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Review Paper

Membrane Technology in Deep Seawater Exploration: A Mini Review

Widda Rahmah [1], Anita Kusuma Wardani [1], Graecia Lugito [1], I Gede Wenten [1,2,*]

[1] *Department of Chemical Engineering, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia*
[2] *Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia*

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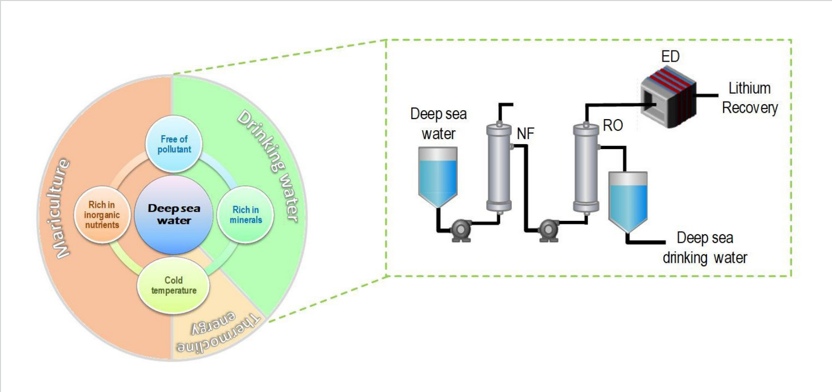
Highlights

- Deep sea drinking water is the main utilization of deep seawater.
- Reverse osmosis has dominated the desalination process of deep seawater.
- Combination of NF-RO-ED is promising for deep seawater utilization.

Graphical abstract



Abstract

Deep seawater is a valuable renewable resource. Due to its outstanding characteristics (i.e., clean, nutrient-rich and cold), deep seawater has been utilized in various subjects, such as mariculture, agriculture, food and beverage, pharmaceutical, medical, and renewable energy. As a result, deep seawater utilization cannot be separated from membrane technologies. Reverse osmosis has become the most common desalination process to prepare deep-sea drinking water with microfiltration and ultrafiltration membranes as the essential pretreatments to remove organisms, biomass and other pollutants. Besides, nanofiltration and electrodialysis have been very useful to reduce fouling, increase water recovery, and extract valuable minerals and metals, such as lithium, uranium, precious metals, and rare earth elements from deep seawater. This review paper discusses these aspects, comprehensively.

Contents

1. Introduction

Deep seawater (DSW) is a general term to describe seawater extracted from more than 200 meters in depth below the sea level. DSW can be alternative, high-quality intake water, yet the quantity is limited to approximately 20,000 m^3/h [1]. DSW has characteristics which have great potentials for mariculture [2–4] restoration of seagrass habitats [5], food [6,7] and beverage [8–12] industry, medical treatment facilities [13–17], cosmetics

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* Corresponding author at: Phone: +6222-6648498; fax: +6222-2511404
E-mail address: igw@che.itb.ac.id (I.G. Wenten)

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[18], cooling water for power stations [19], agriculture of cold climate vegetables [20,21] air conditioning [22–25] and renewable energy through ocean thermal energy conversion (OTEC) process [26–28]. DSW utilization has been intensively studied due to its outstanding characteristics, such as clean, cold, and nutrient-rich as well as mineral-rich by containing magnesium (Mg), calcium (Ca), potassium (K), etc. [29]. It is as a promising renewable resource for the production of energy, nutrients, minerals and fresh water [30–32].

The inevitable growth of human population has led to the increase of the global water demand as much as 1% per year, and the climate changes reduce the availability of pristine-quality water sources [33,34]. More than 2 billion people living in terrain with water scarcity may experience physical and psycological health disturbances, threat in food security and potential conflict among other consumers due to water shortage [35]. Moreover, many people living in developing countries still consume untreated drinking water from surface water bodies with a high chance of adopting cholera and schistosomiasis—the most common water-related diseases [36,37]. To solve this problem, DSW desalination should be considered as an additional route to provide fresh water (after water from springs and rivers). A number of sophisticated methods to collect clean water have emerged, such as water distillation [38], water reuse or reclamation [39], or brackish water and seawater desalination [40]. Brackish water and seawater desalinations have become a common technology in many countries (e.g. USA, China, Australia) around the world to supply water in times of drought and even serve as an indispensable source of water supply on a regular basis in some other countries (e.g. Israel, Saudi Arabia) [41]. In total, desalination plants around the world produced ca. 15.8 (billion gallons per day) fresh water from surface seawater (SSW) in 2013 [41]. A number of contaminants in SSW usually end in more stringent pre-treatment steps to avoid problems, such as fouling in membrane-based desalination (i.e. reverse osmosis) [42]. Due to its cleanliness, DSW is often projected as the intake water for reverse osmosis (RO) system without involving a low pressure membrane process (i.e. ultrafiltration) as pre-treatment, in other words, lower capital costs [43]. However, pumping water from the deeper part of the ocean should cost more energy, and thus the water capacity intake is limited [1]. The study on DSW intake for RO is very limited and industrial-scale plant is not realized yet. Therefore, a comparison of DSW and SSW, as intake water for RO systems in terms of trade-off between CAPEX and OPEX, is a substantial topic to study in the future.

From 1968 to 2018, approximately 397 articles discussed the fundamental characteristics, applications, treatment processes, and the environmental impacts of DSW. A significant increase in the number of publications since the 2000s is shown in Figure 1, where it can be predicted to elevate in the future. The growing number of publications in DSW research area is associated with the expanding investigations on membrane-based seawater desalination (as shown as the inset graph in Figure 1). It is due to the domination of membrane technologies in DSW utilization. One of the most commonly used membrane technologies is reverse osmosis (RO) for the preparation of deep-sea drinking water (DSDW) [13–15]. Meanwhile, microfiltration (MF) and ultrafiltration (UF) technologies have been used as pretreatments to remove microorganisms, biomass, or suspended solids from DSW [44–48]. Electrodialysis (ED) [49] and Nanofiltration (NF) [50] emerged as novel technologies in DSW utilization in the way that they reduce problems met during RO process, enhance mineral, and trace element extraction from DSW.

Among the published articles, several reviews profoundly investigated DSW and its applications. In 1973, Othmer and Roels [31] reviewed the great potential of DSW in mariculture, agriculture, and thermocline energy. Meanwhile, Nakasone and Akeda [51] and Son [52] focused on investigating and exploring the DSW applications in Japan and Vietnam, respectively. Toyama reviewed the potential of DSW utilization to be a catalyst for the economic development at Natural Energy Laboratory of Hawaii Authority (NELHA) [53]. Nani et al. reviewed the health benefits of drinking DSW [54]. In 2012, Takahashi and Huang also updated the potential applications of DSW [30]. Most of the reviews are mainly focused on the applications of DSW, while based on our knowledge, there is no article focusing on investigating the membrane performance in utilizing the DSW. Therefore, this work aims to provide a summary of membrane technologies for DSW and their potentials to produce DSW. In addition, the current and future prospective applications of deep seawater are also discussed.

2. Characteristics and applications of deep seawater

In general, the chemical composition of DSW as well as SSW tends to be constant [55]. It is composed of 96% water, 3% salts, and 1% dissolved inorganic, organic, and atmospheric gases, as shown in Figure 2. The salts are made up off six most abundant ions: chloride (Cl^-), sodium (Na^+), sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+). The quantity of dissolved salts implies that the salinity level of the seawater is measured based on seawater conductivity [55]. The seawater salinity is in the range of 34-37 practical salinity units (psu) depending on the location of the sea [55,56]. The salinity of SSW is greatly affected by evaporation and the addition of fresh water, while the salinity of DSW is only influenced by its depth.

In addition to water and salts, seawater contains dissolved inorganic and organic substances and dissolved atmospheric gases. The dissolved inorganic substances in seawater are dominated by inorganic carbon, bromide, boron, strontium, and fluoride. Meanwhile, the cold and saline DSW contains more dissolved gases, especially carbon dioxide [56]. Towards the deep and bottom water, oxygen levels also increase slightly due to an influx of cold bottom water from the poles. However, at a certain depth, oxygen level reaches a minimum value, while carbon dioxide reaches its maximum value [56].

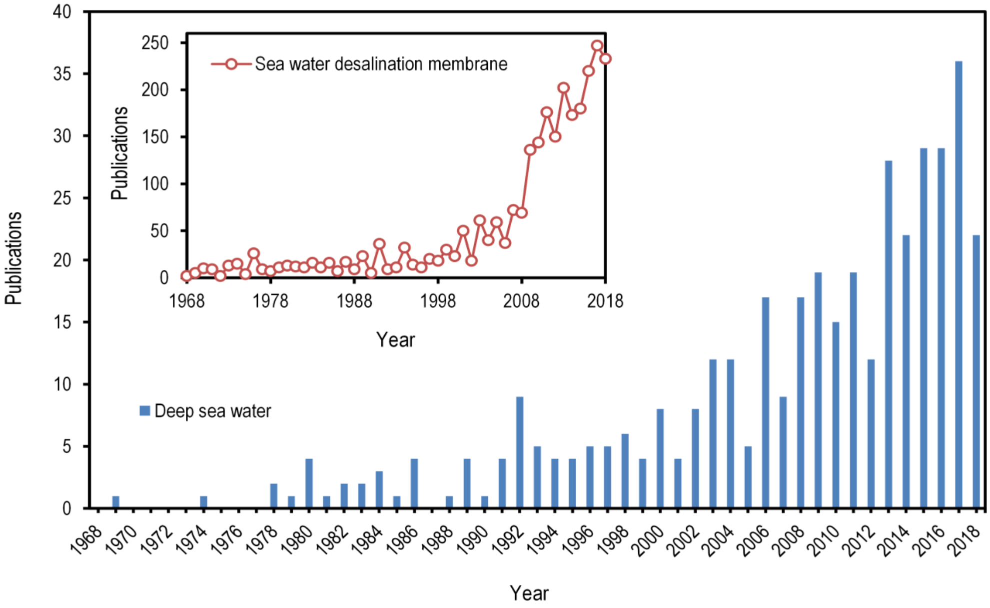

Fig. 1. Annual publication for deep seawater and membrane-based seawater desalination (published article indexed by Scopus on March 2019).

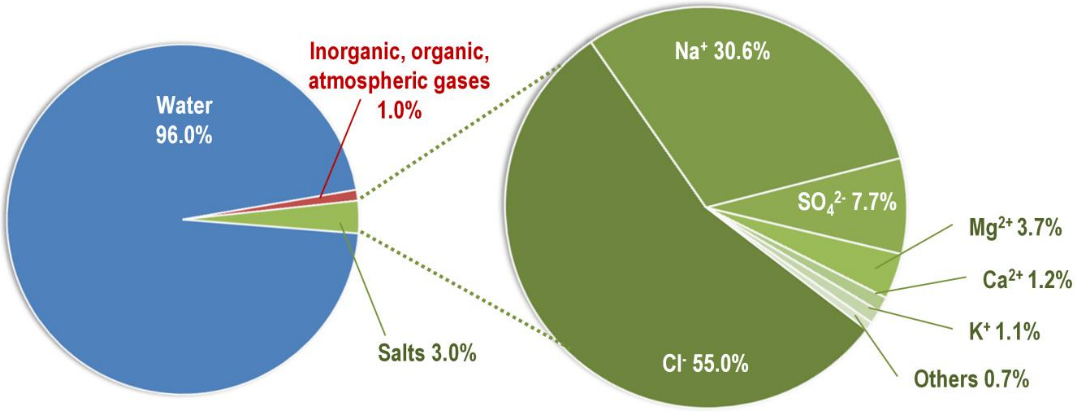

Fig. 2. Composition of seawater.

Compared to SSW, DSW has a higher concentration of inorganic nutrient and lower temperature [2,57], as shown in Table 1. In the deep sea, there is no sunlight; therefore, it is called the 'aphotic zone'. Sunlight and oxygen as the basic requirement for photosynthesis are not available in DSW, and thus the reaction does not occur. Inorganic nutrients which are supposed to be consumed by phytoplankton will sink into the deeper part of the ocean making DSW rich in inorganic nutrients. The content of trace minerals in DSW is also more superior to SSW. The presence of trace minerals is essential to prevent several diseases, such as hyperlipidemia [58], cardiovascular diseases [59], obesity [60] and diabetes [61].

Cleanliness is also the advantage of DSW. It is particularly important in a specific field of industries, which do not require a large volume of water, such as food and beverage, medicine, and cosmetic [62]. Although it is not completely clean from microorganisms and biomass, the biological density in the deep seawater is remarkably low. Several studies [57,63] stated that there are no disease-causing bacteria in DSW, particularly DSW from the sea of Japan. Due to its low concentration of organisms, DSW only requires a simple filtration process to remove them [62].

Many applications of DSW arise from its outstanding characteristics, as shown in Figure 3. In recent years, DSW has been widely used in various industries, such as the pharmaceutical, cosmetic, agriculture, food processing [9], and mariculture industries [64,65]. Furthermore, the presence of some ultra-trace elements or unknown substances in DSW may expand its applications in the future [44]. In mariculture application, four main properties of DSW including cleanliness, coldness, nutrient level, and salinity are required. The cold temperature of DSW permits the culture of plants and animals which could not tolerate tropical temperatures. The use of DSW in mariculture provides an accurate, simple, and cost-effective temperature control by mixing a certain volume of DSW and warm seawater. Meanwhile, the high nutrient level of the cold DSW provides the opportunity for rapid growth rates of marine plants. Since the deep water comes from well below the photic zone, viable plant cells are scarce, so the culture of pure strains of algae is permitted without the need for costly filtration. DSW's cleanliness is also a major strength to mariculture application in avoiding bioaccumulation [62]. Since bacteria and other pathogen in DSW exist in extremely low quantity or none at all, it possible to be used as a medium to culture susceptible animal larval stages [2].

Dr. Oswad Roles from the Lamont-Doherty Earth Observatory at Columbia University undertook the first study of nutrient-rich DSW for growing marine plants (e.g., phytoplankton, seaweeds) and animals (e.g., shellfish, shrimp) at a shore-based facility (mariculture) [66]. Some commodities, such as salmon and trout, have been successfully been produced from the utilization of DSW by NELHA [53,66]. Meanwhile, Japan more intensively utilized DSW for production of various seafoods, such as shrimp [67], Japanese sandfish [68], rainbow trout [69], abalone [70] and multiple species of microalgae [71–73]. Another notable application of DSW besides mariculture is the deep sea drinking water (DSDW). As regulated by the Environmental Protection Agency of the United States, drinking water should be free of contaminants including microorganisms, disinfectant, disinfectant byproducts, inorganic chemicals, organic chemicals, and radionuclides. DSW's cleanliness allows it to be directly used as drinking water as well as medicinal application [62]. The market price of DSDW is quite high considering it has the remarkable attributes originating from it source. For comparison, DSDW is sold at 3 USD per liter in Taiwan meanwhile one liter of tap water is priced at around 0.0003 USD (10,000 : 1) [74]. A number of physiological studies authenticate its benefits to relieve diseases induced by mineral imbalance [29], and those influenced by modern lifestyle and eating habits, [45] such as diabetes [75], obesity [76], hyperlipidemia [45], hypertension [77] and arteriosclerosis [10]. It is due to the high contents of essential minerals such as magnesium (Mg), calcium (Ca), potassium (K), and rare trace minerals such as zinc (Zn), Selenium (Se), and vanadium (V) in DSW.

Minerals in DSW has also been utilized to produce mineral concentrate [49] and/or mineral water [78] for the fortification of foods and beverages. Integrated RO with nanofiltration (NF) and electrodialysis (ED) is commonly used to prepare concentrated mineral and mineral water—rich in calcium and magnesium [49,50,78]. Similarly with DSDW, the objective of food fortification by DSW minerals was to alleviate lifestyle-induced diseases. Minerals extracted from DSW are expected to regulate autonomic nerve activity [79], and cardiovascular disorders which deteriorate the bloodstream due to modern lifestyle (i.e., excessive nutritional intake, unbalanced diet, lack of exercise and sleep, and stress) [50].

The cold temperature of DSW also allows it to be utilized in other practical applications, such as handling of captured fishes [80], air conditioning [24] and energy generation from temperature difference of DSW and SSW [81]. In Japan, DSW has been used to handle captured fishes due to its low temperature and its cleanliness [82]. Captured fishes have to be kept fresh and sanitary for distribution or storage, especially in fish markets. Meanwhile, the cold feature of DSW is advantageous to be used as refrigerant in seawater air conditioning (SWAC) for one or more buildings [83]. On the other hand, electricity generation from DSW or The Ocean Thermal Energy Conversion (OTEC) process is still not fully explored. The process in general makes use of the heat from the ocean as the the 'world's largest collector and storage system of solar energy'. The temperature differences between SSW and DSW can generate mechanical energy and fresh water simultaneously via warm SSW evaporation to and cold DSW condensation to drive a heat engine cycle [84].

Table 1
Differences between SSW and DSW [55,56].

Parameter	Surface seawater	Deep seawater
Depth	0-200 meters	>200 meters
Sunlight	yes	no
Photosynthesis	yes	no
Biomass	rich	less
Inorganic nutrient	less	rich
Dissolved gasses	equal to the atmosphere	less oxygen, rich in CO_2
Temperature	30°c (at sea surface)	-1°c (at seabed)
Microorganism	phytoplankton, algae, bacteria, viruses	few autotropic microbes
Suspended solids	rich	less
Chemical contaminant	rich	less

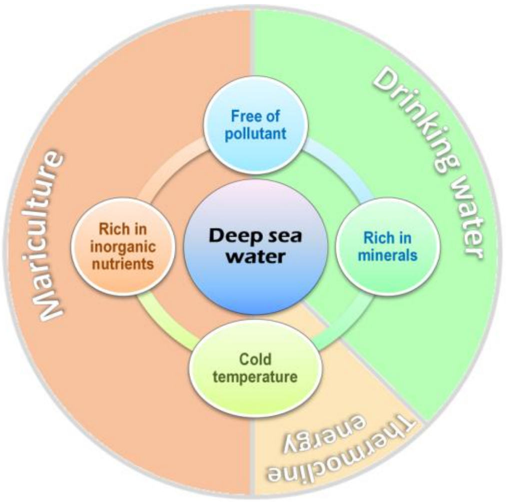

Fig. 3. Application of deep-seawater based on its characteristic

In addition to water and salts, DSW also consists of common elements like silicon, phosphorous, lithium, rubidium, iodine, and barium and some rare metals, such as gold, silver, platinum, and titanium. However, these elements exist in extremely low concentration. A large volume of DSW (>10^3 L) is necessary to obtain a detectable number of trace elements and radionuclides [85]. Therefore, extracting metals from DSW requires considerable economic investment and strategy. Nevertheless, there are several kinds of trace elements which can be recovered from DSW and deemed as economically feasible. Trace elements, such as lithium [86–90], uranium [91–96], vanadium [97,98] and rare-earth elements (REEs), such as Yttrium, Lanthanium, Cerium, Praseodymium, Neodymium, etc. [99–104] are highly valuable and beneficial.

The ocean is estimated to contain 230 billion tons lithium ions. Lithium is electrochemically active, having the highest redox potential value as well as the highest specific heat capacity of any substantial elements making it the hottest commodity for modern life and the key for modern electric vehicle revolution [105]. Due to their desirable characteristics, primary Lithium-Ion Batteries (LIBs) are widely used for powering sophisticated electronics [32]. As for uranium, it is regarded as one of the most valuable metals in seawater [98]. Recent economic analyses also suggest uranium recovery from the oceans can help solidify nuclear energy's potential as a sustainable energy source for the next century [106]. The rare earth industry is experiencing rapid changes, as seen from the manufacturer of highly separated rare-earth elements' point of view [107]. Rare-earth elements are widely applied to metallurgical, glass, ceramics, chemical engineering, nuclear industry, electronics, agriculture and pharmaceutical industries due to their unique physicochemical properties in luminescence, electronics, magnetism, energy catalysis, and so on [100]. Rare-earth elements are becoming uniquely indispensable and critical in many high-tech industries, such as hybrid cars, wind turbines, and compact fluorescent lights, flat screen televisions, mobile phones, disc drives, and defense technologies [101].

3. Advances in membrane technology for deep seawater treatment

Extracting water from seawater by desalination has become a primary practice to supply water in water-scarce regions [108]. Desalination plants around the world produce a total of 15.8 BGD or 60 million m^3 of clean water a day [41], which typically are extracted from SSW. Authors predicted that in the near future desalination plants will start to pump DSW as intake water in order to exploit many kinds of resources, energy, and fresh-water contained in it. In addition, DSW holds an advantage over SSW in terms of cleanliness, namely less capital cost due to less pre-treatment step before desalination process. While it is true that DSW pumping capacity as intake water is limited due to high energy requirement, sophisticated membrane-based technology can reduce operational costs by decreasing the burden of the main desalination process or providing an offset to the energy consumption by generating energy from salinity gradient power (SGP). In the end, when the utilization of DSW comes into fruition, profit from the products can offset the overall operational costs. Economical study of DSW utilization should be able to prove these hypotheses.

Several technologies for seawater desalination are widely available as rane-based desalination. Thermal desalination methods, such as multistage flash (MSF) [109], and multi-effect distillation (MED) [110] include phase-changing which is driven by thermal energy. Meanwhile, membrane-based desalination technologies are categorized into 1) pressure-driven membrane i.e. reverse osmosis (RO), nanofiltration (NF) or low-pressure reverse osmosis (LPRO), 2) thermal-driven membrane which is membrane distillation (MD) and 3) electrical-driven membrane which consists of membrane capacitive deionization (MCDI) and its related technologies i.e. electrodialysis (ED) [111], electrodeionization (EDI) [112], electrodialysis reversal (EDR) [113] and electrodeionization reversal (EDIR) [114]. Table 2 summarizes the advantages and disadvantages as well as their comparisons in terms of energy consumption for each membrane-based desalination technologies.

Due to high energy requirement of thermal-based desalination method, interests have shifted to membrane-based desalination since it consumes less energy and offers a more compact plant while accommodating high water recovery [115–122]. RO has played a great role in providing clean water from seawater desalination. In fact, desalination plants around the world are dominated by seawater reverse osmosis (SWRO) (65%) surpassing the capacity of traditional MSF and MED [123]. For instance, Fujairah 1 (United Emirate Arab), one of the largest desalination plants in the world, is able to produce around 285 million m^3/day fresh water from MSF and around 590 million m^3/day from RO [124]. Another example is Sorek desalination plant (Israel) which is currently the largest SWRO plant—producing ca. 624 million m^3 of fresh water per day [125].

SWRO has been regarded as a conventional method for seawater desalination compared to the emerging technologies. In RO, natural osmotic diffusion, across a semi-permeable membrane that is placed between concentrated solution and dilute solution or pure water, is reversed by an external pressure, resulting water transport from highly saline seawater to pure water. High operating pressure of around 60-70 bar has to be exerted in RO process to counter against the high osmotic pressure of seawater [126]. In addition, the membrane module may reduce the efficiency of RO process, which is determined by parameters, such as the blockage of RO membrane pores due to fouling and scaling, friction coefficient of the module and spacers, the dynamic viscosity of the feed water, the height of the feed reservoir, and the decreased cross-flow velocity of the feed water—naturally decreased along with the filtration module [127]. For this reason, approximately 60% of the total energy cost for typical SWRO plant is consumed by high-pressure (HP) pump with the second and third largest energy consumers, that is, water intake pumping system and product water pumping station which is heavily dependent on the nature of the intake water and product distribution [128].

3.1. Low cost SWRO

Energy saving strategies have been undertaken in order to reduce the energy requirement in SWRO, such as minimizing scaling and fouling, developing high performing/low-pressure membrane, or integrating other processes. In striving to minimize energy consumption, SWRO process is sometimes integrated with energy recovery devices (ERD) or an energy generator e.g. turbine or pressure exchanger (PX)) which catches high pressure—existing in the retentate/brine. Energy produced from these ERD is used to reduce the overall energy consumption of the SWRO plants. The efficiency of these ERDs is as high as 94% (hyperbaric turbine) for SWRO and its around 50% in brackish water reverse osmosis (BSWR) [128]. In around 20 years of development, specific energy consumption (SEC) of SWRO process has been suppressed significantly from around 8.5 kwh/m^3 to < 3 kwh/m^3 due to the integration with ERDs [129,130]. The more stringent energy limitation as well as water quality demand motivated the development of RO membranes that operate at low pressure. Previously studied LPRO has found an application for purification of low salinity feed water, such as brackish water (15 - 20 bar). LPRO membranes may be constructed of thin-film composite membrane, which should be characterized with high permeate flux [131], membrane with wider pore-size (i.e. NF) [132] or charged RO membranes. The interest in charged RO membrane may have been overshadowed by the invention of thin asymmetric cellulose acetate by Loeb-Sourirajan. Regardless, today, charged RO membrane had found applications in the treatment of dilute electrolyte solution, such as water softening, ionic pollutant treatment and recovery of valuable metals from industrial waste [133].

Further attempts to reduce energy consumption are to produce energy from salinity gradient power (SGP) between RO brines and fresh water through technologies which have a positive balance energy, such as forward osmosis (FO), pressure retarded osmosis (PRO) and reverse electrodialysis (RED). Forward osmosis is the opposite of RO process in which water is 'drawn' naturally from saline solution through a semi-permeable membrane due to osmotic-pressure gradient [134]. For seawater desalination, FO's energy efficiency is unlikely to approach the energy efficiency of RO. The integration of FO-RO for pre-diluting seawater prior to RO is more viable. However, pre-diluted seawater reduces energy consumption of the RO module, while the 'drawing' step of FO produces additional energy penalty to this system [135].

In PRO system, a pressure exchanger (PE) is added to the chamber where the 'drawn' water via FO process is accumulated. The increasing volume (pressure) in the chamber turns a turbine converting mechanical energy to electrical energy [135,136]. Typical water recovery from seawater by RO desalination is 35-50% [137]; meanwhile, the remaining concentrated brine is either evaporated or released back to nature by deep-well injection or direct discharge to the ocean which would further cause environmental problems [138]. The integrated RO-PRO process is promising to reduce SEC of a SWRO plant as well as to dilute the produced brine prior to discharging back to the sea. If the brines from SWRO are used as the draw solution in PRO system, a significant amount of energy can be recovered. Integration of RO-PRO system can save 0.71 to 1.13 kWh per m^3 of produced water on a SWRO plant [139].

Another option to generate energy from mixing brine and fresh water is by applying reverse electrodialysis (RED). Ion exchange membranes are placed to separate brine and fresh water to allow voltage generation as a result of ion movement towards its associated electrodes [136]. RED-RO configuration for seawater desalination has been studied and resulted in a significant decrease in SEC as well as the discharged brine concentration. Other options of configuration were also discussed, one of the options being the use of REDs as both pre-treatment for RO and post-treatment to harvest energy from the RO brine and reduce the SEC of the desalination plant lower than 1 kwh/m3 [140]. Higher energy was obtained at higher salinity gradient. Regardless, at high salinity gradient, energy efficiency is reduced due to more salt and water transport through the membrane; in other words, this reduced the membrane permselectivity. Besides, developing better performing membrane (i.e. profiled membrane), reducing spacer and compartment resistance is the main strategies to increase energy gain [141]. Generating energy from SGP is theoretically profitable, however, these ideas are still rendered novel and not yet feasible for industrial application. One problem deterring the development of these processes is the development of high performance membranes suitable for each specific mechanism [142].

3.2. Emerging Membrane-based desalination technologies

Low energy SWRO and emerging membrane-based desalination processes such as MD, MCDI, ED, EDR, EDI and EDIR are now the target for future desalination process. Capacitive deionization (CDI) uses potential difference as a driving force. CDI in general includes porous electrodes to collect charged ions by applying low voltage electrical field. Ion removal in CDI is based on electrosorption and desorption. Electrical double layers (EDLs) are formed when a potential difference is applied on the electrodes, attracting co-ions into their respective electrodes. Desorption then is performed by reducing the electrical current to zero, or by reversing the charge of the electrodes. In conventional CDI, however, co-ions are sometimes desorbed and mixed with the diluted water. One solution to this problem is by adding ion exchange membranes before the electrodes to entrap co-ions which are desorbed from the EDL—this is known as membrane capacitive deionization (MCDI). Salt removal efficiency increased in MCDI rather than the conventional CDI [143].

Table 2
The comparison of some membrane-based desalination process.

Membrane-based process	**Advantage**	**Disadvantage**	**Typical SEC (kWh per m^3 of desalinated water)**
RO	No salinity limitation, no thermal energy, modular configuration [144], integration with ERD allows much lower energy requirement [145]	High pumping power, extensive pre-treatment (in terms of SSW as intake water), chemicals addition, membrane degradation by chlorine oxidation, expensive cleaning [146]	<3.0 – 8.5
LPRO	Low pressure or energy requirements, modularity, in the case of negatively charged RO, negatively charged colloid cannot induce fouling [133].	Membrane is not commercially used [131]	15-20 bar (brackish water)
FO	Low or negative hydraulic pressure, reversible membrane fouling [144], higher water recovery than RO [147]	High initial energy requirement [135], limited availability of drawing solution [147]	2.5 [135]
PRO	Positive energy balance, Seawater or RO brine can act as a draw solution [139]	Limited development of high performing PRO membrane [139]	5.5 – 1.1 (RO-PRO) [139]
RED	Positive energy balance, No requirements for high salinity draw solution, pre-treatment of RO against scaling agents [141]	Reduced membrane permselectivity at high salinity gradient [141]	< 1.0 (RED-RO-RED) [140]
ED or EDR	No need for pressure, little pre-treatment requirement, less scaling and fouling, easy to clean through reversing polarity, higher brine concentration due to zero osmotic pressure limitation [48,129], higher water recovery controlled product concentration, long membrane-life [144]	High costs of electrodes and membranes [129], uncharged species cannot be separated, energy consumption is proportional to feed salinity, high investment cost to produce low concentration dilluate [48].	1.65 – 870 (depends on feed and dilluate concentration) [148–150]
EDI or EDIR	Ability to produce ultra-pure water, more than 90% salt rejection [48], lower energy consumption, ability to process low salinity (low conductivity) feed.	High investment cost, complex equipment hence difficulties in repairing the modules, pressure drop in ion exchange resin compartment [135]	0.2 -0.8 [48]
MD	Operates on low thermal energy and low pressure gradient, less stringent membrane mechanical properties [144], high salt rejection, treatment of high salinity water [151], modularity, easy operation [152]	Relatively low permeate flux over RO [152], Prone to inorganic scalling, scalling-induced membrane wetting [151]	1.25 [153]

Water purification by ED includes a series of anion and cation exchange membranes arranged in an alternating pattern between anode and cathode. Spacers which are either inert or conductive materials are placed in between each ion exchange membrane. When a DC potential is applied, positively-charged cations move toward the cathode by passing through an anion exchange membrane (AEM), while negatively-charged anions are retained by this membrane. The same process also applies for negatively-charged anions; they move towards the anode by passing through a cation exchange membrane (CEM). By this process, compartments which hold the anode and cathode are filled with ions of the same species, and the other compartment (dilute compartment) is free of ions [154]. ED has been applied in a wide range of fields, such as water desalination, production 1q of acid and bases [155], and the removal of hardness in water [143,155]. A feature which distinguishes ED from other water purification methods is the ability to selectively recover charged species, for instance, zinc recovery from electroplating effluent or nickels and iron recovery from plating-industry waste. This feature of ED has also used in a profound application of mineral extraction from DSW which will be explained in more detail in the following chapter. ED performance is determined by a series of process parameters, such as stack construction, feed and product concentration, membrane permselectivity, flow velocities, current density, recovery rates and so-on [156]. ED is more suitable for purification of brackish water than seawater due to a couple of reasons: 1) high energy requirement for the highly saline seawater desalination, 2) efficiency losses due to water transport increases for high feed salinity, and 3) low coulombic efficiency at high salinity [157]. Desalination of seawater (>35,000 ppm) to brackish water (~5000 ppm) by ED is viable economically, and thus pre-desalination of seawater by ED prior to brackish water desalination by RO can reduce energy consumption in SWRO plant. The accumulation of ions, especially bivalent ion near the ion exchange membrane as a result of separation by electrical current, can lead to ED membrane scaling. Reversing the electrodes' polarity periodically, such as in electrodialysis reversal (EDR) can help clean the membrane from precipitant build-up, and thus increase the membrane's shelf life [158]. EDR has been studied as a pre-treatment step of RO in petrochemical wastewater treatment and achieved water recovery of about 40% with <90% removal of phsycochemical parameters [113].

EDI is a modification to ED, while dilute compartment is filled with electrically active media, such as ion exchange (IE) resin, IE textile, or organic porous IE material [159]. EDI shows a better performance compared to ED especially for purification of more dilute solution due to higher electrical conductivity provided by ions in the IE resin [48]. When used to purify low concentration solution (i.e. brackish water), ED experiences a decrease in current efficiency and required high cell voltage, hence higher operational cost. EDI was proven to be more effective in brackish water desalination with salt rejection as high as 94% [112]. Compared to conventional ion exchange process, EDI does not require chemical regeneration since the resin beads in EDI are continuously regenerated by protons ($H^{+)}$ and hydroxyl (OH^{-}) ions via water-splitting reaction using low electricity, this feature is regarded as 'electro-regeneration' [160]. In EDI, loose resin beads sometime block channels, and thus add an extra hydraulic resistance. Therefore, most engineers replace the conventional resin with a resin wafer (RW-EDI) in which the beads are molded into a porous, solid matrix. EDI can achieve higher salt rejection (~90%) as well as removal of weakly ionized substances, such as boron and silica, which are not achievable with RO or ED [48]. Industrially, EDI has been applied to produce ultra-pure water for semiconductor, pharmaceutical industries [160]. Similarly like ED, in EDI process, scale formation on the surface of membranes and resin can decrease the process performance. Periodic reversal of polarity in electrodeionization reversal (EDIR) as well as in EDR can prevent scale formation without using any scaling agents. Lee et al. [155] compared the performance of EDR and EDIR for hardness removal from water. The result showed that EDIR consumed lower energy for the same softening capacity and current density compared to EDR. In terms of desalination, EDIR was able to produce good quality drinking water from brackish water under reasonable voltage requirements [114]. In DSW treatment and utilization, however, EDI or EDIR application is very lacking or none at all. Even though, the ability of EDI and EDIR in removing boron and silica should be beneficial in DSDW production since boron and silica can be harmful when consumed in a certain amount [161,162].

Electromembrane-based desalination offers many potentials, not as the main technology for SSW and DSW desalinations, but as extra steps to reduce energy cost by acting as pre-treatment to protect RO membrane against fouling and scaling. This is believed to improve the produced water quality or recover valuable species from RO brine. Nevertheless, industrial scale-up of these technologies is difficult since the cost of the investment is high, and there are limitations of the feed and product salinity [163]. In contrast to electrical-driven membrane process, there are no concentration limits for MD. In MD, hot saline solution is fed to the membrane where water vapor pressure is increased from higher temperature. Water vapor are drove through the pores; meanwhile, liquid saline water is repelled by a hydrophobic microfiltration membrane [164]. MD had theoretical 100% rejection of both macromolecules and ions and does not require complex pumps and pipes like RO, and so is applicable for small-scale systems in remote areas. Currently, MD desalination process is viable only in lab-scale processes. Scaling under high temperature and fouling due to hydrophobic nature of the membrane in MD are one of the problems hindering its development. Operating conditions, such as pH, temperature and design parameter especially those which relates to concentration polarization, should be considered to minimize the formation of scaling and fouling on MD membranes [165]. Combining MD with a crystallization (MD-C) process has been proposed for zero liquid discharge (ZLD) approach on seawater desalination. Processing hot brine with a MD unit can reduce volume factor as high as 83.6% by adding RED after MD to increase the factor to 92% [166]. The extraction of minerals and other valuable resources from DSW may become more approachable with the MD-C configuration. A complete utilization of DSW should be in-line with ZLD policy, where all water is extracted (no brine waste), while mineral and other trace elements, such as metals which are recovered as solid products. However, this configuration is energy intensive and calls for the use of renewable energy [151]. Solar energy can be harnessed for MD desalination. Nevertheless, many technological aspects remains to be discussed especially for large desalination facilities. Currently, MD process is more suitable for conjunction with solar energy for small capacities, for example in remote regions and urban areas [167].

3.3. Drawbacks in membrane-based desalination

Despite various offered advantages, the efficiency of membrane-based desalination process is still limited by membrane fouling. This is a common problem found in membrane-based process due to the presence of dissolved substance in the intake water. Fouling is associated with the accumulation of substances on the membrane surface or within the membrane pores, it leads to a significant impact on the reduction of permeate flux [168]. It occurs through one or more of the following mechanisms: feed component adsorption, pore clogging, chemical interaction between solutes and membrane material, gel formation, and bacterial growth [169]. This fouling not only leads to productivity decline, but also requires an additional energy supply to keep the membrane performance constant [170–173].

Fouling is inevitable but can be controlled. The usage of suitable fouling control strategies allows for longer membrane life and lower operational costs. It is important to ensure the membrane technology is favorable and competitive in comparison to other technologies. Various attempts have been undertaken in order to control fouling in UF membrane, for example optimization of operation condition by increasing both pH and cross flow velocity or decreasing initial flux. Fouling control can also be done by the addition of pretreatment or fundamental modifications of the membranes [174,175]. The selection of appropriate pretreatment can be used to inhibit the fouling formation by reducing foulant concentration in the feed water. In addition, fouling formation can be inhibited by making the membrane surface more hydrophilic, negatively charged and/or smooth. The incorporation of nanomaterials with antimicrobial properties can also be done to avoid interaction between a membrane surface and microorganisms. Lately, researchers are focused on modifying the surface of the RO membrane into having enhanced anti-fouling characteristics. Modifications, such as surface hydrations [176], surface grafting with graphene oxide [177], surface layering by poly-electrolytes [178], are proven to decreases the odds of membrane fouling in RO.

For DSW desalination, stringent pre-treatment steps which came with RO process can be eliminated since DSW is less polluted compared to SSW. However, even though the quantity of pollutants (e.g. microorganisms, biomass, suspended solids, and other chemical contaminants) in DSW is very small, they can still hinder the utilization of DSW by the formation of fouling on the membrane surface. Figure 4 shows a combination of several pretreatments which are mostly used to process DSW before fed to RO. For handling colloidal and biological fouling, colloid, organic matter and microorganisms must be removed from DSW before reaching the RO membrane. It can be obtained by both conventional processes (e.g., conventional/lamella sedimentation, dissolved air flotation, granular media gravity/pressure filtration) [179] and low-pressure membrane processes (e.g., MF and UF) [180]. However, MF and UF technologies are also limited to fouling if used directly to filter DSW; hence, another pre-coagulation step is required before MF/UF filtration [181].

One of the main goals of membrane-based desalination is to obtain salt recovery as high as possible. The higher the recovery, the higher the salt concentration—accumulating in the feed side of the membrane. However, the salt concentration will exceed its solubility limit and deposited on the membrane, a phenomenon known as scaling [182]. Salt crystal accumulation in the membrane could reduce permeate flux and increase pressure drop. Moreover, chemical cleaning is required to remove scaling and consequently shorten membrane lifetime [182]. Scaling is further severed by the concentration polarization (CP) which is a gradient in salt concentration occurred in the vicinity of membrane surface due to the salts left behind as water permeates through the RO membrane [182]. Calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, calcium fluoride, and silica are examples of the most common scalants as well as iron, manganese, and aluminum [183].

In conventional RO process, antiscalant agents are usually added to the system to control scaling on RO by complexing metal ions in the feed stream to prevent precipitation [183]. The used antiscalant is preferred to be the one of which is proven not to foul the membrane, approved by the environmental protection agencies in case of potable water production. It is effective in handling the common scalants and more preferably silica which has a good tolerance to aluminum, iron and manganese oxides, disperses particulate foulants, works over a wide range of feed water pH and temperature, has no adverse effect over continuous use, has biocidal effect to protect against biological fouling, has a compatibility with coagulant in pre-treatment stage [183]. Emerging membrane processes have a high potential to replace chemical addition in the attempt to prevent scaling, for instance NF, ED, and EDR processes as pre-treatments can separate multivalent ions which are responsible for scaling formations in RO membranes.

4. Deep seawater reverse osmosis for drinking water production

RO has become almost indispensable in DSW utilization as shown in Table 3. Several researchers [9,29,44,45,184] successfully produced DSDW by DSW reverse osmosis processes (DSWRO). DSDW is widely accepted as a healthy drink especially to relieve lifestyle induced diseases, such as hyperlipidemia [58], cardiovascular diseases [59], obesity [60] and diabetes [61]. DSDW production is closely related to membrane technologies. The membrane has been used as a desalination method to produce balanced-salinity DSW which is safe for drinking. Most of the time, the desalination procedure is carried out by RO membrane [9,29,44,45,184], although ED was also able to be used to prepare DSDW [60]. RO process makes use of a high external pressure difference on a semi-permeable barrier which is only permeable to fresh water. Meanwhile, in ED fresh-water is produced by a DC field generated by electricity across a stack of flat sheet ion exchange membranes in a cation-anion arrangement [185,186]. Production of drinking water by RO requires a post remineralization step since it provides a total desalination, while ED gives a possibility for partial and selective desalinations [187]. Desalination of DSW using ED results in a higher recovery of minerals compared to RO, and thus DSDW prepared by ED harbor higher hardness compared to DSDW produced by RO [60,188]. However, a dietary habit of overly high salt, especially sodium, can lead to hypertension and renal hypertrophy or even renal fibrosis [8]. Moreover, saltiness due to the high content of monovalent ions such as sodium [189] or bitterness due to sulfate ions [78] in food and beverage products leads to consumer dissatisfaction. Later, it was found that monovalent perm-selective ED membranes utilized at specific operating condition can remove monovalent ions from the final product of DSDW [50,190].

The production of DSDW mostly includes pretreatment, desalination of DSW to produce fresh water and concentrated retentate, and then mixing both freshly desalinated water and the RO concentrate (brine) [61,184]. In most articles mentioning DSDW, the preparation step includes only one module of SWRO for DSW desalination. However, the product from SWRO mostly still contains more than 1000 ppm of minerals. LPRO can be added to reduce the concentration of minerals obtaining fresh water that is readily used as drinking water. The fresh water from LPRO permeates, and then mixed with a part of LPRO brine to control its salinity regarding magnesium (Mg^{2+}) and calcium (Ca^{2+}) content (hardness). Meanwhile, the rest of the LPRO brine can be returned to SWRO feed water, as shown in Figure 4.

Table 3
Recent membrane technologies used in applications of DSW.

Membrane	Application	Methods	Result	Ref.
MF - RO	DSDW preparation with anti-obesity and antidiabetic effects studied on feeding induced-obese mice	DSW was pumped from a depth of 1.1 km and a distance of 18 km from the shore of Gangwon-Do, Korea. Phytoplankton and microorganism were removed by microfiltration (0.2 μm) before processed with RO. Brine and desalted water were mixed with mineral ratio of Mg/Ca/K/Na = 3:1:1:1.	DSDW showed antidiabetic and anti-obesity activates via activation of diabetes- and obesity-specific molecules	[61]
MF - RO	Preparation of Deep-sea Drinking water for Diabetes type I	DSW was pumped from a depth of 0.5 km, 6.7 km from the shore at Oho-Ri, Gangwon-Do, Korea. The DSW was microfiltered before passed to RO membrane. DSDW was prepared by mixing mineral extracts and desalinated water with ratio of Mg: Ca was 3:1. Before the tests, the DSDW was diluted to a series of different hardness.	DSDW illustrated an ability to suppress hyperglycemia and improve glucose intolerance on high-fat diet-induced diabetic mice.	[184]
RO	Preparation of Deep-sea Drinking water for atopic eczema /dermatitis syndrome	The tests used refined DSDW Amami no Mizu hardness 1000 (Ako Kasei Co., Ltd.) which was obtained from 344 m below the sea in Japan.	Out of 33 patients treated with DSDW, 27 patients showed improved skin symptoms	[29]
RO	Preparation of Deep-sea Drinking water for Hypercholesterol	DSW was pumped from ca. 344 m below the sea level of Cape Muroto, Japan. After RO, NaCl was removed from the RO brine with evaporation. Brine with small amount of NaCL then mixed with desalinated water to produce DSDW with hardness of 1000. The refined DSDW was then filtered for disinfection and battled.	Hyperrcholesterolemic rabbits that were given DSDW periodically showed an improvement in its cardiovascular hemodynamics.	[44]
RO	Preparation of Deep-sea Drinking water for Hypercholesterol	DSW was pumped from 662 m below sea level 5 km off the coast of Hualien County, Taiwan. The pumped DSW was then processed with filtration, RO and concentration. Mixed brine and pure water was controlled to hardness of 350 and 1400 mg of Mg per liter.	DSW was found to be effective in reducing blood total cholesterol, low-density lipoprotein-cholesterol and lipid peroxidation in hypercholesterolemic subjects	[9]
RO	Preparation of Deep-sea	DSW was pumped from 374 m below sea level	Minerals in DSDW promotes the	[45]

	Drinking water for Hyperemia	off Muroto Cape, Japan. The DSW was desalinated by RO and concentrated to remove Na and other excessive ions. DSDW was prepared having hardness of 28, 300, and 1200.	reduction of serum lipid in hyperlipemia rabbits	
ED	Production of DSW minerals for food and/or drinks to regulate autonomic nerves	Multiple ED stage was applied for DSW desalination. Both EDs used a monovalent-selective cation IX membrane. The first ED process was run until the DSW conductivity was 12 mS/cm or less, then subjected to the second ED to obtain mineral water with electrical conductivity less than 6mS/cm. The produced mineral water has Mg and Na concentration of 740 mg/L and 2 mg/L respectively. It was diluted with RO treated DSW to prepare DSDW with controlled hardness.	Electrocardiograms tests were carried out to 21 adult males that were given DSDW for 5 weeks. Minerals composed in the DSDW were capable of alleviating a disturbed state of autonomic nerves and the symptoms caused thereby.	[79]
ED	Mineral extraction from DSW for food or beverage or its additive	DSDW was prepared by ED using monovalent-selective cation IX membranes and electric conductivity < 10 mS/cm. The ED desalination was repeated plurality of times in order to obtain the best result.	Mineral water for the production of DSDW as well as other food and beverage products was successfully obtained from DSW. Sodium and chloride were removed to < 4 mg/L while magnesium concentration remained at >20 mg/L.	[49]
ED	Desalting used DSW from OTEC plant before dispersed back into the upper ocean to increase the nutrient level of the photic zone	A submerged ED device was located in the depth of the ocean. Desalinated seawater that produced therein rises naturally upward through a conduit leading to OTEC plant.	Such configuration led to a reduced energy requirement to transfer cold DSW to the OTEC plant which usually require high pumping energy. In addition, the remaining nutrients in DSW were mixed with SSW, and then increased fishery production and harvest.	[191]
ED	Desalination of DSW for hydroponics vegetables	DSW was pumped and subjected to ED to remove the NaCl content. Treated DSW with different electrical conductivity (50-10 dS/m) and dilution factor were used to grow hydroponics spinach.	Salinity content in treated DSW with electrical conductivity lower than 16 dS/m was negligible to spinach growth. The highest spinach yield was obtained using treated DSW with 5dS/m electrical conductivity.	[192]
ED	Study of DSW on biochemical and mechanical properties of bone and the related gene expression in mice	DSW and SSW (612 and 15 m depth) were desalinated with ED unit with monovalent – selective cation IX membranes to prepare drinking water. All seawater was desalinated to electrical conductivity of 10 mS/cm before diluted and fed to mice.	DSW had higher Si content than SSW. Soluble Si as well as other natural material in DSW stimulated cell growth in osteoblast and osteoclasts in cell culture and promoted bone formation in mice.	[193]
RO - ED	Extraction of organic component for Helicobacter pylori infection inhibition	A selection of organic components with molecular weight of 685 to 690,733 to 738 and 1,070 to 1,075 were extracted from DSDW by gel, dichloromethane (DCM), acetone and chloroform extractions. Mg and Ca were removed by EDTA in some tests.	Patients with gastroscopy and *Helicobacter pyroli* infections were given DSDW. Clinical result showed a significant decrease in H. *pyroli* infection symptoms. Magnesium and calcium were not included in the bacteria deactivation mechanism	[189]
RO - ED	Production of mineral balanced DSW to enhance inhibitory effects of chitosan oligosaccharide on atopic dermatitis-like inflammatory response	DSW was pumped from 0.5 km depth and 6.7 km far from a shore at Oho-Ri, Gangwon-Do, Korea. DSW was then subjected to a microfiltration, then RO to produce mineral extract. DSDW was prepared from the extract to a series of sample with controlled hardness. DSDW was mixed with chitosan oligosaccharides (COS) before tested on mice.	Pro-inflammatory factors in atopic dermatitis induced by lipopolysaccharides (LPS) were inhibited by COS treatment. The inhibition was further enhanced by DSDW and it was dependent to DSDW hardness.	[194]
UF – NF – NF - NF - RO - ED	Production of RO permeate water and mineral water from DSW	The obtained DSW was initially filtered by sand-filtered and UF. The filtered DSW was then subjected to the first NF. First NF brine was subjected to a second NF. Both NF permeate was mixed in a pH and TDS adjustment tank before filtered by a third NF in which the permeate is further purified with RO apparatus. Pure desalinated RO water was then mixed with the second NF brine in another adjustment tank prior to selective ion separation by ED.	This configuration allows pH adjustment by adding acid or base while TDS may be adjusted with distillation, evaporation, RO or dilution with water. Produced DSDW may contain CL and Na ions in the range of 300-8000 mg/L and 200-5000 mg/L respectively. Meanwhile Ca, Mg and sulfate ions was in the range of 600-15000; 3000-20000; and 50-2500 mg/L respectively.	[50]
UF – RO – ED	Studi of DSW with	The DSW was pumped from 618 m below sea	DSDW was fed to exercise-induced	[195]

	adjusted hardness on exercise-induced fatigue in rats	level in Hua-Lien County, Taiwan. DSW was treated with UF then RO to produce desalinated water of 25 ppm hardness. The desalinated water was then mixed with the adjusted divalent salt fraction to get hardness of 100 ppm, and 600 ppm.	fatigued rats. The weight gain, kidney-body weight ratio, spleen-body weight ratio, and total plasma protein level in the rats showed no significant difference to the un-fed group. However, biochemicals related to fatigue: the ratio of lactic acid elimination to lactic acid increment and the exhausting time were significantly better for the experiment groups.	
UF – NF - RO - RO - Pasteurization & ED - Pasteurization	Study of DSW effect on cardiac abnormally in high cholesterol dietary mice	DSW was obtained from 700 depth below sea level in the outer of Hua-Lien County, Taiwan. DSDW preparation by RO treatment constituted of pre-treatment, UF, NF and two units of RO. Other DSDW was prepared by ED treatment for comparison. Both were also pasteurized at 80℃ for sterilization.	DSDW treatment relieved dietary-induced cardiovascular diseases and improved HDL-C/non-HDL/C ratio and blood pressure in mice. ED-treated DSDW showed better activity in this regards than RO-treated DSDW.	[188]
UF – RO - RO – ED - Pasteurization	Study of DSDW effect on hepatic lipid accumulation and oxidation on mice with a high-fat diet	DSW was pumped from a depth of 618 m in Chisingtan Bay, Hua-Lien County, Taiwan. DSDW was prepared by a combination of RO-ED to prepare DSDW with controlled hardness (300 900, and 1500 ppm) and pasteurized at 80℃ for 60 seconds.	DSDW treatment to fat-diet hamster reduced serum/liver lipids, lipid droplets in liver, liver sizes, serum aspartate aminotransferase and alanine aminotransferase. The treatment also up-regulated hepatic peroxisome, proliferator-activated receptor-alpha, retinoid X receptor alpha, and uncoupling protein-2 gene expression.	[8]
NF – RO – ED	Production of hardness drinking water from DSW	DSW was subjected to both RO and NF to produce pure water and mineral-rich water respectively, RO permeate and NF concentrate were then mixed and further treatment with ED. Operating ED above 20mS/cm allows concentrating Mg and Ca while removing Na and Cl continuously.	Mineral extract with hardness of 12,600 mg/L and Cl concentration of 2,446 mg/L was obtained with this configuration. Diluting this mineral extract ten times would result in DSDW that passed the drinking water standard.	[196]
NF - NF - RO	Production of mineral water rich in calcium and magnesium ions	DSW was desalinated with RO to remove NaCl content. RO concentrate was then treated with NF to retain sulfate ions. The permeate of the first NF was then subjected to a second NF to obtain mineral water rich in magnesium and calcium ions.	Selective filtration by two units of NF may remove sulfate ions from the mineral rich DSW extract. Second NF retentate has Mg and Ca content ranging from 300-5000 mg and 200-2000 mg respectively.	[78]

Due to its high concentration of essential minerals (particularly Mg^{2+}) and the availability of trace minerals, DSDW is considered as water with physiological activity. Katsuda et al. [44] investigated that Mg^{2+} has become the main contributor in DSDW for reducing blood cholesterol level, proven by a slight increase of Mg^{2+} in the serum. The same result was obtained by Fu et al. [9]. They studied DSDW effect in reducing total blood cholesterol which also signed with an increase in Mg^{2+} level in the blood sample. The presence of Mg^{2+} in DSDW is also proven to have antidiabetic and antiobesity effects [61]. Beside Mg^{2+} which has been proven to have antidiabetic and antiobesity effects [61], trace elements in DSW may also have a physiological activity that has not been studied yet. Selenium in DSW is predicted to be able to promote antioxidant and anti-inflammatory qualities as stated by Li et al. [197]. This theory was supported by Yang et al. [198]. In their study, aqueous selenium solution and DSDW successfully reduced intestinal inflammation but not aqueous MgCl solution. Another supportive example was the reduced symptoms of chronic skin inflammation disease, atopic eczema by DSDW intake. Magnesium level in patient’s hair after DSDW treatment did not show a noticeable change. However, selenium level increased significantly along with potassium level [29].

5. DSW mineral extraction using ED and NF

ED and EDR have been employed for many separation industries, such as brackish water desalination; lithium recovery from seawater and brines; salts, acids and bases production; separation of monovalent from multivalent cations; and selective recovery of heavy metals cations from industrial waste [190,199]. The mechanism of separation in ED and EDR processes was explained briefly in the previous subchapter. One important feature in ED method is the selective separation of monovalent ions (e.g., Na^+, K^+, NH_4^+, Cl^-, and NO^{3-}) from multivalent ions (e.g., Ca^{2+}, Mg^{2+}, Fe^{3+}, SO_4^{2-}, and PO_4^{3-}). This process is achievable via the use of monovalent perm-selective IEMs and/or operating at lower current density [190]. Ion perm-selective IEM membranes have fixed functional groups which serve as ion-exchange sites and provide electrostatic interactions with the counter-ions in the solution. Typically, these sites have larger attraction force towards multivalent ions than towards monovalent ion. When ED or EDR are operated at lower current density (e.g. <10 mS/cm), concentration polarization (CP) effects are lower; therefore, membrane selectivity will more likely be governed by the membrane affinity towards ions which are higher for multivalent ions. In result, multivalent ions will be transported at a higher rate [186,190].

Similarly to ED, NF offers a simpler method to separate monovalent and bivalent ions, based on the size of the ion and electrostatic interaction. By this feature, NF has found many applications in separation industries, such as water-hardness treatment [200], metal recovery [201], and heavy metal removal [202]. Heavy metal removal by NF combines the rejection of uncharged components by sieving mechanism and electrical (Donnan) effects between the metal ions in solution and the membrane [203,204]. Therefore, the pore size and the presence of charged groups on NF membrane surface play an important roles in the efficiency of heavy metal removal. NF membrane with smaller pores and highly charged surface provides a better performance in removal of the metal ions. In desalination application, NF is able to remove multivalent anions, such as sulphate up to 99% [205], while rejection of monovalent anions, such as chloride ion which is only 5-45% [206,207]. It is due to the strong electrical repulsion between the negative charges of multivalent anions and the negative charge on membrane surface [208]. Meanwhile, the rejection of cations is high when the they are associated with multivalent anions to maintain electro-neutrality. For example, when sodium is associated with sulphate, the sodium would be rejected to roughly the same degree as the sulphate ion [209]. The uncharged dissolved materials and some positively charged ions can also be rejected if they are larger than NF molecular weight cut off.

ED and NF technologies were involved in the history of DSW exploration, especially those mentioning mineral extraction or selective ion removal from DSW. In 2005, a patent utilized RO-ED membranes to obtain fresh water and mineral water recovery from DSW [49]. A patent published in 2008 used three stages of NF before RO desalination to produce fresh water, the NF concentrate was subjected into monovalent cation selective ED to separate sodium and other foul tasting monovalent ions from mineral water, so it would contain mostly magnesium and calcium [50]. In Wang et al. (2009), RO concentrate was treated with ED to separate divalent salt fraction, and monovalent salt fraction. Next, some of the divalent salt fraction was added into RO permeate water while adjusting the hardness of the product [195]. Moon et al. produced DSDW by subjecting a combination of RO permeate, and NF concentrate into an ED membrane, and thus this method obtained a deep seawater brine, and mineral enriched deep seawater [195]. The latest patent for DSDW production was in 2016 which includes two stages of NF prior to RO desalination; the first NF stage was to remove sulfate ions, the second NF was to extract calcium and magnesium ions while ED unit can be omitted to reduce capital and energy cost [78].

In summary, hybrid configuration of SWRO can solve problems associated with SWRO membranes, i.e. scaling, fouling and high energy requirement. Schematic illustration provided in Figure 5 offers an excellent configuration option for DSW utilization. NF as pre-treatment for DSWRO process can actively reduce microorganism, hardness, and most multivalent ions, and thus reduce the chance of fouling and scaling of the RO membrane as well as lowering energy requirement as a consequence of the reduced osmotic pressure of the seawater. Besides, by this configuration, NF may serve as mineral extractor required to produce DSDW with high essential mineral concentration as well [210]. By configuring NF as divalent ion extractor from DSW, the resulting NF permeate is supposed to have low Mg/Li ratio which is suitable for lithium-ion recovery [211]. ED or EDR processes can further recover lithium for a profound DSW exploration.

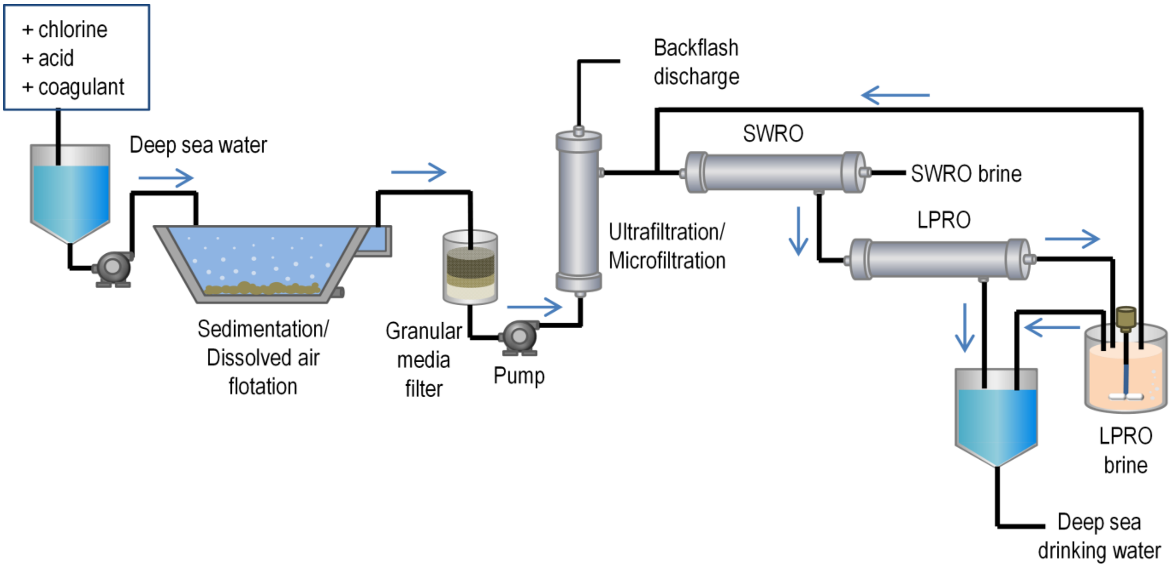

Fig. 4. Schematic illustration of membrane processes for the production of deep-sea drinking water.

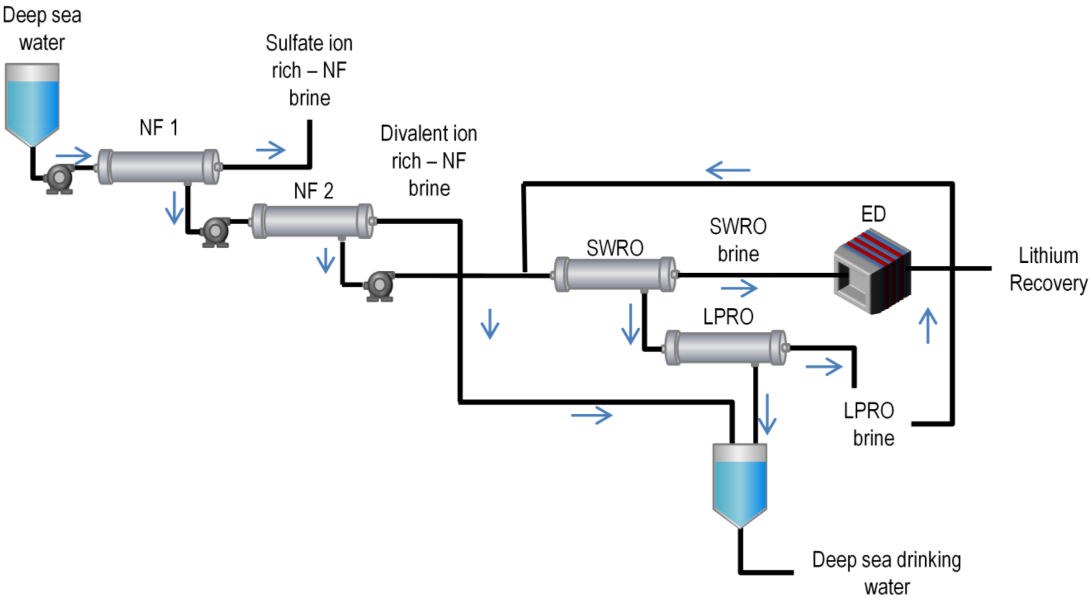

Fig. 5. Schematic illustration of hybrid RO/NF/ED technology for complete utilization of DSW.

6. Conclusion and future prospect

DSW outstanding characteristics led to its wide range of applications particularly DSDW production. The presence of magnesium in DSW was proven for having antidiabetic, anti-obesity, and cardiovascular-diseases relieving activities. Meanwhile, rare trace minerals, such as zinc, selenium, and vanadium, may have a physiological activity which have not not studied yet. They are suspected of having antioxidant and anti-inflammatory qualities. Due to its cleanliness, stable salinity, and unique characteristic, DSDW has much higher economic value compared to plain tap water. Moreover, the concentrated retentate (brine) produced from DSDW preparation could be further concentrated to produce valuable salt, minerals, and rare trace elements such as lithium, uranium, vanadium, rare-earth elements (REEs) and precious metals, such as gold, silver, platinum, and titanium—available naturally in DSW.

Utilization of DSW cannot be separated from membrane technology. RO has dominated the desalination process of DSW. The process is generally composed of intake, pretreatment, RO, and post-treatment. Pollutants, such as microorganisms, biomass, suspended solids, and other chemical contaminants, must be removed to prevent the formation of fouling on the membrane surface. MF, UF and emerging technologies, such as NF, RED, or ED has been studied as RO pre-treatment and illustrated a great improvement in both product qualities and operational costs. In the application of DSW for preparing drinking water, LPRO can be added after SWRO to obtain fresh water with a low concentration of minerals. The fresh water is then mixed with a part of LPRO brine to get drinking water with controlled hardness.

Furthermore, NF and monovalent cation selective ED have great potentials in DSDW preparation as it can remove monovalent ions and recover beneficial multivalent ions. Furthermore, by combining ED with NF, the trace element recovery from DSW has become more feasible since ED can further concentrate the recovered minerals before solidification by evaporation. Therefore, the complete utilization of DSW can be achieved while fulfilling ZLD requirements. Integrating RO desalination of DSW with NF and/or ED or EDR will increase the probability of recovering valuable trace elements from DSWRO brines for additional profits. Further integration with MD and crystallizer would fulfill ZLD requirements and profit from salt and other solid product recovery. By those advantages, further studies in a combination of NF-RO-EDR-MD-C for DSW utilization are needed in the future to optimize the applications of DSW.

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