial pressure of ethanol than that of water, which implies ethanol vapor can preferentially transfer through the membrane pores. Both direct contact air gap MD are common configurations coupled with fermentation for ethanol production. Udriot et al. [609] reported that 87% increase in ethanol productivity was achieved. Although this integrated fermentation-MD system can overcome the drawbacks of the conventional batch production, its studies have been limited to the lab scale. Larger scale operations need to be investigated. Moreover, the membrane selectivity of current MD materials (PTFE, PVDF and PP) is low [604] and hence higher performance MD membranes are needed. However alcohol and biological surfactants which might be present in the fermentation reduces the surface tension and promote liquid intrusion in the membrane pores, making MD application challenging.

Pervaporation (PV) is the most studied membrane technique for ethanol recovery from dilute fermentation broths. The separation of this process is based on the chemical potential difference generated by either vacuum or a sweep gas on the permeate side of the membrane. The separation mechanism predominantly relies on the preferential sorption (solubility) and diffusion (diffusivity) of the target component across the membrane. To recover ethanol, the membrane should be hydrophobic to possess higher affinity (solubility) towards ethanol that allows ethanol to preferentially pass through. Polydimethylsiloxane (PDMS) is the dominant polymeric material used to recover ethanol from water because of its superior performance as compared with other polymeric materials [610]. From the aspect of energy consumption, the separation factor of pervaporation membranes must be larger than 20 to compete with distillation [611]. This is the one of the main challenges to restrict the industrialization of polymeric membranes in this application. Although inorganic membranes (e.g. zeolite and 1-silicalite) produce the separation factor of over 20, they pose problems in processability of large-sized membranes and they are often expensive. In addition, performance degradation in practical separation system is another issue needed to be solved before the system can be industrialized [612]. This degradation is mainly due to the complex compositions in the fermentation broth. Even with very small concentration, the present of by-products in the fermentation broth can significantly reduce membrane performance. Thus, exploring higher performance and reliable membrane materials are critical for pervaporation applications in ethanol recovery.

3.3.2.3. Biogas. Biohydrogen is generated in fermentation processes while biomethane is produced during anaerobic digestion of biological waste [613]. Anaerobic membrane bioreactors (AnMBRs) have an advantage in producing both biohydrogen and biomethane in a single membrane system because in anaerobic digestion, the hydrogen production phase occurs prior to the methanogenic phase [614]. Besides biogas, many other gases and volatiles exist in the system in trace amounts (ppm) such as nitrogen, oxygen, carbon dioxide, hydro sulfide and volatile siloxanes [615]. They must be removed to upgrade biogas because their presence not only reduces the calorific value of biogas,

but also causes corrosion to the transport and distribution system and reduces the possibilities of compression [613].

Membrane technology is also gaining importance in biogas [613]. Also for this application polymeric membranes have clear advantages over ceramic for operation in temperatures below 150 °C. Several companies are currently developing gas separation membranes on commercial scale such as Membrane Technology Research, Air Products, UOP, Air Liquide, Praxair, Cynara, UBE and GKSS Licensees [616]. Continuous attempts have still been made to improve the performance of these polymeric membranes. The two commonly used effective approaches are (1) chemical modifications, especially introduction of bulky functional groups such as $-\text{Si}(\text{CH}_3)_3$, $-\text{C}(\text{CF}_3)_2$ or bromine groups [617, 618]; which increase permeability without sacrifice of selectivity and (2) crosslinking to improve selectivity of highly permeable membranes [619]. Although polymeric membranes have high potential for gas separation, they (especially glassy polymers) usually pose problems with densification, ageing or plasticization. Plasticization occurs when gas molecules are dissolved into micro-voids of the polymeric matrix, leading swelling or permanent damage to the matrix and hence drastic increase in gas diffusion and reduced selectivity [620]. To overcome plasticization, considerable attempts have focused on membrane modification by heat treatment [621,622], chemical modification [623] and polymer blending [624,625].

Also, mixed matrix membranes (MMMs) are promising candidate for gas separation by synergistic combination of easy processability from polymeric membranes and high selectivity and permeability from inorganic membranes. The attractive inorganic materials for gas transport are zeolites, carbon molecular sieves (CMS), carbon nanotubes (CNTs), metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). To achieve the improvement of MMMs, the problems in their fabrication must be conquered, which are particle sedimentation, agglomeration and interfacial voids. Sedimentation causes inhomogeneous filler and polymer phase whereas agglomeration and interfacial voids lead to non-selective voids decreasing selectivity. These problems are possibly solved by [613] (1) preparing polymer solutions at high concentrations to increase viscosity and lessen the particle sedimentation, (2) quickly solidifying membranes to offer the fillers less chance to settle, (3) matching the polarity of polymer chains and filler structures, (4) subsequently thermally annealing MMMs, (5) developing a priming protocol of MMM preparation (e.g. coating an ultrathin layer of the matrix polymer on the particle surface) and (6) using melt extrusion technique.

4. Prospects and conclusion

Membranes have been long used as sustainable solution for seawater desalination by reverse osmosis. The successful use of membrane technology in other applications requires new materials and tailored separation characteristics. Although high flux and rejection of salt and small neutral molecules can be achieved by commercial membranes, membranes with specific functionalities, better defined pores or functionalized transport channels could provide breakthroughs in the separation and recovery of valuable products for instance in mining industry, heavy metals and rare elements, as well as in the biotech industry. Membranes could supply partial desalinated water and play a more important role for agriculture providing the needed water in arid regions. For situations in which drinking water quality is not a requirement and alternatives to RO can be used, new membranes with higher flux but lower salt rejection may be an option. Providing the right composition of nutrients or selectivity for ions, preferentially for crop growth, would require membranes with tailored pore size and functionality and is still an open challenge. Industrial effluents treatment will offer more opportunities for membrane technology in the future. Membrane materials with good thermal and chemical stability would allow their application in chemical processes, which are so far not extensively explored with membranes. This is the case of recovery of valuable

products such as catalysts from reaction medium containing organic solvents. Membrane materials with better resistance to harsh cleaning treatments (chlorine, acid and alkali treatments) would increase the membrane life time in chemical separation and also in regular wastewater treatment, for which fouling is a serious problem. This would also facilitate the use of membranes for a separation task of growing importance, the treatment of produced water in the oil and gas industry.

In the energy sector, membranes already play a role in the production of biofuels. They are also the key components in different energy conversion or storage technologies, whose performance and competition with other technologies depend on the availability of better materials. For fuel cells proton conductivity even above 100 °C and low humidity aligned to high chemical and oxidative resistance are important specifications to achieve. There has been important achievement and innovative approaches in this area in the last decade. More incremental improvements in membranes for fuel have been reported in recent years. The technology as a whole has progressed becoming more mature for market penetration. A combination of other characteristics is needed for battery separators, a sector which has grown faster than fuel cell. Longer term options, such as osmotic power, are also on the horizon. However, osmotic power requires significant advances in the membrane technology, while maintaining cost and competitiveness. In summary there are a large number of open challenges and opportunities for new materials in membrane technology. With the advent of better materials in this area, new sustainable technologies and separation processes will be implemented, a task for the current and new generation of material scientists.

Abbreviations

AEM	anion exchange membrane
AMPS	2-acryloylamido-2-methylpropanesulfonic acid
AnMBR	anaerobic membrane bioreactors
BOD	biochemical oxygen demand
CAS	conventional activated sludge
CHP	combined heat and power
CMS	carbon molecular sieve
CNT	carbon nanotube
COF	covalent organic framework
DABCO	1,4-diazabicyclo-2,2,2-octane
DMFC	direct methanol fuel cell
ED	electrodialysis
EDC	endocrine disrupting chemical
EDR	electrodialysis reversal
FAME	fatty acid methyl ester
FCD	fixed charge density
FO	forward osmosis
HEV	hybrid electric vehicle
HFP	hexafluoropropylene
ICD	ionic complexation degree
ICP	internal concentration polarization
IEC	ion exchange capacity
IEM	ion exchange membrane
LbL	layer-by-layer
LIB	lithium ion batteries
MBR	membrane reactor
MD	membrane distillation
MMM	mixed matrix membrane
MOF	metal-organic framework
NF	nanofiltration
NIPS	non-solvent induced phase separation
PEMFC	polymer electrolyte membrane fuel cell
RED	reverse electrodialysis
REE	rare earth element
RO	reverse osmosis
PAFC	phosphoric acid fuel cell

PAN	polyacrylonitrile
PBI	polybenzimidazole
PDA	polydopamine
PDMS	polydimethylsiloxane
PE	polyethylene
PECH	polyepichlorohydrin
PEM	polymer electrolyte membrane
PES	poly(ether sulfone)
PET	poly(ethylene terephthalate)
PhAC	pharmaceutically active compound
PMMA	poly(methyl methacrylate)
POP	persistent organic compound
PP	polypropylene
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)
PRO	pressure-retarded osmosis
PS	polystyrene
PTFE	polytetrafluoroethylene
PV	pervaporation
PVA	polyvinyl alcohol
PVC	polyvinylchloride
PVDF	poly(vinylidene fluoride)
SDI	silt density index
SPARRO	slurry precipitation and recycle reverse osmosis
SRO	seeded reverse osmosis
SSA	sulfosuccinic acid
TDS	total dissolved solid
TFC	thin-film composite
TFE	tetrafluoroethylene
TFN	thin-film nanocomposite
TIPS	thermal induced phase separation
TOC	total organic compound
TrOC	trace organic contaminant
TRO	tubular reverse osmosis
TSS	total suspended solid
UF	ultrafiltration
VOC	volatile organic compound

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