

Microbial Desalination Cells: Progress and Impacts

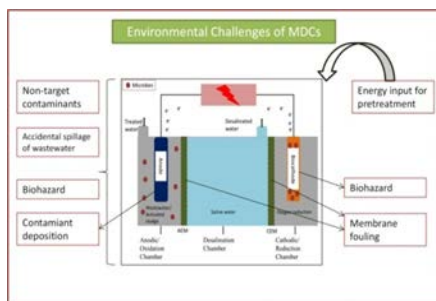
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Abstract

Microbial desalination cells (MDCs) have attained substantial importance in the recent years. The high energy consumption and environmental impacts of present desalination process has put mounts pressure to search for alternative desalination techniques. In search for sustainable and low cost desalination alternatives, microbial desalination at present has been known as self-sustaining (in terms of energy) and low cost process. Additionally, MDCs provide a dual benefit of waste treatment in line with power production. Numerous studies have reported advancements in MDCs that could potentially increase the efficiency of process. This present review mainly highlighted the various configurations of MDCs that could give possible large scale deployment of this technique. Additionally, the underlying limitations that affect the cell performance have also been critically discussed. The possible environmental impacts such as the release of unidentified microbes, the accidental leakage of high COD water, and fouling of membranes etc. have been identified as important factors to achieve environmental sustainability through the desalination process. Further, the authors identified a dire need to conduct LCA of different cells to identify the possible impacts of the preparatory phase of MDCs. Most of the research on MDCs indicated that it is virtually a self-sustaining process in terms of energy supply, thus the actual amount of output energy was also identified as a missing fact in most of the research studies. This review specifically covered the significance of research carried out on the current progress towards the commercialization of MDCs with possible environmental impacts.

Graphical Abstract



Keywords: Antimicrobial Activity, Methanolic Plant Extracts, Disk Diffusion Method, Gram Negative and Positive Bacteria.

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Introduction

The critical element for the survival of mankind on earth is the provision of safe and hygienic drinking water. Water is the most abundant resource on earth, where the most plentiful type of water is available in sea which is brackish that limits its direct use for the drinking purpose (Eltawil et al., 2009). The fact that fresh water resources have regional distribution and are not evenly distributed has diverted the attention of scientists to convert brackish and saline sea water to safe and clean water. Therefore, presently freshwater comes from two sources, natural and treated. The natural freshwater resource involves surface and ground water in the form of rivers, lakes, ponds, aquifers etc. Natural fresh water sources are globally either over exploited or contaminated due to the industrial discharge that has led to water scarcity in different regions. These problems would further foster the water crisis due to the deterioration of the water quality in fresh water resources (Moruno et al., 2018). Accepting the challenge of deficiency in the provision of fresh water, desalination of sea water would provide a practicable solution to meet the demands of freshwater in the areas of low or no natural freshwater resources (Elimelech and Phillip, 2011; Al-Mamun et al., 2017). Desalination process would provide a suitable technique to convert the highly concentrated salt solution of sea water into drinking water or tab water. According to an estimate of International Desalination Association (IDA), currently there are 18,426 operational desalination units globally, with a capacity of producing 86.8 millionm³ daily and thus serving 150 countries and around 300 million inhabitants. However, existing practices in desalination like thermal-desalination and high pressure membrane-desalination technology demands an extensive energy input, for instance, they consume 3.7 to 650 kWh energy for the desalination of a single metric cube of water (Mehanna et al., 2010). This number is continuously increasing from the past 50 years as the demand for water is increasing (Fritzmann et al 2007). However, these treatment plants are limited only to the developed countries specially located geographically around the coastal areas. Moreover, the operational cost of desalination is high due to its energy requirements and production of membranes and other materials required (Avlonitis et al., 2003). Around 60% of existing desalination has been operated by flash distillation process, where the energy demand has been met by fossil fuels utilization (Gude et al., 2010). Considering the importance of energy in desalination units, a considerable research has been performed using renewable energy resources. However,

the conversion of traditional units to renewable energy based system requires a high capital cost (Al-Karaghoul and Kazmerski, 2013). Compared to the conventional technologies such as reverse osmosis (RO) (Lee et al., 2011), nanofiltration (NF) (Muhammad et al., 2015), electrodialysis (ED) (Hong et al., 2015), more sustainable and energy efficient technologies are under consideration. One of the most established alternate that has been reported in recent years is the deployment of microbial distillation cells (MDCs). MDCs follow an interdisciplinary approach with the combination of membrane science, electrochemistry and microbiology, these cells work on the principle of mass transfer that ensures the continuous power generation and salt removal (Santoro et al., 2017a). On lab scale MDCs are found to be self-sustaining in terms of energy supply where additional benefits could also be achieved e.g. production of hydrogen gas (Mehanna et al., 2010), acid-base (i.e., HCl and NaOH) production (Chen et al., 2012a, 2013), production of valuable chemicals (Chen et al., 2012a, 2012 b, 2013), removal of hardness (Zhang and Angelidaki, 2013), and nitrates (Brastad and He, 2013). Therefore, theoretically MDCs have a potential to stand alone for the treatment and supply of freshwater to meet the current demands. Along with providing a freshwater directly, the MDC process could also be used as pretreatment to decrease the salt stocking in prevailing reverse osmosis (RO) process which results in reducing the membrane fouling (Al-Mamun and Baawain, 2015, Jacobson et al., 2011b). Considering the importance of MDCs, different reviews focused on the configuration and operational challenges (Ziaedini et al., 2018; Sophia et al., 2016; Seveda et al., 2015; Saeed et al., 2015). The robust development of MDCs has been evident from the large number of articles in the previous years. Though, MDCs have been attractive options which had proved their extraordinary strength on lab scale (Brastad and He, 2013), broad applications of MDCs require comprehensive information about hidden environmental impacts. To date, there is a lack of information on the environmental impacts of MDCs, therefore in the present manuscript, possible impacts due to the operation of MDCs and during their production have also been highlighted along with different types of MDCs.

Types of microbial desalination cells

Various studies have been reported different types of MDCs having varying potentials as desalination and power density, a few examples have been described as follows (Table 1).

Biocathode MDC

Biocathodes are innovative electrodes which promote the electrochemical reduction reactions where the prime catalysis is carried out by micro-organisms. Thus, biocathodes do not require high cost catalysts due to their lower construction and operational cost, self-regeneration potential, and ease of scale-up (Zhang et al., 2012a, b; Al-Mamun et al., 2018). In biocathode MDC, microbial communities carry out the reduction reactions which either take place in the catholyte or at the surface of electrode surface itself (Croese et al., 2011). The bacteria were electro active and acted as a catalyst in the cathode chamber to enable the oxidation reduction reaction and in result, an improvement in water desalination

coulombic efficiency could be achieved (Wen et al., 2012). Therefore, biocathodes aimed to mediate the reduction of the targeted oxidant indirectly or directly using the microorganisms as catalysts (Al-Mamun et al., 2018).

An innovative derivation of Biocathode MDC is a microbial desalination cell which consists of three main chambers including cathode, middle, and anode chambers. The reactions in aerobic cathode and anaerobic anode chambers are the similar as in microbial fuel cell, however, the middle chamber is filled with saline seawater which conducts the desalinated reaction by the potential gradient between anode and the cathode where ions such as Na, Cl migrate to the cathode and anode and generate freshwater out of sea water (Bard and Faulkner, 2004). In case, if the biofilm growth is higher, more will be the potential at the anode and more power will be produced (Wang et al., 2009). If the optimum conditions are provided to biocathode, startup duration of a MDC can be noticeably reduced, thus the overall performance of cell will be improved (Tchobanoglous et al., 2003; Li et al., 2017)

Various microbial consortia may be applied as biocatalysts in biocathodes which include nitrifying and denitrifying bacteria and algae to produce electron acceptors at cathode required for the reduction reaction (Clauwaert et al., 2007). Microalgae biocathodes can be applied for the sequestration of left behind nutrients and dissolved organic matter for microalgae biomass production that can be used for bioenergy production (Gude, 2016; Arana and Gude, 2018).

Different types of biocathodes have been successfully deployed in MDCs. The specialized microbes called electro-trophs have the potential to accept electrons either directly or routed from the cathode, and can exploit different terminal electron acceptors which includes iron, sulfate, nitrate, oxygen or carbon dioxide (Zaybak et al., 2013; Saeed et al 2015). Few significant examples of electro-trophs have been described below:

- *Micro-algal biocathode MDC*

The development of algal MDC is a novel technique to achieve economic benefits and environmental sustainability through dual benefits of desalination and bio-energy production. The microalgae utilize high carbon materials such as bicarbonate and CO₂ to produce O₂ with the provision of solar energy where under suitable condition, the oxygen saturation level may be achieved. *Chlorella vulgaris* is microalgae, that has been most commonly used as biocathode MDC (Zamanpour et al., 2017). *Chlorella vulgaris* is easily accessible and is highly efficient in reducing CO₂ and producing O₂ which has made it an appropriate oxygen provider in biocathode (Powell et al., 2009). Zamanpour et al. (2017) developed an MDC uses *Chlorella vulgaris* microalgae at saline water concentration of 35 g/l in a desalination cell with 20.25 mW m² power density, and achieved 0.341 g/l/d of salinity removal which was attained with higher algal growth (38%).

- *Bacterial biocathode MDC*

Bacterial *biocathode MDC* can be used as electro-troph in biocathode MDC. However, this is an intricate and laborious process. A more efficient and practically feasible approach has been developed in which anaerobic facultative autotrophic biocathodes are supplied through pre-enrichment of heterotrophs (Zaybak et al., 2013). In this mechanism, acetogenic bacteria transform CO₂ into organic byproducts by substituting hydrogen with cathode; which act as an energy and electron source.

Keeping the facultative autotrophic behaviour of acetogens in view, a pre enrichment process was also developed where, bacteria were initially enriched heterotrophically with carbon rich supply for instance glucose. Afterwards, CO₂ was supplied as carbon source, and an electron acceptor which assists in transforming the microbes from heterotrophic towards the autotrophic metabolism (Zaybak et al., 2013; Saeed et al 2015).

Table 1- Types of MDC and their efficiency desalination and current production efficiency

S. No.	MDC Type	Salt Removal Efficiency	Power and current potential	Reference
1	Photo MDC	Salt concentration was below ca. 1.4 mg/L Salt removal efficiency higher than 96%	Power density = 8.8 A m ²	Liang et al., 2016
2	Biocatalyst/ biocathode in MDC	Higher than 90% of ammonium removal achieved	power density = 0.092 Wm ⁻³ Current density = 0.814 A m ⁻³	Kokabian 2018a
3	Sulfonated sodium poly(ether ether ketone) membrane MDC	Salinity reduction = 78.6 %	Power generation = 235 ± 7 mW m ⁻²	Moruno et al., 2018
4	Ozone-cathode MDC	Salinity reduction = 74%	Power density = 4.06 W m ²	Gholizadeh et al., 2017
5	Photosynthetic MDC	TDS removal = 32.2 %	Power densities = 675 mW/m ³	Kokabian et al., 2018a
6	Silver-tin dioxide (Ag-SnO ₂) composite MDC	Desalination efficiency = 72.6 %	Maximum power density = 1.47 W/m ³	Anusha et al., 2018
7	Up-flow MDC	TDS removal rate = 7.50 g TDS L ⁻¹ d ⁻¹	Maximum power density of 30.8 W/m ³ .	Jacobson et al., 2011 a
8	Osmosis MDC	Desalination rate = 86%	Power density = kWh/m ³	Luo et al., 2017
9	Recirculation MDC	Salinity reduction = 39 %	The maximum power density was 931 ± 29 mW/m ²	Qu et al., 2012
10	Microalgae MDC	TDS removal > 40%	Power density = 625 mW/m ³	Arana and Gude , 2018
11	Quadripartite microbial desalination cell	Desalination rate = 72.8%	Max. Power density = 8.16 W m ⁻³	Ebrahimi et al., 2018
12	Biocathode microbial desalination cell	Desalination = 92%	Maximum voltage = 609 mV	Wen et al., 2012
13	Static photosynthetic microbial desalination	Max. TDS removal = 32.2%	Power density = 753.75 mWm ⁻²	Kokabian et al., 2018 b
14	Anammoxbiocathode	-	Power density = 0.092 Wm ⁻²	Kokabian et al., 2018 b
15	Biocathode microbial desalination	Desalination > 40%	Power density = of 3.178 Wm ⁻²	Meng et al., 2014

Photo-MDC

Bio-photoelectrochemical cells have recently gained significant curiosity as a novel approach as they can enhance the output energy of MDC by utilizing sunlight potential as a driving force without inflating any cost of the operational process. Some examples of this kind of cells have been reported such as hematite nanowire photoanodes MDC for an efficient operation (Qian et al., 2014), nanowire photocathodes for solar powered photochemical MDC (Liu et al., 2015), nanowire-bacteria hybrids for unaided solar CO₂ fixation (Zang et al., 2014). Liang et al. (2016) introduced a high-performance photo-MDC in which the anode was modified with nanostructured α-Fe₂O₃. It was observed that the highest current density of the photo-MDC during the process was 8.8 Am² twice of the unmodified MDC using 20 g/L of initial salt concentration. Moreover, the salt concentration observed in the middle chamber was below 1.4 mg/L of effluent, and the salinity removal efficiency was 96%. These studies revealed that combining MDC with bio-photoelectrochemical cell could be highly attractive to attain a high efficacy in photo-MDC.

Upflow MDC

The up-flow MDC is a unique type of cell in which mixing of solutions within the chambers can be attained without shaking, and recuperate 100% water (He, 2011). In up-flow MDC, water

osmosis is a practicable option which allows the microorganisms in anode chamber to remain in suspension form, and efficiently carry out maximum oxidation of organic matter (He et al., 2006; Saeed et al., 2015).

The up-flow MDC designed as a tubular unit composed of two compartments where the inner compartment (anode chamber) is filled with graphite granules to provide a higher surface area for oxidation reactions. In the graphite granules, two graphite rods are immersed as current accumulators which allow transmission of electrons. Anode chamber of the cell is enclosed with anion-exchange membrane tube. The external unit containing saline water represents desalination chamber which is further protected by cation-exchange membrane tube. Thus, the surface area is increased as the tubular nature of the electrodes as maintained in the desalination process to progress (Jacobson et al., 2011a).

The catalyst used in up-flow MDC is a mixture of carbon and platinum, which layers to the outer layer. Furthermore, it is coated with carbon cloth around the reactor to form cathode, therefore, the requirement for the separate cathode chamber is eliminated (Jacobson et al., 2011b). In up-flow MDC, the saline water normally enters from the bottom side, where, the desalinated water is released from the top side of anode chamber.

Stacked MDC

The working of MDC can also be improved using multiple pairs of ion exchange membranes implanted between the cathode and anode chamber, in order to enhance the efficiency of charge transfer, and enable the high saline water to flow over a series of MDCs which promote more salt removal (Gude et al., 2013). This setup is referred as the stack structure MDC system. The desalination efficiency has been reported up to 98% for saline water using Stacked MDC (Chen et al., 2011). The insertion of membrane in stacked MDC enhanced the charge transfer capability and salt removal due to the transfer of ions through the pairs of membrane (Gude et al., 2013). The MDC system comprised of a series of concentrated and diluted cells developed with the attachment of CEMs and AEMs in alternate arrangement (Al-Mamun et al., 2018). The transport of electron through the electrodes of MDC was responsible for the movement of a pair of ion across the membranes in each chamber which leads to the enhanced CTE and total rate of the desalination process (Kim and Logan, 2013a).

The stacked MDCs are highly useful due to their efficiency in retrieving more energy as compared to the other MDC systems, and therefore they are more economical. In stacked setup, the organic material is oxidized by amicroorganism (bacteria) in anodic chamber, thereby more recovery of energy can be achieved (Shehab et al., 2013). Since stacked configuration works on the mechanism of bio-electrochemical reaction, where varying their setups and operational parameters such as connection of electrodes; either series or parallel and hydraulic flow methods may affect the process of desalination (Cheng et al., 2010). The misbalancing of pH between the cathode and anode chamber is another important factor that affects the desalination process, in case when more than one chamber is utilized between the electrodes. High reduction in the pH values at the anode, can lower the activity of microorganisms in anode chamber, whereas a boost in the pH value in cathode chamber may lead to the substantial loss in potential, thus reducing the overall process efficiency (Qu et al., 2012).

Osmosis MDC

Microbial osmosis DC has been developed by substituting AEM with osmosis membrane. In an osmosis MDC, ions are transported across the membrane, whereas water is forced from anode to salty water because of greater osmotic pressure of the central chamber. In middle chamber, regardless of the dilution of saline water, the absence of membrane selectivity routes other unwanted ions which hinders the efficacy of MDCs (Zhang et al., 2012; Zamanpour et al. 2017).

In Osmosis MDC, forward osmosis process is used in water desalination. It is a technique which develops a water flux across two solutions, that is the draw solution and the feed solution (Zhang et al., 2011; Zhao et al., 2012). The feed solution has more water potential compared to the draw solution that creates a concentration gradient, therefore a water flux is developed (Zhang and He, 2012; Werner et al., 2013). Attempts to integrate forward osmosis with MDCs have been reported in which the ion-exchange

membranes are replaced with forward osmosis membrane (Kim and Logan, 2013a). The forward osmosis membrane permits water passage, while at the same time it reduces the transfer of ions from the middle chamber of the anodic and cathodic chambers (Zhao et al., 2012). The salts were actually not removed in this case, but they became rather concentrated. In a study of Zhang and He (2012), a high-energy process of osmotic MDC results in higher desalination efficiency of approximately 95.9% and 0.16 kWh/m³ of energy production using saline water. Moreover, 85% decrease in conductivity was also achieved with a salt solution of 10-50 g/L of NaCl (Saeed et al., 2015).

In general, the osmotic MDCs are capable to achieve three main goals at the same time, which includes: generating electricity, treating wastewater, and diluting salty water (Zhang, et al., 2012). Some challenges are associated with replacing the ion exchange membrane with forward osmosis membranes that are needed to be addressed. Forward membranes are more vulnerable to fouling than that of ion exchange membranes, which results in significantly increase in internal resistance of osmosis MDC and drop water flux (Kim and Logan, 2013a). A few studies showed that fouled forward osmosis membrane may increase the current generation (Ge and He, 2012). In fact, forward osmosis membranes in MDCs are still undiscovered and require further research.

Bipolar membrane MDC

Bipolar membrane MDC is an additional alteration in the MDC. The bipolar membrane entails a cation and anion discerning layers coated with either heat-press or glue together as a one membrane (Buck, 2014). Bipolar MDC is developed by bipolar membrane; layered with discerning coatings of CEM and AEM which are placed subsequently to the anode CEM and AEM. The additional chamber between saline water and anode evades Cl⁻ transfer to anode and thus results in a reduction in the pH. Therefore, the accretion of H⁺ and Cl⁻ in this chamber results in the production of acids in the cell (Chen et al., 2012; Zamanpour et al. 2017). Membrane characteristics may significantly influence the performance of the MDC. These properties include electric resistance and low water splitting voltage drop, high per-selectivity, the ability to allow only one type of ions to pass through, and a long-life duration (Alvarez et al., 1997). Enhancing the membrane ion-exchange capacity can potentially enhance the desalination potential from 50 up to 63% (Mehanna et al., 2010). Bipolar membranes are more susceptible to biological and organic fouling because of their exposure to wastewater in the anode chamber. Water across the membrane while passing through, splits up into hydroxyl ions and protons that develops a high potential gradient. The organic compounds get oxidized in anode chamber and release the hydroxide ions from the bipolar membrane into the anode chamber, whereas the hydrogen ions are drifted into the extra fourth chamber to produce HCl. Simultaneous to this process, salt removal from saline water (sea water) takes place in desalination chamber, and NaCl is separated at cathode chamber. Overall, the integration of bipolar membrane with the MDC is very advantageous, especially in sustaining pH of anode chamber (Kim and Logan, 2013a). Though, despite their incredible efficiency, one major disadvantage of bipolar MDCs is that they need an extra

source of energy in order to split water into OH⁻ and H⁺ ions in anodic and cathodic chamber; respectively (Saeed et al., 2015).

Recirculation MDC

A major problem in conventional MDCS ascends from the obstruction of these membranes to both hydroxyl and protons produced in the redox process, in both the cathode and anode chambers; respectively (Kim and Logan, 2013a). In the anode chamber, the oxidation of the organics releases protons which are incapable to diffuse to cathode chamber, whereas hydroxyl ions are being produced by the reduction reaction (Luo et al., 2011; Qu et al., 2012). This may lead to a momentous pH inequity inside the cell, where pH increases in cathode and decreases in the anode.

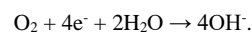
In an MDC reactor, the supplementation of a pair of ion exchange membrane between the electrodes is related to the acidification of anolyte. The potential gradient has been attributed to the electrochemical reactions following the flow of electrons over the external circuit creating the prime flux through the ion exchange membrane that established salt ions in its place of hydroxyl ions and protons. This situation possibly enables the buildup of hydroxyl ions and protons in both electrode chambers, that leads to a difference in pH inside the cell. The most harmful effect of this pH variation has been found on anode efficacy compared to cathode due to the reduction in microbial metabolism and proliferation in anode chamber. Nevertheless, the imbalance in pH in the cathode chamber can result in potential losses (Kim and Logan, 2013b; Al-Mamun et al.2018).

A more inspired technique has been newly under developmental stages in which anolyte and catholyte solutions have been consecutively recirculated through the MDC in order to offset the pH (Luo et al., 2011). Such technique has been known as recirculation MDC. Various studies have been conducted aiming to eliminate the imbalance pH in MDC chambers, these comprised the addition of buffers and the introduction of excess volume of anolyte (Al-Mamun et al.2018). Where, the recirculation of the catholyte and anolyte has had a positive consequence on energy production and desalination. Rendering to some previous investigations, recirculation MDC operating with 50 mM of phosphate (buffer solution) generated 33% more power, however, under normal conditions, cell working with 25 mM generated a 53 % increase in power (Luo et al., 2011). Thus, an increase in the buffer concentration is not essentially required to enhance the power density, so an optimal concentration of buffer should be identified. Recirculation could also improve the desalination performance up to 48 % with 25 mM phosphate buffer concentration. However, the recirculation of catholyte and anolyte solutions could decrease coulombic efficiency of the cell. Importantly, the recirculation of the solutions must take place through very thin tubes in order to avoid formation of equal potentials in anode and cathode chambers (Chen et al., 2012).

Combination of Microbial electrolysis desalination with the chemical-production cell

An amalgamation of microbial electrolysis cell with electro dialysis potentially performs the function of desalination and this type of

cell has been referred as microbial electrolysis DC (Mehanna et al., 2010). At MDC, the insertion of a bipolar membrane is done along with acid production chamber, and forms a combination of the microbial electrolysis desalination with the chemical-production cell (MED-CPC), which can concurrently produce HCl, NaCl, and desalinate seawater (Chen et al., 2013). With MED-CPC, the production of OH⁻ at the anode chamber assisted in solving the difficulties of pH variations, whereas this job is performed by Cl⁻ in conventional MDC. The degree of desalination in the MED-CPC is usually 1.4 times higher than the rate of a conventional cell with a single chamber (Chen et al., 2011). In these circumstances, an electric field permits splitting of water molecules on bipolar membrane. The hydroxyl ions drift through the cell into anode chamber in order to control pH, where the H⁺ ions drift from acid production chamber for the production of acids as a byproduct. To produce alkali, the subsequent reaction takes place at the cathode (Saeed et al 2015).



Capacitive microbial desalination cell

One major reported problem with the progress in working of MDCs is the accumulation of negative Cl⁻ and sodium positive ions inside anode and cathode chambers; respectively. This accumulation of ions affects the pH of the catholyte and anolyte that results in the inhibition of microbial metabolism. Thus, it requires a recurrent replacement of the catholyte and the anolyte, and also loads TDS for water reutilization (Xu et al., 2008; Saeed et al 2015; Al-Mamun et al 2018). To address this problem associated with MDCs, the microbial electrochemical desalination structure has been advanced with another concept termed as capacitive deionization (Al-Mamun et al., 2018). Capacitive deionization is based on using carbon materials having a greater surface area at two electrodes. Potential alteration is supplied between the porous electrodes (anode and cathode). Capacitive deionization is developed on two resulting procedures of the desorption and adsorption, where ions are initially divided from the saline water and thus water is desalinated. Secondly, in the adsorption process, double electrical layers are formed on both charged anode and cathode due to the attraction of ions parted from the water. Thereafter, the solution present between electrodes is substituted, and the electrodes are completely discharged to zero voltage, energy is supplied, and ions are discharged into the solution forming waste stream thereafter (Wen et al., 2012; Walter et al., 2013).

Saeed et al. (2015) also described the similar phenomena related to capacitive microbial desalination cell, they reported that the a double-layered capacitor was formed on high surface area electrodes, the ions were adsorbed when a salt solution ran between the anode and cathode. These ions from the salt water were adsorbed on the surface of electrodes by double-layer capacitor, and when the potential gradient got detached, ions were permitted to drift back into the solution. In this way, the saline water was directly deionised by the adsorption over the electrochemical salt on the electrodes without the contamination of cathode and anode chamber by the salt (Zhang and He 2012). Santoro et al. (2017b)

has developed a super capacitive MDC in which the electrodes were self-polarized due to the redox reactions, and thus the cathode acted as a positive electrode, and the anode acted as a negative electrode of the interior super capacitor. This cell system was practically operated with Pacific seawater for 15100 cycles where maximum power generated was up to 1.63 W m⁻² whereas the solution conductivity was reduced by 60% after 44 h.

In capacitive MDC technology, a slightly different and modified form of the cell has been developed with the introduction of membranes, called as membrane capacitive deionization, in which cation selective membrane was integrated on the negative electrode, while anion exchange membrane was integrated on the positive electrode (Chenget al., 2010; Zaybak et al., 2013). Compared to the captive microbial desalination cell, the membrane captive had the capability to operate at lower energy input with more salt separation potential. Though, the addition of membranes increased the overall capital investment in the desalination cell. Moreover, in both types of technologies, the release processes took place with a very low potential generated ranging between 200–300 mV, therefore, recovered energy could not be used for further practical application (Saeed et al 2015).

Microbial desalination processes, issues and challenges in general cell configuration

The significance of MDCs could be noticed from various studies indicating the effective salt removal for instance, 98% salt removal could be achieved using 35g /L NaCl solution (Yuan et al., 2012). Researchers have highly encouraged the use of MDCs over the conventional distillation cells due to the associate multiple benefits. MDCs could be called as an advancement to MFC (microbial fuel cells) that carried out the bio-electrochemical process. The slight difference between MFCs and MDCs was that MFC required the auxiliary microbial supply to degrade the substrate where, in MDCs no supplementary microbes were required it depended on the internal sludge which was already electroactive. The wastewater with organic loading entered the anodic side of MDCs where the proliferation of bacteria created a bio-film, and thus during the degradation of organic matter, electricity was produced (Elimelech et al., 2011). The biofilm adhered to the surface of the anode and bio-catalyzed the oxidation of the pollutants to release the electrons extracellularly for the respiration (Lovley, 2012; Yuan et al., 2017) and protons in the wastewater electrolyte present in the cell. These released electrons and protons were captured by cathode for the reduction of electron acceptors (e.g., oxygen) and anode attached to the external circuit. The transfer of electrons to the cathode generated an electrostatic force which in the saline water pushed the anions towards the anode, and the cations to cathode (Kim and Logan, 2013a). The Anodic chamber of the MDCs could possibly be aerobic or anaerobic. The electrochemically active microorganisms in the anode degraded the organic matter in wastewater and released electrons. The electrons were transferred to the cathode..

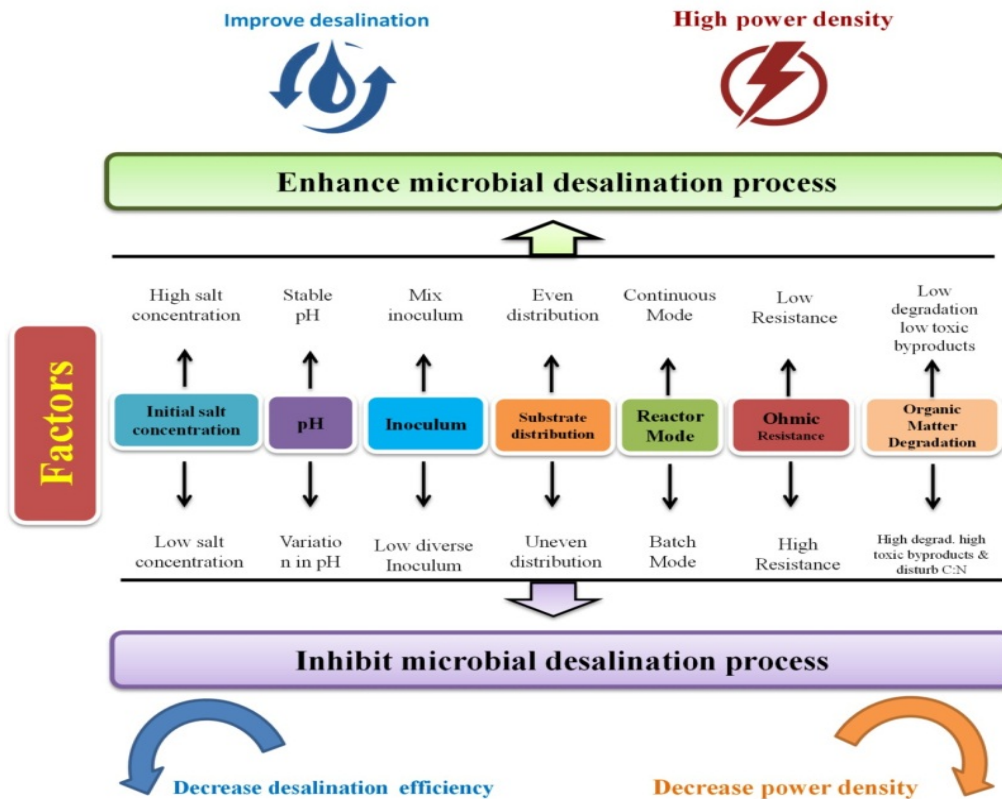


Figure 1: Summary of factors effecting efficiency of microbial desalination process.

The MDCs provided the dual benefit of waste treatment and bioelectricity. The potential difference across the chambers of electrode produced bio-electricity in the MDCs. The positively charged ions were diverted towards the cathode by cationic membrane during the combination of positively charges species to the electrons, and oxygen produced clean water (Sophia et al., 2016). The expedition of this process was a factor of the desalination process in the MDCs which was controlled by the initial salt concentration, and higher salt concentration promoted the high desalination rate by reducing the ohmic resistance. The stabilization of pH could be enhanced by using anode-cathode recirculation (Fritzmann, et al., 2007).

The operational mode of MDC also controlled the performance of the MDC. The desalination decreased with the passage of time in batch mode due to the increasing resistance (Ping et al.,2013). Where in the case of the continuous mode using air cathode, the pH variation decreased the conductivity and overall MDC's performance (Chen et al., 2011a). However, using mixed inoculum

could enhance the power generation and simultaneously de-salinated the wastewater. Where in up-flow MDC and stacked MDC, the continuous distribution of substrate increased the performance of MDC both in terms of the current generation and desalination (Gude et al., 2013; Jacobson et al., 2011a). Various factors effecting the desalination process have been summarized in Fig. 1. A typical MDC consists of three different chambers (illustrated in figure 2), the anodic chamber carries out the oxidation of the organic matter through active bacteria followed by the desalination chamber where the high concentrated saline solution desalinated the two chambers are separated by Cation and Anion exchange membrane. The last chamber is the cathodic chamber where the oxygen is reduced. The cathodic chamber is separated from the desalination chamber by cation exchange. Where during the desalination process, the sodium and chloride ions are transferred to their respective electrode by the selective membrane that is sodium through cation exchange membranes and chloride through anion exchange membrane (Moruno et al., 2018).

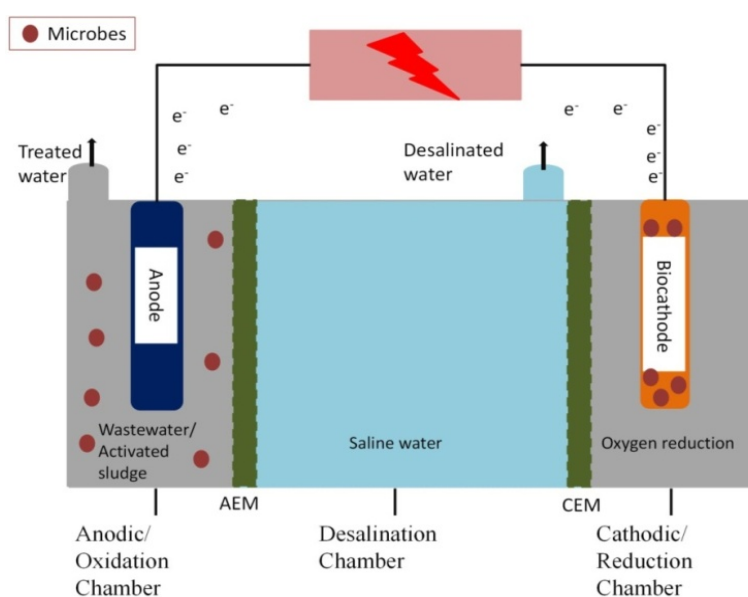


Figure 2: Typical microbial desalination cell configuration.

But, the practical application of MDCs is hindered by different operational factors, therefore, the true challenge in achieving commercialization of the MDC has been comparing the existing desalination technologies (Zhang and He 2012; Morel et al., 2012; Chen et al., 2011a). The different issues in MDCs have been:

- i) Low desalination rate
- ii) Degradation of organic matter
- iii) Poor electrochemical performance
- iv) Membrane fouling
- v) Low microbial activity

Low Desalination Rate

The low desalination rate of the MDCs has been mainly related to the inherent potential of microbes to work with excessive salt

solutions. Where other factors like the provision of the sufficient nutrients carried out the desalination process. The proper balance of C: N ratio and the sufficient supply of micro-nutrients have been the key factors to control the effectiveness in working of MDCs. Additionally, the large ohmic overpotentials potentially caused by electro dialysis of membranes might lead to the low desalination rate (Sophia et al., 2016; Saeed et al., 2015).

Degradation of Organic Matter

The degradation of organic matter contributed in two ways, either the degradation products could be toxic to the active desalination colonies, or the organic matter could disturb the C: N of the MDCs. The removal of COD has always remained an important factor in wastewater treatment cells (Zuo et al., 2017).

Poor electrochemical performance

Poor electrochemical performance would lead to low power generation by the MDCs. This could be attributed to the low anodic kinetics, or to the high cathodic activation. The membranes in MDCs also contributed to ohmic resistance, thus leading to the low power generation.

Membrane fouling

The key part of an MDC is its membrane, which can undergo the continuous wear and tear, thus decreasing the efficiency of MDC both in terms of energy production and desalination process (Kokabian et al., 2018b). Several studies have reported the possible alterations that increase the membrane life without decreasing the efficiency of the overall system. During the exchange, the membranes control the electrochemical process as they contribute to the considerable resistance that is the ohmic over potential or the ohmic losses, reducing the overall electrochemical and desalination performance of the cells in the assembled cells affecting the overall power generation and desalination rate.

Low Microbial Activity

In MDCs, the operational cells are a batch mode type, so with the passage of time, the overall concentration of the nutrition for microbes in the cell declines a continuous supply of essential nutrients in the MDCs, which are pivotal for the proper functioning of the MDCs. Also, during the operational procedure, the salinity of the anolyte increases with the salt removal creating a hypertonic solution for the micro-organisms to work that could potentially reduce the microbial activity, and correspondingly MDC performance (Kim and Logan, 2013a).

Several studies have focused on the importance of low electrochemical and desalination activity in MDCs and provided attractive alternatives to ensure the efficacy of MDCs. For instance, iron-based cathode catalysts (Shehab et al., 2013; Zhang and Angelidaki, 2013), different selective membranes (Subramani et al., 2015; Chen et al., 2016) integrating supercapacitors electrodes (Jacobson et al., 2011b; Luo et al., 2012), recirculating the solution have been a few attractive options that increase the MDCs performance. Other modifications involve the prevention of ions to enter into the anode chamber (Forrestal et al., 2012). Another considerable option to increase the cell performance is to recover different byproducts during the cell operation. Zhang and Angelidaki (2015a) have developed submersible microbial desalination cell (SMDC) for the reduction of ammonia. Later, Zhang and Angelidaki (2015b) developed bipolar and electrochemical cells, and recovered volatile fatty acid (VFA) from the waste, and routed it to produce hydrogen and alkali (Sophia et al 2016). For the practical application of MDCs, different key aspects have been needed to be overcome. However, the strength of any technology not only lies in overcoming the operational issues, but also on its impacts on the environment to make it sustainable. Therefore, the current article not only focused on different types of MDCs but also on the environmental impacts.

Pollutants of mdp (microbial desalination process)

Desalination processes have been usually associated with the refusal of waste brine of high concentration of the plant, the pretreatment unit or plant itself, during the time of cleaning period. In thermal processes such as multistage flash, thermal pollution may occur which increases the temperature of seawater, water current, salinity and turbidity. These results disturb the environment of the oceans causing fish to migrate, while increasing the algae, tiny mollusks and nematodes. In some cases, micro-elements and toxic materials have been present in discharge distillation and brine (Kim and Logan 2013b; Mehanna et al., 2010).

Increasing the efficiency of desalination has extensively been studied by different researchers in the past few years, however little has been known about the effect of desalination on the environment. Few studies have focused on the possible impacts of the desalination units of environment due to the discharge of concentrated brine and possible air pollutants, but the possible impacts of MDCs still needs further investigation before practical application on large scale. Al-Mamun et al., (2018) has pointed out that desalination plants could contribute to climate change by GHG emission and also demand high energy. For MDCs, the emissions from the possible burning of fossil fuels are eliminated, as theoretically MDCs require no energy, and are self-sustaining cells. However, the possibility of other pollution types still exists.

Water pollution

MDCs have been known for their effectiveness in treating wastewater along with energy production. On a lab scale, few MDCs have been found to remove up to 90% salinity removal (Cao et al., 2009). The efficiency of these cells could be extended to other pollutants with few modifications (Zhang and Angelidaki, 2013; Brastad and He, 2013;). But for the desalination from the sea water, MDCs have shown little efficacy as compared to the other DCs. Similar to the other DCs, the disposal of rejected brine is a serious environmental concern. The discharge can be comprised of the high concentration of nitrated and phosphates and other salts. The disposal of such high concentration of salts in the open water channels leads to high pollution load, and thus could be toxic to aquatic life where if discharged near soil could lead to high salinity of the soil.

The treatment of wastewaters using MDCs has been extensively studied in recent years, and numerous researchers have attained impressive salinity removal rates during the wastewater treatment (Kokabian et al., 2018 c). Where in other cases the treatment efficiency was higher, but the salinity removal was lower as compared to the conventional DCs.

Air pollution

Other DCs have been known to produce carbon monoxide, hydrocarbons, nitrogen oxides, and sulphur oxides. Where the use of MDCs requires no foreign energy source, thus the potential hazard of these gases is eliminated. However, there is a dire

possibility of development of bioaerosols and other gaseous emissions from the MDCs.

Impacts on Environmental Quality

Manufacturing MDCs has had higher impacts as compared to the environment. A complete LCA indicated 22.7 % contribution during manufacturing, and 58.7% during the operation in global warming. The manufacture of MDCs involved the development of membranes that usually involved ion exchange carriers where the polytetrafluoroethylene (PTFE) binders also contributed to the environmental pollution. And, the operational impacts have been related to the electricity required for continuous pumping of water (Zhang et al., 2018).

The impacts of MDCs could also be related to the potential biological hazards, where the competition of native microbes in wastewater was not addressed in the present research work. Therefore, three different scenarios could be presented for the operation and manufacturing of the MDCs which have been discussed below:

Scenario 1: No pretreatment was given to the wastewater for the removal of the indigenous microbe.

Scenario 2: Thermal sterilization of the wastewater was used to remove the indigenous microbe.

Scenario 3: The oxidative sterilization of wastewater was done to remove the indigenous microbe.

The impacts of these different scenarios have been critically discussed in table 2.

Challenges and prospects of future technology

Different configurations which have been provided above, greatly focused on the performance aspects of the MDCs, and the improvement in cell configuration to ensure the environmental safety requires serious attention in this field. Studies have widely focused on the key challenges in the true commercialization of this technology, and identify the low desalination rate or the electrochemical performance as the key issue in the technologies (Sophia et al., 2016) where none of these have focused on the

impacts of membrane formation and discharge of wastewater to the open water channels. Further, the work was mainly done on NaCl solution, however, the efficacy in working with salts (sea water) yet need more exploration. The use of microbes for desalination of actual sea water with the simultaneous power generation has been a matter of great interest as the efficiency of bacteria could be reduced in a mixture of salts. The disposal of electrolyte and electrodes after significant wear and tear also needs attention. One of the possible alterations is to use more stable membranes that will not only result in cost reduction (Moruno et al., 2018), but will also be beneficial for the environment in the long run. Similarly, the photo-microbial desalination cell can be another possible alteration (Kokabian et al 2018c).

A LCA analysis carried out by Zhang et al (2018) indicated a negative GHG emission by MDCs compared to the conventional wastewater treatment option. This provided a hope for the sustainability of the technology with the environmental feasibility in future. However, the role of different pretreatment methods in cost reduction also needed to be addressed in future studies. Further, the performance of key micro-organisms along with the other native microbes in the waste also need the cost-effectiveness study of MDC technology. Although, the above-discussed experimental studies provided the substantial indication that MDCs can be used to fabricate high energy effective technology, but it is generally difficult to synthesize a controlled system while working with original water. Therefore, the deployment of sustainable membranes for the processing of MDCs is highly desired. Another issue could be the cost of manufacturing and pretreatment of sustainable membranes like of carbon Nano tubes (Goh et al., 2013). Recently, Membrane fouling and its control has been critically focused by Goh et al., (2018). Membrane cleaning has been identified as the direct factor to contest fouling issues in desalination cells. The chemical cleaning could lead to the considerable damage of the membranes; therefore, cost-effective membrane cleaning options are needed to be considered (QU et al., 2012). The same is applicable to the already present chemicals and ions; thus, regardless of the types of membrane, it is imperative to procure thorough understanding about the nature of foulants and their corresponding complex interaction with the membrane surface before any sludge or water is supplied to the MDCs.

Table 2- Environmental Impacts of the operation and manufacturing of the MDCs in different scenarios

Scenarios	MDC efficiency	Energy input	Environmental impacts
Scenario 1: No pretreatment given to the wastewater for removal of the indigenous microbe	Lowered down due to the competition among the indigenous and augmented microbes for resources	No energy input required	<ul style="list-style-type: none"> • No GHG emissions • Self-sustaining system • Implications only by the discharge of contaminated wastewater
Scenario 2: Thermal sterilization of the wastewater to remove the indigenous microbe	High efficiency due to the provision of surplus nutrients for the selected species	<ul style="list-style-type: none"> • Renewable energy resource • Fossil fuel powered energy resource 	<ul style="list-style-type: none"> • Reduced GHG emissions if renewable source is used. However, the risk of discharge of untreated non targeted toxic contaminants was there. • For fossil fuel powered thermal treatment process <ol style="list-style-type: none"> 1. GHG emissions 2. Thermal pollution 3. Resource competition 4. Risk of discharge of untreated non targeted toxic contaminants

Scenario 3: Oxidative sterilization of wastewater to remove indigenous microbe	High efficiency due to the provision of surplus nutrients for the selected species	<ul style="list-style-type: none"> • External energy source to power the oxidative source • Chemical input 	<ul style="list-style-type: none"> • GHG emissions • Radiation emissions • Public health hazard during operation • Chemical contamination could be toxic to the indigenous species
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Conclusion

The demands of MDCs of desalination applications could be generated in the coming years. Low desalination rate, microbial activity, organic matter degradation and membrane fouling have been the utmost bottlenecks for the commercialization of this technology to compete with the conventional high energy demanding desalination technologies. The overall study indicated that operational issues of MDCs have been greatly addressed by offering different types of MDCs discussed above, but the cost-effectiveness of these different types of MDCs could be an area of exploration for the commercialization of this technology. Similarly, although the MDCs offer lower environmental impacts as the emissions are greatly controlled by the use of self-sustaining, energy systems but the role of thermal pretreatments and their energy emissions could be harmful for the environment. Further, most of the studies have only focused on the treatment of specified contaminants, where in actual wastewater, a mixture of contaminants and different salts could result in lower efficiency of the microbial activity. Additionally, the environmental risk and public health impact due to the accidental release of active microbial electrolyte solution in the cell has been a thoughtful concern. These features should be proactively assessed to be regulated at risk estimation and regulations for the development of safety guidelines. Although, the associated environmental risks have been thoroughly assessed for all the possible alternatives to enhance the electro-chemical performance of MDCs, the application of this technology for large-scale water desalination systems has been doubtful in the near future. As the complete elimination of environmental impacts is practically not approachable, but the approaches that offer the minimization and remediation should be established to reduce the impacts of MDCs.

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