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Review

A Review on the Near-Future Integration of Microbial Desalination Cell with Reverse Osmosis Technology

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The combined negative effect of both fresh water shortage and energy depletion has encouraged the research to move forward to explore effective solutions for water desalination with less energy consumption. Reverse osmosis (RO), the most common technology for desalination today, uses much less energy than thermal processes. Several modifications and improvements have been made to RO during the last four decades in order to minimize energy consumption, and the process is now near thermodynamic limits. To further reduce energy requirements for desalination, other approaches are needed. A microbial desalination cell (MDC) is a recent technology that could be used as an alternative to RO. An MDC uses electrical current, produced by electrochemically active bacteria, to concurrently generate bioenergy, treat wastewater, and desalinate water. In an attempt to answer the question of whether this emerging technology has the ability to stand alone as an efficient replacement for RO, or it is best if used as an RO pre-treatment setup, this review addresses the recent approaches and limitations of both MDC and RO technologies in order to highlight the near-future application of MDC integration with RO operation.

1. Global Fresh Water Crisis

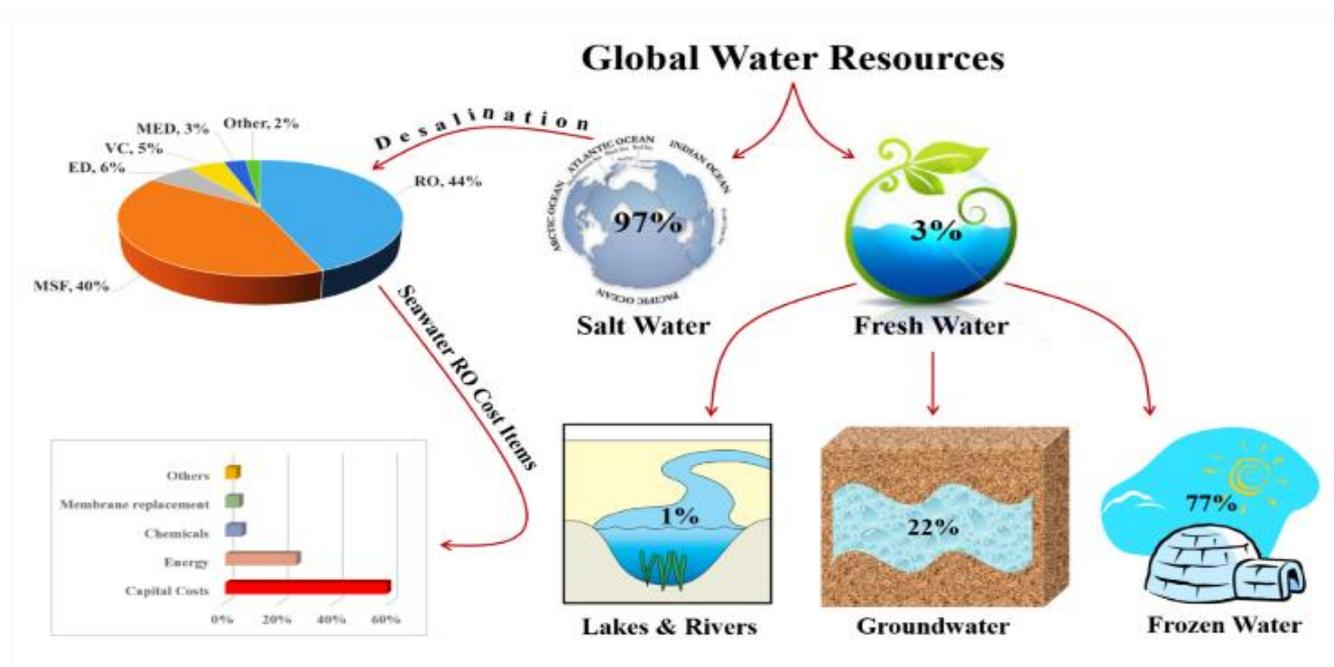


Fig. 1. The global distribution of fresh and salt water resources, with different technologies used for desalination and the main cost items accompanied with the RO as the main wide spread desalination technology. MED: Multi-effect distillation; VC: Vapor compression; ED: Electrodeialysis; MSF: Multi-stage flash distillation; RO: Reverse osmosis.³⁷

Fresh water constitutes a very small percentage of total water on earth, accounting for only 3% with the remaining amount in the form of saline-based and oceans. Moreover, only 1% of fresh water is easily reachable, with the majority of it locked in snowfields and glaciers difficult to obtain due to laborious efforts or lack of significant financial resources. Although desalination technologies are commonly used for producing clean water from sea and brackish water around the world (Fig. 1), most of these technologies require significant capital and energy resources.¹ The shortage of fresh water (salinity < 0.5 g/L) has become one of the major challenges for societies all over the world.¹ All of these technologies still require electrical or thermal energy, with today's reverse osmosis (RO) desalination units consuming 3-5 kWh/m³.¹ Therefore, developing desalination technologies sustained by renewable energy, i.e. wind and solar generated electricity, are being seriously considered.² Alternatively, novel membrane technology is being developed for use with forward osmosis (FO) as a pre-treatment step,³ which reduces the requirement for high water pressure, and hence energy. In the next two decades, it is predicted that the average amount of fresh water per person will decrease by one-third,⁴ with two thirds of worlds' inhabitants living in fresh water-stressed conditions.⁵ Water for agriculture and irrigation accounts for approximately 70% of fresh water use, and may reach 90% in some industrialized nations. Approximately 276 cross-border river basins cover the earth (25% in Europe, 23% in Africa, 22% in Asia, 17% in North America and 13% in South America). Due to topography, weather, engineering, and other reasons, some

areas have ample fresh water, while others are faced by the prospects of drought or polluted water sources. In most of the developing countries, the desalination capability is estimated to increase from 44×10^6 to 98×10^6 m³/day of water in 2015,^{6,7} with energy consumption accounting for 40% of the desalination operating cost. The leading desalination technologies presently used are distillation, RO, and electrodeialysis (ED). Progress on the development of desalination processes and equipment, mainly between 1990 and 2000, rendered these technologies more reliable with diminished capital cost. However, the relatively high energy cost continues to be a major concern.⁸ The present review highlights the potential near-future integration of microbial desalination cell (MDC) with RO system, as one of the novel technologies for economic water desalination in terms of energy consumption.

2. Technological Principles of MDC and RO

MDC technology is a derivative of microbial fuel cell (MFC), in which electrons are generated from the catabolism of microorganisms, which are then passed to an anode across the cell membrane.⁵⁶⁻⁵⁸ Electrons flow from the anode to the cathode, through a connected external circuit, due to the existence of redox potential difference between anolyte and catholyte solutions,⁴⁹ in which electron acceptors are reduced. Once an additional chamber is introduced, between the anode and cathode chambers (which are separated by a couple of ion exchange (IE) membranes), the desalination process may occur.

In such configuration, the MFC is transformed into the MDC mode offering a new method for desalination. The growing bacterial cells on the anode oxidize the organic substrate and trigger the electrons flow, which deploys the migration of anions and cations from the middle chamber towards the anode and cathode chambers, respectively, while simultaneously producing an electric current.^{9,11,13,27,59} The migration of ions to the middle chamber is powered by the difference in potential between the anode and cathode, in which anions (i.e. chloride) move to the anode chamber through an anion exchange membrane (AEM) and cations (i.e. sodium) move to the cathode chamber through a cation exchange membrane (CEM).⁶⁰ Hydrogen ions are consumed in the cathode chamber as they react with oxygen and electrons to form water, with the charge being equalized by the transient cations (Na^+) from the desalination chamber across the CEM towards the cathode chamber. This process can reach a desalination level up to 99% while, concurrently, produce energy. That's why MDC technology could be considered a promising approach for concurrent desalination and energy generation.^{9,13}

While MDC uses electromotive force produced by the bacteria to desalinate water, RO uses external energy source to pressurize salt water to be desalinated. Normally, the RO membrane is fabricated from a polymer material with layered network structure. It permits filtration by pore flow, as a positive hydrostatic pressure is applied on the fluid to be forced through the membrane. Therefore, the filtered water follows a twisted pathway across the membrane to pass to the permeate

side. The fluid flow is influenced by the membrane permeability, the portion of membrane volume containing void gap which can hold liquid, and the ratio between the travelled distance by liquid across the membrane to the membrane thickness.⁶¹ While monovalent ions and the tiniest contaminants could be rejected by RO membrane, additional nanofiltration (NF), microfiltration (MF) and ultrafiltration (UF) membranes are usually utilized to block larger size contaminants.

Fluids transport across the RO membrane is controlled by a mechanism called "solution-diffusion", in which the open channels used for pore flow are absent.⁶² Hydrostatic pressure, higher than the osmotic one of the solution, is required to operate the RO membrane. The positive pressure difference develops a transversely chemical concentration gradient through the membrane that pushes the liquid across the membrane in a direction opposite to the natural osmosis, i.e. the migration of water molecules from high concentrated area to low concentrated area. In the meantime, salts are rejected and concentrated on the membrane inflow surface.⁶³ The power required to pump the water influent represents the main energy consumed by RO systems and is directly affected by the flow rate and feed pressure.³⁷ Hydrostatic pressure up to 7 MPa is required for the high salt content of seawater. The greater the salt content, the higher the pressure required to generate a preferred permeate flux.

3. Desalination Setups

The first small-scale setup of MDC was presented in 2009 by Cao *et al.*, who used a salt water chamber with a volume of 3 mL, later increased to 1 L in a larger scale MDC created by Jacobson *et al.*^{9–11} Since then, the MDC technology has evolved on several fronts including reactor design, process, and

decade, to increase product permeability, and as a result, RO membranes were then used for seawater desalination.¹⁵ Nowadays, more than 15,000 desalination facilities are operating around the world, with about half of them applying RO technology. Approximately half of the world's desalination

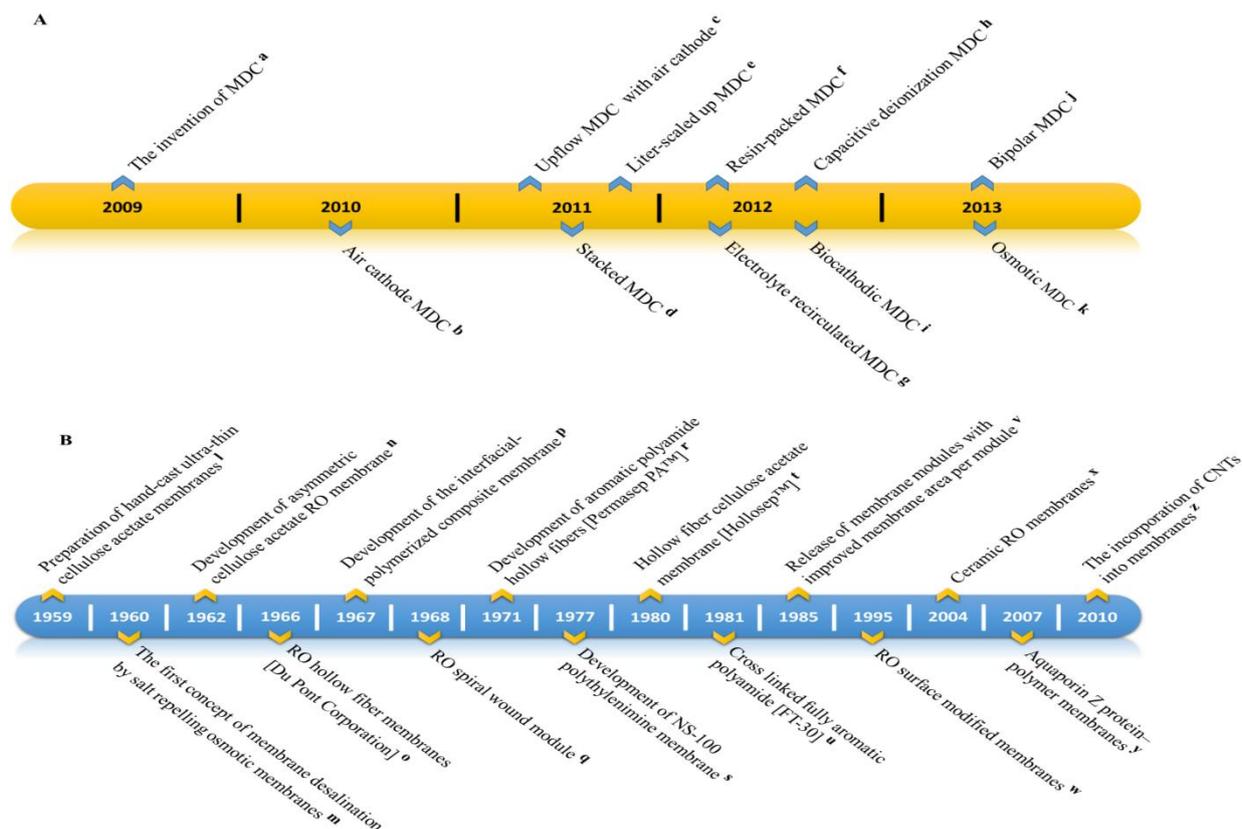


Fig. 2. The timeline of the key milestones developments of (A): MDC and (B): RO; a:¹¹, b:¹³, c:⁹, d:^{22,23}, e:¹⁰, f:^{35,120}, g:²⁷, h:¹²¹, i:¹²², j:³⁰, k:³², l:¹²³, m:¹²⁴, n:¹²⁵, o:¹²⁶, p:¹²⁷, q:^{128,129}, r:¹³⁰, s:¹³¹, t:⁷⁸, u:¹³², v:⁷⁸, w:⁷⁸, x:¹³³, y:¹³⁴, z:¹³⁵.

productivity (Fig. 2A).¹² In most lab-scale MDC setups, the anolyte contains a synthetic substrate solution, i.e. acetate, while the catholyte contains efficient ferricyanide or the applicable dissolved oxygen as a terminal electron acceptor, and NaCl is used as a salt solution.¹³ Contrary to the infancy of MDC technology, RO was introduced almost 40 years ago. Remarkable advancements in fabrication and materials of RO membrane, over the last four decades, positioned RO technology as the main option for new desalination plants (Fig. 2B). Seawater distillation facilities were initially established in the 1950s, with the first application on the industrial level launched in Kuwait in the 1960s. After these initial trials, membranes started to be commercially available with the first RO facilities running brackish water feed in the late 1960s.¹⁴ Membrane materials were further improved in the following

capacity is located in the Middle-East, which has been the pioneer in industrial-scale seawater desalination. In 2005, two seawater reverse osmosis (SWRO) desalination plants were commenced by United Arab Emirates and Israel, with production capacities of 454×10^3 and 330×10^3 m³/day of fresh water, respectively.^{16,17} The key milestones along the evolution path of both MDC and RO technologies are summarized in Fig. 2. The main configurations of both MDC and RO technologies are schematized in Fig. (3 and 4), and reviewed in following sections.

3.1. MDC Configurations

Microbial electrodesalination cell (MEDC) and MDC are among the bioelectrochemical systems (BESs) developed recently for saltwater desalination at reduced energy consumption (Fig. 3). After the invention of MDC by Cao *et al.*,¹¹ it has been demonstrated that 93% of used 35 g/L NaCl solution could be removed via the MDC, which was later successively improved by incorporating air cathode.¹³ MEDC was combined with each of the MDC and microbial electrolysis cell (MEC) to reject 68% of 20 g/L NaCl and 99% of 10 g/L NaCl, respectively.^{18,19} Furthermore, in order to improve the desalination rate of MEDC, Chen *et al.*^{20,21} proposed the microbial electrolysis desalination and chemical-production cell (MEDCC). Results obtained from all these experiments confirmed the potential for high desalination efficiency of MDC, and its suitability for being utilized as either a stand-

alone technology, or pre-treatment process for the conventional desalination technologies.

The configuration of an MDC setup has improved through the use of stacked cells to enhance the effectiveness of charge transfer,^{22–24} or by applying up-flow tubular reactors for potential scale-up.^{9,10} Such stacked or up-flow MDC types were built to enhance the desalination rate.^{9,22,23} It was found that the desalination capabilities of the MEDCC and stacked MDC (SMDC) are around 1.4 times that of the classical three chambers desalination reactor.^{20,22} Also, MDCs connected in series can remove up to 44% salinity of 60 mL synthetic seawater using only 120 mL of anolyte.²³ MEDCC is one of the multi-chamber designs used to improve desalination rate of MDC coupled with the production of some byproducts. This could be accomplished by assembling four chambers, in which

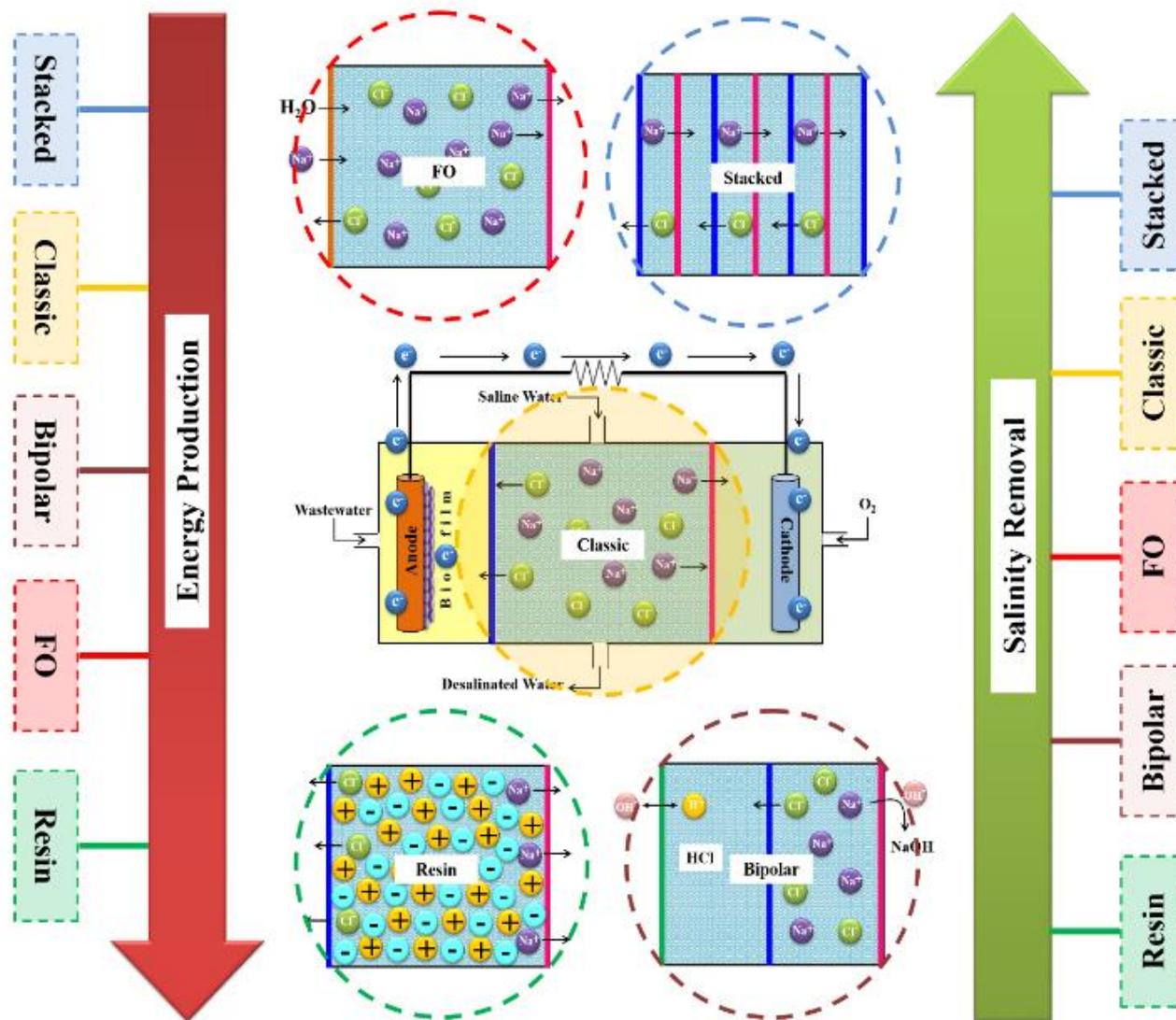


Fig. 3. Schematic diagram of the various types of MDCs configurations based on the unique features of their middle chamber. The centred design represents the classic three chambers setup, with focus on the middle chamber of the other four designs. The green and red arrows indicate the increment and decrement trends of salinity removal and energy production, respectively, for different MDC types.

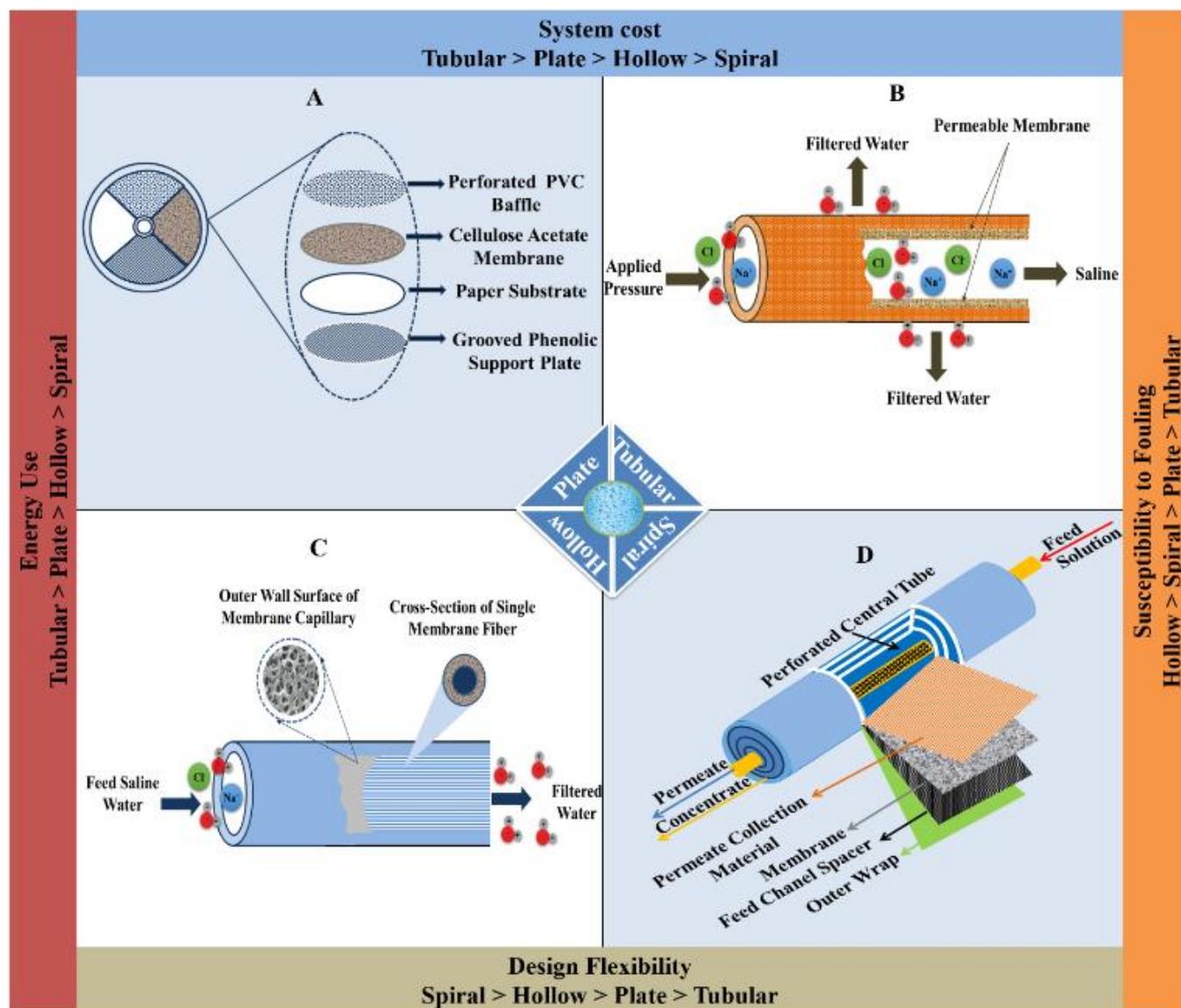


Fig. 4. Schematic diagram overviewing the various types of ROs membrane modules and their main features.¹³⁶

an acid-production compartment is inserted between the anode compartment, and the AEM and equipped with a bipolar membrane (BPM), which has the ability to split water into OH^- and H^+ , to simultaneously produce hydrochloric acid, sodium hydroxide and desalinate saltwater.^{21,25,26}

Several trials were conducted to recirculate the electrolyte between the cathode and the anode for the pH buffering, in order to diminish the operating cost of the catholyte buffer solution.^{27,28} In order to achieve this, novel strategies were followed, such as incorporating BPM to generate alkali and acid,^{21,29–31} or using an external voltage to generate hydrogen gas in the cathode compartment.^{18,19} It was observed that the recirculation can effectively overcome large deviations in pH. However, with recirculation, the capacity of desalination was limited by the mandate to operate the MDC as a single cell in

fed-batch running mode. Although continuous mode of operation has been applied to enhance the productivity of MDCs, the cathode or anode solutions were recirculated only within the same electrode compartment during earlier trials.^{10,23} Also, the increase of the anode solution volume¹¹ or the addition of bases or acids²² are among other options used to reduce the negative consequences of pH on electrode productivity.

Further improvement of desalination performance was attained by replacing the AEM with FO membrane to achieve water dilution, resulting from water drawing out from wastewater, along with desalination powered by electric potential.^{32–34} Within the same context, low-salinized water was also treated by MDC equipped with ion-exchange resins.^{35,36}

3.2. RO Configurations

The RO process set-up has a quite simple design comprising feed water input, feed pre-treatment unit, high pressure pump, modules for the RO membrane and, in some configurations, post-treatment stages. The four different types of RO membrane modules that are used for desalination processes are the spiral, hollow fiber, tubular and plate and frame modules (Fig. 4).³⁷

Plate-and-frame is old RO module made up of layers of supported plane sheet membrane, with a spacer between each support and membrane in order to drive the feed through each membrane while flowing the permeate outside the module (Fig. 4A).^{38–40} Although this type of module is fouling resistant, it has a low packing density which puts a lot of demand on space requirements making it a high cost option. Another RO desalination configuration is the tubular membrane units, which comprise membrane tubes wrapped around punctured stainless steel cylinders (Fig. 4B). The feed runs across the tubes and the permeate flows out from the membrane and support.^{38,41} The tubular modules share the same advantages and disadvantages of plate-and-frame one, and as a result they are both used mainly for extreme foul feeds. In order to overcome the disadvantages of above types, hollow-fiber modules were invented with a large packing density, in which multiple fine hollow fiber membranes are laid in a pressure vessel, and the feed runs outside the membranes (Fig. 4C).^{38,39,41} While these units have high productivity per module, they are highly susceptible to fouling and thus not practical for use in some applications.

One of the most widely used modules, nowadays, is the spiral-wound. A spiral-wound module contains plane layers of membrane parted from each other by spacers wrapped around a punctured collection tube (Fig. 4D). The feed flows across these wrapped membrane layers while the permeate flows through the membrane to the collection tube.^{38,41} This type of module has a high packing density along with reasonable fouling resistance. Moreover, this is the cheapest module setup to be produced from flat sheet thin film composite (TFC) membrane.^{42,43}

In addition to the development of spiral wound module several decades ago, progresses on materials, manufacturing techniques, feed channels and the size of vessels and spacers have contributed to better adjustment of the internal fittings between module elements and liquid transport features, thus reducing both pressure drop shortfalls and fouling. The sales of spiral wound modules made from polyamide (PA) membranes are currently leading the RO/NF market (91%), followed by the hollow fiber modules made from asymmetric cellulose acetate (CA) membranes.⁴⁴ Although the PA membrane has a high salt rejection and efficient energy consumption, the CA membrane is superior in chlorine resistance, allowing it to inhibit the growth of microorganisms by chlorine disinfection.⁴⁵

4. Limitations and Challenges

In spite of its advantages of lower energy and chemicals consumption, and the added value of wastewater treatment, the MDC technology currently suffers from a number of limitations. One of such limitations is the inability to produce huge amounts of concentrated acid or salt solutions by IE process, for strong or weak acid cation exchange resins, respectively. Moreover, prolonged time is typically needed by MDC process due to the decelerated anodic biological metabolism.⁶⁴ Also, the existence of competitive ions, other than those representing hardness, consume electrons and consequently reduce desalination capacity. Another key challenge with the MDC process is the gradual increase in salt concentration in the anode and cathode compartments upon the removal of these salts from the middle compartment, which leads to highly salted anolyte and catholyte.⁶⁰ Even though, the accumulation of these ions can be suitable for wastewater treatment as it promotes conductivity.^{59,65} It is worth mentioning that RO membranes suffer from the same phenomenon due to the accumulation of chlorine ions on the membrane (i.e. commercial PA) resulting in the degradation of membrane.⁶⁶ The power generation from complex wastewater is considerably lower than that from simple substrates, because of the low conductivity, buffer capacity and biodegradability of wastewater.⁵⁹

Throughout the desalination process by MDC, ohmic resistance considerably increases as water conductivity and salinity decreases, limiting electricity production and desalination speed, particularly for low saline waters.^{11,13,22} The different ions existing in water influence the efficiency of MDC productivity in several ways. For instance, soluble cations, i.e. Mg^{2+} and Ca^{2+} , may deposit on the surface of the membrane causing the scaling phenomena, in which the flow of ions through membrane is hindered and the electrical resistance of MDC is substantially amplified. In addition, a possible reaction between these ions and the natural organic matter in water may develop compressed fouling layers on the surface of an operating membrane.^{67,68} Furthermore, anions, i.e. SO_4^{2-} and NO_3^- , that moved from the salt water to the anolyte, may affect the functionality of the anode as the electron accepting electrode, which eventually leads to electron loss and decreases system output.⁶⁹ Additionally, the molecular size and ionic strength of various ions may differ considerably, which influence their transfer activity in salt water. It was noticed that the MDC productivity is reduced by 22% when synthetic seawater was fed into the desalination compartment to substitute pure NaCl solution.¹⁰

In the same context, membrane fouling is one of the main obstacles for the efficient (SWRO) desalination process.⁷⁰ Biofouling is an important phenomena that occurs as a result of a microbial adhesion or absorption on the surface of the membrane, developing a gluey polymeric layer of biofilm (transparent exopolymer particles (TEP)).⁷¹ Such polymeric biofilm is hard to regulate and eradicate, leading to reduced flux and overall decline in productivity.⁷⁰ Biofouling depends

on many factors including the existence of organics and microbes in water, oxygen accessibility and temperature.⁷² Therefore, biofouling in membrane-based desalination techniques is very difficult to control compared to other fouling types, which could be overcome by proper physical or chemical procedures.

Another major challenge is the scale-up of the MDC system, where the liquid volume in the real practical applications of MDC can range from hundreds to thousands cubic meters.⁶⁴ Regardless of the MDC configuration, i.e. tubular or stacked, the MDCs are commonly constructed out of three compartments enclosed in a reactor; salt, anode, and cathode. Altering the liquid volume or replacing any of the separate chambers, while carrying out maintenance or responding to operational problems, would require the disassembly of the whole setup. This lack of sub-modular assembly of an MDC is a real practical obstacle towards the fulfilment of the vision for large-scale MDC setup comprising several MDCs modules.⁷³ One of the concepts introduced to overcome such scale-up obstacle suggests the insertion of multiple chambers between the same electrodes. However, pH imbalance may occur between the anode and cathode compartments. A pronounced decline in anode pH below 6, as a result of the discharged protons, will hinder microbial metabolism and can limit the interval of the desalination cycle.^{11,18} Protons are then consumed in the cathode chamber leading to pH increase and subsequent potential loss of 95 mV for each pH unit, which considerably reduces the reactor productivity.^{18,27,74–76} Similar effect of pH was also observed on RO membrane. However, such effect depends on molecular size as well as ionic charge. Fluctuations to the feed pH may change the charge of the membrane surface, which may consequently influence the membrane productivity.⁷⁷ On the other hand, although RO for seawater desalination has been commercially scaled-up for several decades, it is still suffering from the major problem of its high capital investment as well as increased operating costs, which must be reduced in order to be affordable by developing countries. On the other hand, although RO for seawater desalination has been commercially scaled up for several decades, it is still suffering from the major problem of its high capital investment as well as increased operating costs, which must be reduced in order to be affordable by developing countries. Energy, chemicals and labor contribute to around 87% of the entire RO costs.⁷⁸

5. Evaluation of Desalination Process: MDC versus RO

5.1. Membrane Efficiency

As MDC uses AEM and CEM between the desalination compartment and the anode and the cathode compartments, respectively, it is mainly considered as a membrane-reliant technique, where the features of membrane are vital to MDC's productivity. It was observed that the desalination performance of MDC can be improved by 50% to 63% by increasing the

capacities of the IE membranes.¹³ Nevertheless, assessment of permanence and reliability of the membranes used in MDCs after prolonged operation is still blurry and does need more focus and research. Membrane scaling and biofouling are among the main reasons for low productivity in conventional electrodialysis desalination technologies, as they elevate the internal resistance and decreases both the permeable membrane selectivity and current.⁷⁹ The AEM in MDC is more prone to biological and organic fouling compared to the CEM due to microbial attack and wastewater in the anode compartment. The extra cellular production of polymeric materials by the biofilm, as an interconnected and adhesive matrix, may lead to membrane fouling.^{80,81} Alternatively, the surface scaling of CEM may also occur as a result of inorganic precipitations, i.e. magnesium and calcium hydroxide⁸² and phosphate, when ferricyanide is applied as the cathode solution.⁸³ This was confirmed after eight months long operation of MDC, in which the membrane biofouling on the AEM was identified as the main reason leading to degradation in performance due to associated ion transfer inhibition and enhanced internal resistance. It was also observed that the current density, desalination rate and Columbic efficiency were reduced by 47%, 27% and 46%, respectively, whereas the organic matter removal remained constant. The CEM was entirely concealed by crystalline sphere-shaped aggregates with a rough texture, while, a smooth layer was noticed on the other side of the membrane fronting the middle chamber of the cell. On the other hand, a sparingly crystalline flakes were distributed on the used AEM surface facing the desalination chamber.⁸² Moreover, the increase in anolyte acidity (i.e. pH drop from 7 to 5.4) and catholyte alkalinity (i.e. pH increase from 7 to 9.5) negatively affect the MFC performance,⁸⁴ in terms of electrode potential, voltage and power density.⁸⁵ Accordingly, BPM was suggested to work as a separator in MFC in order to maintain neutral pH in the cathodic and anodic compartments.^{86,87}

The BPM is an alternative type of the electro-filtration membranes, in which a functionalized membrane composite containing interchangeably anion exchange and cation exchange layers, can separate water to H^+ and OH^- concurrently between both layers under electrical field.^{88,89} Therefore, BPM can generate alkali and acid *in situ*, i.e. NaOH and H_2SO_4 from Na_2SO_4 , thus considerably decreases the cost of alkali and acid.^{90,91} Nevertheless, neutral pH was not strictly maintained due to low water ionization efficiency of BPM.^{86,92} The large polarization resistance of BPM is an additional disadvantage, which could lead to drop in the MFC voltage and power density.⁹³

On the other hand, FO membranes could be utilized in bioreactors to recover water during wastewater treatment.^{94–96} The FO pressure gradient between solutions of high and low water chemical potentials is employed to power the flow of water through the semi-permeable FO membrane.³ Under such conditions, water naturally flows, without the need for hydraulic pressure, resulting in a process with less consumed energy, as compared to RO.^{97,98} The low tendency for membrane fouling represents additional advantage of the FO

technology,⁹⁹ with an improved removal of wastewater derived impurities upon the use of wastewater as the feed solution.¹⁰⁰ FO is less prone to fouling compared to RO due to the difference in desalination driving force, i.e. osmotic versus hydraulic pressure, respectively.³ Alternatively, the low rate of water flux and the leakage of some solutes (e.g. NaCl) through commercial FO membranes are among the main disadvantages of FO process.¹⁰¹ FO membrane has been employed in a microbial osmotic fuel cell (MOFC) between the electrodes to recover desalinated water while generating power. Earlier setups applied aeration at the cathode compartment, counterbalancing the gains in power production by its consumption for cathodic aeration.³²

In contrast to electro-filtration membranes in MDC, the osmotic size-exclusion filtration membranes are commonly used in RO plants. RO membranes range from cellulosic and aromatic PA to TFC membranes. Cellulosic membranes are fabricated from thin materials with dense porous in the form of hollow fibers or sheets. On the other side, aromatic PA membranes, are relatively similar to cellulose with an improved reaction towards organic substances and high durability. The TFC membranes are fabricated from thin dense membrane with high salt rejection capability, which is then placed on the surface of a porous material.¹⁰²

Based on the aforementioned discussion, the two major membrane options for MDC and RO to produce desalinated water are IE and RO membranes, respectively. Both IE and RO membranes are well developed with progressive levels of improvement. Although both membranes are pre-treated to eliminate suspended solids to circumvent fouling, IE membrane is more resistant to suspended solids.¹⁰³ Also, membranes are exposed to scaling by the feed water hardness, which needs either to be softened, as a part of the feed solution pre-treatment process, or to be eliminated by the utilization of anti-scaling chemicals. However, both membranes could suffer from fouling by organic materials present in the feed solution. Nevertheless, IE could be easily cleaned, compared to RO membranes.¹⁰⁴ Other than its main utilization in desalination process, IE is also employed as a post treatment for eliminating boron in some desalination factories. Commonly, the exclusion of boron with RO is achieved at pH 9. At this pH, boron has a partial negative charge and the rejection efficiency can reach 90% with SWRO. However, further RO processing of the first permeate is required, i.e. by a complete or partial dual pass scheme, in order to obtain less than the target 0.5 mg/L boron concentration in permeate, and the pH in this case, needs to be adjusted before the second pass. Post treatment with IE membrane could be a good replacement for this process.¹⁰⁵ The same process could be also applied to selectively eliminate several heavy metals, e.g. arsenic, after RO process. Although, the IE membrane has innate characteristics that render its performance effective at eliminating ions with lower molecular weight from a feed solution. It is not efficient in removing immobile high molecular weight or non-charged ionic components. This could be a drawback when fresh water is generated from a feed solution with heavy suspended solids or

microorganisms. In such case, pre-treatment is required before the desalination process.¹⁰⁶

5.2. Desalination Capacity

Desalination in the various three-chamber configurations of MDCs may exceed 90% from initial concentration¹⁰⁷ of 30-35 g/L of NaCl solution, which is the typical concentration of seawater (Table 1). Unfortunately, high desalination rate requires huge volume of fresh water, for the anolyte as well as the catholyte, accounting for 55 to 133 times the capacity of desalinated water.¹²

The desalination capacity of MDCs can be improved by loading several membrane pairs between cathode and anode.^{13,18,19,22,23,27,33,59} However, in early versions of SMDC, as that demonstrated by Chen *et al.*²² in which they introduced dual cell pairs between the air cathode and anode, the desalination productivity was reduced due to internal resistance developed by wide desalination compartments (~1 cm). Kim and Logan suggested some novel approaches to overcome complications related to SMDCs, including the use of seawater catholyte to exclude chemical buffers, the integration of effective water flow setup across the stack and the decrease of ohmic resistance by minimizing the thickness of the utilized stack. Accordingly, a novel flow setup was evaluated, where the dilute and concentrate solutions are running in series inside each desalination cell in the stacked setup which led to improved desalination rate and efficiency.²³ Another reported problem with SMDCs is the migration of the diluted water to the concentrate as a result of osmosis. This phenomenon can be diminished by decreasing the hydraulic retention time or the membrane area. In this context, the reliable method to improve the desalination performance is to connect seawater flows to several MDCs in series, rather than adding multiple stacks in single MDC unit.²³

Furthermore, the use of SMDCs may decrease the requirement for huge volumes of salt-free electrolyte. Desalination efficiencies up to 98% may be obtained from NaCl feed with 35 g/L employing five cell pairs of SMDCs. In such configuration, the SMDC used about 13 times less anode solution amount of fresh water,²³ compared to standard MDC. Luo *et al.*¹⁸ achieved desalination efficiency of 99% from 10 g/L NaCl with the ratio of salt-free electrolyte to desalinated water was around 14. These findings demonstrated the effect of the initial percentage of water salinity on the required volume of wastewater in MDCs.

The salt permeation is influenced by the amount of both divalent ions and total dissolved solids (TDS) in solution, as a result of reactions between the membrane surface and the ions.³⁷ The total surface charge on RO membrane is negative, which allows the repelling of negatively charged molecules or ions,¹⁰⁸ and the presence of more cations in the vicinity of membrane surface, resulting in electric potential recognized as Donnan potential phenomenon.^{109,110} Although this phenomenon facilitates the repelling of ions from the membrane, its

influence diminishes with high divalent ions or salinity content. The variation of the extent of salt removal of a particular membrane on the composition of water and the strength of membrane charge. Bartels et al.¹⁰⁹ observed the increase in salt permeation, using a number of RO membranes for brackish water, from around 0.4% to 2.6% upon an increase from 1 to 10 g/L NaCl.

By any standard of judgment, the MDC technology today is in its infancy in spite of the progress made over the past five years. Accordingly, it is conceivable that MDCs be only partially integrated in the existing desalination technology of seawater, rather than being considered as a replacement of RO technology. With such mindset, one may think of MDC technology as a pre-treatment step for RO process. Since the RO process efficiency largely depends on feed water salinity, in which salt permeation through the membrane increases proportionally with salt concentration of the feed water, pre-treatment of the feed water with MDC will reduce its salinity and, hence, contributes to RO process efficiency.

of 1 m³ of wastewater.¹⁰⁷ This emphasizes the ability of MDC technology to concurrently treat wastewater and generate energy in the form of hydrogen gas or electricity.^{10,11,18,23,59,82} The power densities generated by the MDC were comparable to those generated by single chamber MFC without desalination compartment (Table 1). The obtained recently demonstrated efficiency 86%, corresponds to the splitting of 4.3 pairs of sodium and chloride ions for each electron travelled over the circuit. Studies reported an increase in H₂ energy production of 180 - 231%, compared to the input energy, upon the desalination of 5 - 20 g/L NaCl solutions.^{13,18} Another study estimated that liter-size MDC can generate up to 58% of the electrical energy required for the operation of a RO system.¹⁰ Also, the power density was enhanced by 33% by utilizing recirculated MDC.²⁷

6. RO and MDC: Reality and Prospects

The concurrent consideration of water recycling and desalination is a strategy for developing the available sources of

Table 1 Comparative overview of some MDC and RO modules and their productivities.

Desalination Technology	Configuration	Membrane Type	Feed NaCl ^l Solution (g/L)	Salinity Removal (%)	Power Density (W/m ³)	Energy Consumption (KWh/m ³)	Water Flux	Ref.
MDC ^d	C-MDC ^c	IE ^h	35	9.5	3.1	-	N/A ^m	111
			35	90	31	-	N/A	11
	MOFC ^d	FO ⁱ + IE	35	95.9	2.44	-	0.82 L/m ² .h	34
			35	35	43	-	4.1 L/m ² .h	32
			30	99	30.8	-	N/A	9
UMDC ^e	IE	30	99	30.8	-	N/A	112	
RO ^b	SW ^f	PA ^j	32	99	-	2.32	28 m ³ /day	78
					-	2.88	24.6 m ³ /day	113
					-	4.35	21.5 L/m ² .h	114
HF ^g	CA ^k	35			-	5	63.5 L/m ² .h	114

^aMDC: Microbial desalination cell; ^bRO: Reverse osmosis; ^cC-MDC: Classic MDC; ^dMOFC: Microbial osmotic fuel cell; ^eUMDC: Upflow microbial desalination cell; ^fSW: Spiral wound; ^gHF: Hollow fiber; ^hIE: Ion exchange; ⁱFO: Forward osmosis; ^jPA: Polyamide; ^kCA: Cellulose tri-acetate; ^lNaCl: Sodium chloride; ^mN/A: Not available.

5.3. Energy Consumption

The sustainable recovery of fresh water by desalination of saltwater has considerably improved in the last century. However, the process is still challenged by high energy consumption.⁶⁰ As mentioned earlier, it is expected that the global capacity of desalination will escalate to 140% in 2015 with 40% of the overall desalinated water cost¹¹⁵ attributed to energy consumption during the process. The focused efforts on reducing concentration polarization and fouling, along with increasing energy recovery and permeate flux, have diminished the energy usage from 12 to 3.7 kWh/m³ over the period from 1970s to 2006, respectively.⁷⁸

The developing MDC technology is considered as an energy saving, cost-effective and eco-friendly desalination method. MDC operates under neutral pH, pressure and temperature conditions,¹¹⁶ and utilizes the produced bioelectricity to achieve desalination. It is predicted that around 1.8 kWh of bioelectricity can be produced from MDCs from the handling

fresh water,¹ and therefore is indeed relevant for fulfilling the escalating universal demand for fresh water. Thermodynamically, the required energy to retrieve 50% of fresh water, from a 35 g/L TDS simulated seawater solution by RO, is 1.06 kWh/m³.¹¹⁷ At the maximum efficiency of SWRO configuration, an energy consumption of 1.8 kWh/m³ was reported,¹¹⁸ not counting the energy required for the pre-treatment of feed solution and pumping. However, this value increases to 3-4 kWh/m³ once the energy consumption of the entire system is considered.¹¹⁷ Such significant reduction in energy consumption is a direct result of the focused attention RO technology has attracted over the last five decades, as evident from the number of publication on this technology. Fig. 5 shows that searching 'ScienceDirect', using the keyword 'reverse osmosis', reveals that an almost 65% growth in the total number of scientific publications over the last two decades (1995 - 2014). Also, the reported consumed energy by the RO process tremendously decreased over the recent years, with notable increase in flux and salt rejection. Further reduction in

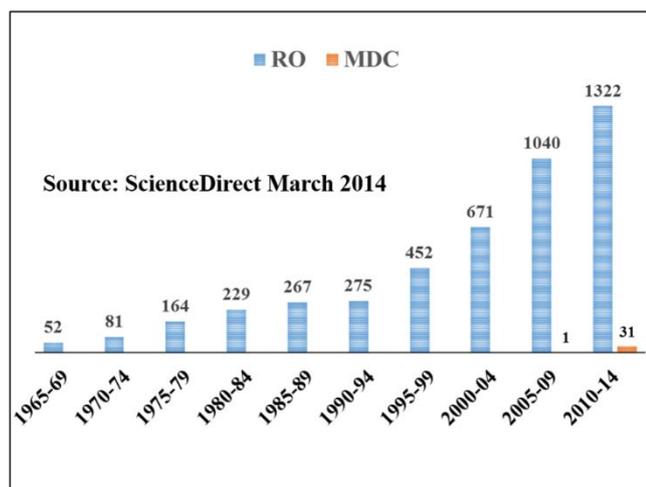


Fig. 5. Histogram highlighting the scientific progress in MDC and RO based on the number of articles in the "ScienceDirect" database till March 2014.

energy consumption for seawater desalination will require novel approaches and strategies. On the other hand, 'ScienceDirect' search with keywords "microbial desalination cell" returns only 32 articles published over five years (2009 - 2014) (Fig. 5). In addition to the obvious need for more work to understand the fundamentals of the MDC, scale-up, engineering, reliability and performance challenges are yet to be investigated at a reasonable level.

The energy required for RO decreases with the decrease in the salinity of the feed water. Accordingly, decreasing the conductivity of the salt water by 60% or more would significantly help in reducing the overall amount of energy consumed by the RO modules. This suggests that MDCs may be advantageous as a pre-treatment process for water desalination by RO. Also, the MDC importance is magnified, due to the production of more than 82% of the total desalination volume ($441 \times 10^5 \text{ m}^3/\text{day}$) from saline water (63% from seawater, 19% from brackish water and 5% from wastewater sources).⁷ The ability to remarkably decrease the saline content of the feed water without any external energy source may be considered a promising approach to cut-off energy expenditures for water desalination. Thus, the MDC is proposed as a preceding partial desalination step for RO.¹³

Recently, a configuration termed as upflow MDC (UMDC), was proposed by Jacobson et al.¹⁰ to examine the durability of the scaled-up 2.7 L MDC. It was observed that the UMDC could generate 58% of the theoretical electrical energy required for the RO process. In a setup that uses the UMDC as a preceding desalination step for RO process, if the UMDC removes 30% of TDS in saline water, the energy requirement for RO process will then drop from 3.7 to 3.5 kWh/m³ due to reduced salinity. Also, the bioelectricity generated in the UMDC can additionally decrease the energy consumption to 2.9 kWh/m³, restoring about 22% of overall energy cost of an RO system without the UMDC.

The UMDC configuration of Fig. 6 was proposed as an

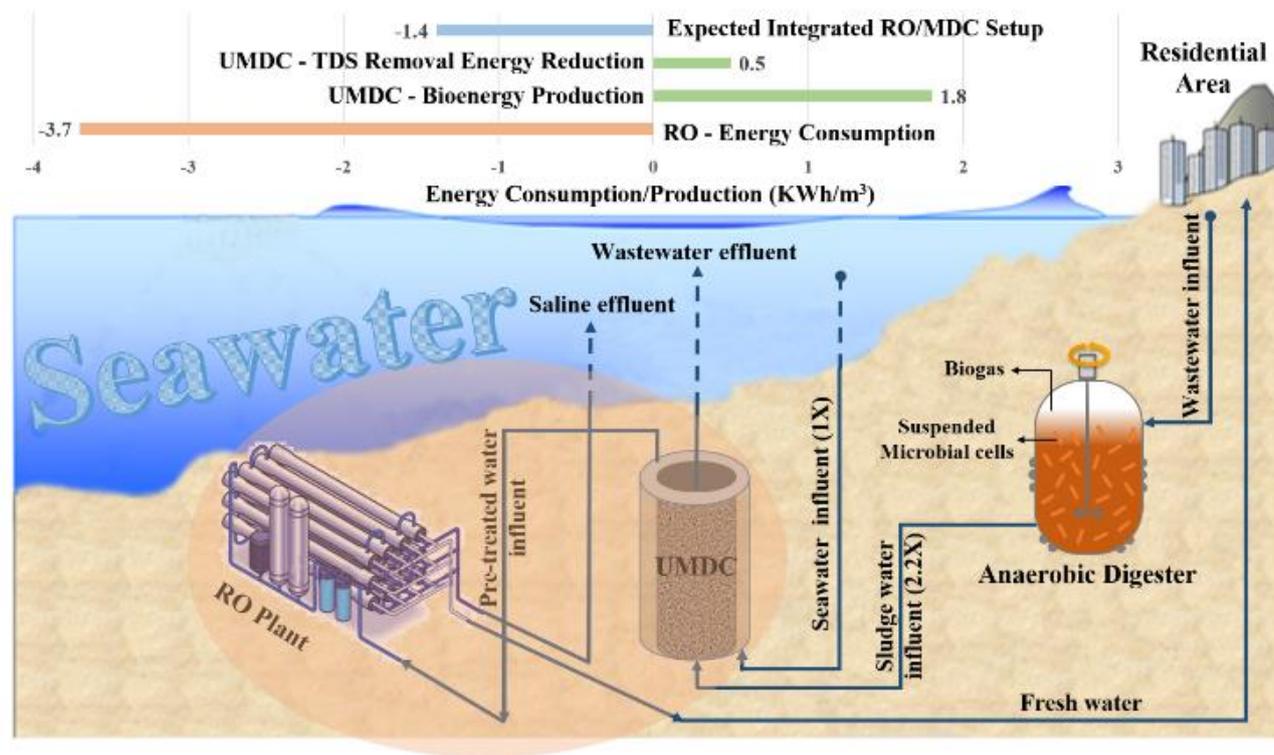


Fig. 6. Graphical diagram exemplifying the assumption of the UMDC integration with RO system as a pre-desalination step and its impact on net energy gain.¹⁰

example of a scale-up integrated loop for efficient and economic utilization of MDC as a pre-treatment technology for RO. The integrated loop includes the initial treatment of municipal wastewater in anaerobic reactor to produce biogas, and in the meantime using the effluent of the reactor as a fuel for the UMDC, which is used to desalinate seawater partially (70%), before it is fully processed by the RO membrane modules. However, industrial scale integration between MDC and RO systems requires innovative scale-up designs and integration schemes.

7. Concluding Remarks

In spite of the prospective advantages, there are several endeavours before the real practical application of MDCs is realized. This is partly due to the increased capital investment accompanied with the bioelectrochemical technologies, as well as the low water productivity of MDCs. The MDC needs a longer retention time than RO process, in order to obtain comparable water production, which may be balanced by the great volume of the reactor, irrespective of the high capital costs. MDC reactor could have a complex assembly that may require more consideration on maintenance and operation,⁶⁴ among which developing effective method to reduce or clean the membrane fouling. The scaling up of MDC from lab to applied scale requires step-wise increments of the desalination bioreactor volume from milliliters to several liters, and then to the industrial scale cubic meters, while at the same time performing research to recognize the main limiting aspects at the larger scale. The whole desalination efficiency could be improved by installing stacks of IE membranes between the working electrodes to develop the exchange of charge per electron shuttled to the circuit, and by running the saline water across multiple MDCs, connected in series, to improve the desalination degree.^{22,23} The advantages of wastewater treatment in MDC must also be considered, since MDCs are a combined method of both water desalination and wastewater treatment. This system best to be constructed in a location near wastewater and saline water sources.¹¹⁹

To recapitulate, MDC technology has a promising potential as a sustainable process for water desalination, compared to more conventional technologies of desalination, i.e. RO. MDCs could be either employed as a stand-alone technology for distributed water treatment and recycle or integrated with the traditional membrane-based RO to decrease salinity of the feed water and subsequently reduce energy requirements. The later approach seems to be more appropriate in the near future, unless the efficiency and durability problems of MDCs are fully explored.

Acknowledgements

Dr. Ahmed ElMekawy acknowledges the Egyptian government for the ParOwn scholarship for the stay at Flemish Institute for Technological Research (VITO), Belgium. The research of Dr

Deepak Pant on bioelectrochemical systems at VITO is supported by a grant from VITO's strategic research fund. Additionally, the authors are grateful to Prof. Bruce Logan, Penn State University for his very useful suggestions on an earlier version of this work which helped us in improving the present article.

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Graphical Abstract

