Journal of Cleaner Production 183 (2018) 458–480

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

A review of microbial desalination cell technology: Configurations, optimization and applications

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ARTICLE INFO

Article history:
Received 28 September 2017
Received in revised form
4 February 2018
Accepted 5 February 2018
Available online 8 February 2018

Keywords:
Microbial desalination cell
Wastewater treatment
Seawater desalination
Bioelectricity
Fuel cell design. contents

ABSTRACT

Seawater could be a potential source of freshwater to manage the intensified demand of drinking water for new generations. The recent techniques for desalination and wastewater treatment are energy intensive and unsustainable. Therefore, an integrated and sustainable approach is essential to achieve cost-effective desalination through wastewater treatment. Microbial desalination cell (MDC) has been proven to be one of the emerging technologies capable of simultaneous wastewater treatment, seawater desalination and eco-energy production. This technique generates electricity through the bio-electrochemical oxidation of organics present in wastewater. The produced electricity is utilized to drive the migration of ions in MDC system. This ionic migration will result in desalination as well as formation of value-added by-products. The review summarizes the recently investigated MDC configurations along with their critical evolution of designs and operational parameters on the desalination and power generation capabilities. The review also acknowledges the emerging applications of MDC for microbial electrochemical desalination, bio-remediation, nutrients recovery, water softening, and value-added chemical production. The key findings included that the MDC system achieved a remarkable desalination without any external power input, and treatment of wastewater, and recovery of power without intermediate steps. The technical challenges associated with their practical applications were maintaining the pH in cathodic and anodic fluids, higher internal resistance, usage of catalysts on electrodes, and membrane fouling and durability. However, for certain configurations especially for microbial electrolysis and desalination cell (MEDC)/microbial electrolysis desalination and chemical production cell (MEDCC), the integration with electrodialysis module can significantly increase their performances. The installation of ED module will establish the pH neutrality and increased water recovery through recirculation of electrolytes between chambers of ED module and these MDC configurations. However, the sustainable development of MDC technology and its scale-up requires future investigations related to prevention of membrane fouling, materials feasibility, electron transfer kinetics, microbial growth and durability of catalyst. The feasibility studies are also needed to be conducted for determining the suitability of MDC operation in terms of reactor performance and stability.

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https://doi.org/10.1016/j.jclepro.2018.02.054
0959-6526/

1. Introduction

Safe and clean drinking water is one of the vital elements for human life on earth. Although water is an abundant natural resource, 97% of the earth's water is seawater, it cannot be used directly for drinking purposes without further treatment (Eltawil et al., 2009). Moreover, although the remaining 3% is freshwater, only 1% of it is available for use. The factors contributing to intensified utilization of clean freshwater include rapid industrialization, a massive growth in the human population and the blockage of a major portion of clean water in the form of glaciers and snow. The availability of freshwater is a key challenge for the development of many countries, where desalination can provide a feasible solution to meet the demand of freshwater supply (Elimelech and Phillip, 2011; Al-Mamun et al., 2017a). According to International Desalination Association, 18,426 desalination plants are currently operated worldwide, producing 86.8 million cubic meters per day, serving 300 million people in 150 countries. However, conventional thermal-desalination and high-pressure-membrane-desalination technologies are highly energy intensive; they consume 3.7 to 650 kWh energy per m^3 of water desalination (Mehanna et al., 2010a). More than 60% of the desalination plants worldwide use a multi-stage flash distillation process, which is powered by fossil fuels (Gude et al., 2010). Thus, current desalination processes are not only required the supply of abundant energies but also contributed to the emission of greenhouse gases and climate change. Aeration, sludge treatment, thermal distillation and high-pressure membrane operations are the specific factors responsible for making these techniques high energy demanding.

As a result, meticulous research efforts need to be made to develop inexpensive and efficient desalination technology, in order to fulfil the increasing demand for freshwater. Indeed, significant attention has been given to the construction of desalination processes powered by renewable energy. However, the adoption of these renewable energy technologies by existing desalination plants requires high capital investment (Al-Karaghouli and Kazmerski, 2013). In contrast, recently developed microbial desalination cells (MDCs) have shown a significant potential as a sustainable approach for water desalination, with simultaneous organic waste and wastewater treatment. Technologically, MDCs are a modified version or extended form of bio-electrochemical systems (BES) that produce electrical energy from the direct oxidation of organic matters coupled to extracellular electron transfer by anode-respiring bacteria (ARB); thus, they can be operated in self-powered mode.

Multi-chamber designs of MDCs deploy ion-exchange membranes (IEM) in a way that permits salts to be extracted from saline water (e.g., seawater, brackish water) to maintain charge neutrality in the system. Several lab-scale studies have demonstrated that MDCs could provide complete (>90%) salinity removal (Cao et al., 2009). For instance, one lab scale prototype of MDC exhibited 90% desalination efficiency along with 1.8 kWh energy production per m^3 of water treatment (Jacobson et al., 2011a). With a small amount of exogenous power supply, electricity produced by MDCs can be diverted to produce hydrogen gas (Mehanna et al., 2010a). As an additional benefit, MDCs can be engineered to add more features, such as acid-base (i.e., HCl and NaOH) production, denitrification, and water softening. Chen et al. (2012c, 2013) achieved the production of valuable chemicals in treating the wastewater using a type of MDC (Chen et al., 2012a, 2013). Brastad and He (2013) and Zhang and Angelidaki (2013) utilized a modified MDC for removing the hardness and nitrates from wastewater and groundwater, respectively (Brastad and He, 2013; Zhang and Angelidaki, 2013). Thus, MDCs have the potential to be a stand-alone desalination process. Furthermore, they can be retrofitted as a pre-treatment process to alleviate salts or dissolved solids loading in the existing reverse osmosis (RO) system, which will mitigate membrane fouling and energy consumption (Al-Mamun and Baawain, 2015; Brasted and He, 2013; Jacobson et al., 2011b; Mehanna et al., 2010b).

Different lab-scale designs of MDC have been explored, such as air cathode, biocathode, capacitive, electrolyte recirculation, photosynthetic, osmotic, stacked, bipolar membrane, ion-exchange, resin packed, and upflow configurations (Chen et al., 2012a; Forrestal et al., 2012a; Mehanna et al., 2010b; Qu et al., 2012; Shehab et al., 2014; Wen et al., 2012; Zhang and He, 2012b). However, none of these configurations have been tested in a pilot or full-scale study. To date, there have been several review articles featuring various MDC configurations, their desalination efficiency and resource recovery potential, and operational challenges (Chen et al., 2016; Gude et al., 2013; Saeed et al., 2015; Sevda et al., 2015; Sophia et al., 2016).

Since few years back, a large number of literature articles addressing various aspects of MDC implies strong interest and robust development of this technique. However, the scale-up of MDCs requires a deeper understanding of the challenges associated with different MDC designs and their operation. Therefore, this review article aims to provide a critical review of various MDC configurations, focusing on engineering developments and strategies to overcome operational challenges. Apart from that, it identifies the gaps for future research in order to improve the sustainable approach of MDC types in desalinations and energy recoveries.

2. Methods

2.1. Literature search

Various Scopus scientific data bases were used in literature search for this review. Most of the cited bibliometric references were selected from Web of Science, Scopus and Google Scholar. The key words used in literature search include “microbial desalination cell”, “microbial electrochemical desalination”, “wastewater treatment using microbial desalination cell”, and “optimization of microbial desalination cell”. The inserted references in this review were mainly comprised of research articles, book chapters, thesis and conference proceedings.

2.2. Screening process

The searching used the aforementioned keywords resulting into hundreds of articles. In order to narrow down the screening, specific keywords, such as, stack, upflow, osmotic upscaling challenges, parametric study, techno-economic, sustainable, eco-friendly microbial desalination cell were used.

2.3. Selection of literature

The relevant literature was selected by analyzing the abstract as well as the full text of the references filtered in the screening process. The abstracts were carefully read in order to find the relevant content such as configurations/operation/sustainability. The relevance of full texts of references was affirmed using the available online data bank. Therefore, the selection of literature was based on keywords, used in screening process, found either in article title, abstract or keywords.

2.4. Inclusion process

The selected 140 references were read in order to extract the useful information related to sustainable operation and associated technical shortcomings of MDC technology. Careful analysis of data in selected references was ensured to estimate the desalination and power generation efficiencies of respective MDC type. Special attention was paid to units in reporting the data as they use to differ from reference to reference for a same parameter. Moreover, the review articles were carefully examined to filter the required information by avoiding any type of superfluity.

3. Microbial desalination cell configurations

Various MDC reactor configurations and their specific pros and cons are summarized in Table 1. Elaborated discussions for each specific configuration are presented in subsequent sections.

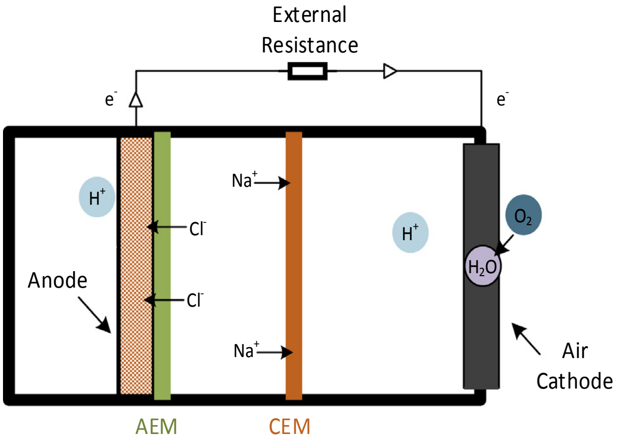
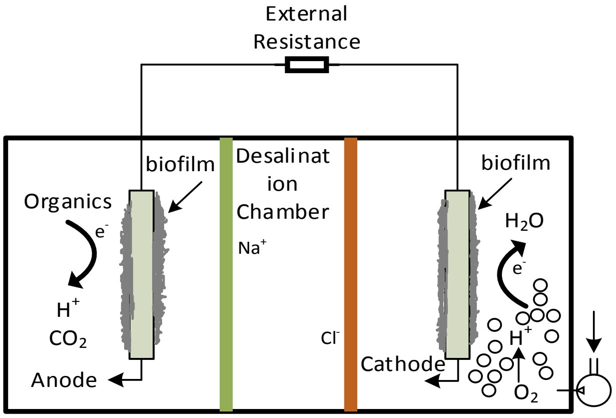
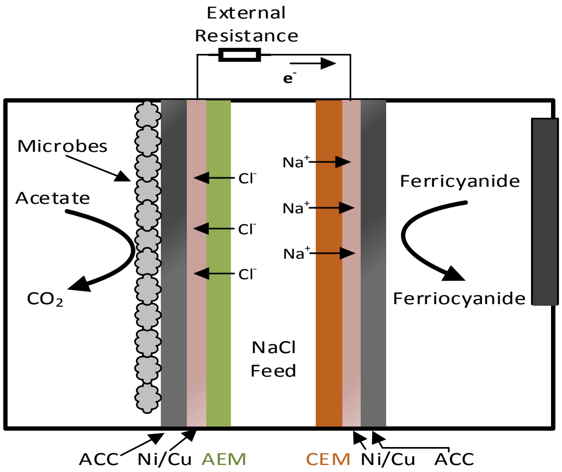
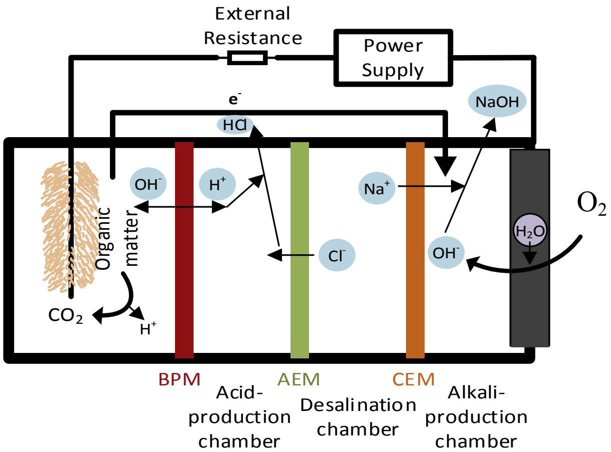
3.1. Basic configuration of MDC (three-chamber cubic design)

When the concept of MDC was first introduced, the cubical reactor was made of polycarbonate material. The MDC consisted of three chambers; anode, cathode and desalination chamber, as shown in Fig. 1. The desalination chamber was produced by placing AEM and CEM between the electrodes. The AEM and CEM were facing to the anode and cathode electrodes respectively. The empty volumes of the anode, desalination and cathode chambers were 27, 3 and 27 mL respectively. By inserting carbon felt into the anode and cathode chambers as electrodes, the net volume of each chamber was reduced to 11 mL. The electrodes were connected by 5 mm diameter graphite rod for external electrical connection. The anode and cathode chambers were fed with 1.6 g/L solution of sodium acetate and potassium ferricyanide, respectively. The desalination chamber was fed by three different concentrations of NaCl at 5, 20 and 35 g/L. The operating external resistance for the MDC was 200 Ω. The potential gradient developed across the electrodes was utilized to drive the desalination by the migration of anions (e.g., Cl^{-1}) and cations (e.g., Na^{+1}) from the middle chamber to the anode and cathode chambers respectively. A maximum power of 31 W/m^3 was produced in the MDC system, while simultaneously removing 90% of the salt in a single desalination cycle. In conjunction with efficient salt removal, the ohmic resistance of the MDC was observed to be increased from 25 to 970 Ω towards the end of the cycle. The use of potassium ferricyanide as an electron acceptor in the cathode chamber facilitated high cathode potential and faster reduction kinetics. However, the drawbacks related to its toxic features and high cost have limited its use for large scale processes. As a result, a cathode chamber equipped with ferricyanite solution cannot be recognized as sustainable technology in spite of its generation of high power density. This basic configuration has been modified for sustainable applications aiming to achieve higher capabilities of desalination and power-generation. This newly developed technology offered the great advantages of utilizing the domestic sewage and municipal solid and liquid wastes for desalination and power recovery (Al-Mamun et al., 2017b; Baawain et al., 2017).

3.2. Air cathode MDC

The chemical catholytes such as ferricyanide solution possessed lots of limitations. However, oxygen had been identified as a favorable and practical terminal electron acceptor because of its high reduction potential, cost effectiveness and wide availability. The concept of air cathode MDC with Platinum/Carbon (Pt/C) as catalyst was first attempted by Mehanna et al. (Mehanna et al., 2010b). The graphical representation of air cathode MDC was given in Table 1 as Figure A. This air cathode MDC operation reduced the salt-water conductivity by 43 ± 6%, while producing a maximum power density and coulombic efficiency of 480 mWm^{-2} and 68 ± 11% respectively. Hydrogen peroxide (H_2O_2) obtained as an intermediate product in the redox reaction of oxygen had also been treated as cathode oxidant (Park et al., 2004). Air cathode MDC processes with oxygen was used in various studies due to the negligible toxic effects of atmospheric oxygen and the harmlessness of the end products (Alvarez-Gallego et al., 2012). However, the shortcomings associated with this air cathode MDC were slow

Table 1
Various modified MDC configurations with their major pros and cons.

MDC configuration	Specific pros and cons	Reference
A. Air cathode MDC 	- Oxygen act as terminal electron acceptor - Achieved salinity removal of ~63% - High reduction potential - Environmental sustainability due to negligible toxic effects of oxygen - Cost effectiveness	(Alvarez-Gallego et al., 2012; Mehanna et al., 2010a; Mehanna et al., 2010b)
B. Biocathode MDC 	- Microbial catalytic reduction reactions - Self-generating and sustainable - Increased water desalination - Reduced start-up time - Low pH variation - High produced power output of ~3.178 W/m^3 - Efficient salt removal efficiency of 92%	(Sharma and Kundu, 2010; Sun et al., 2012; Wen et al., 2012)
C. Capacitive MDC 	- Utilization of capacitive deionization concept - Formation of double-layered capacitor on electrode surface - Continuous/periodic removal of salts from electrodes - Reduction in electrodes contamination - Easier ions migration - Salinity removal of ~69.4%	(Liang et al., 2015; Wen et al., 2014; Zhang and He, 2012a)
D. Microbial electrolysis desalination and chemical production cell (MEDC) 	- Incorporation of acid-production chamber and bipolar membrane in MEDC - Increased desalination rates - Reduced pH imbalance	(Chen et al., 2012a; Heijne and Liu, 2010; Xu, 2001)

(*continued on next page*)

Table 1 (*continued*)

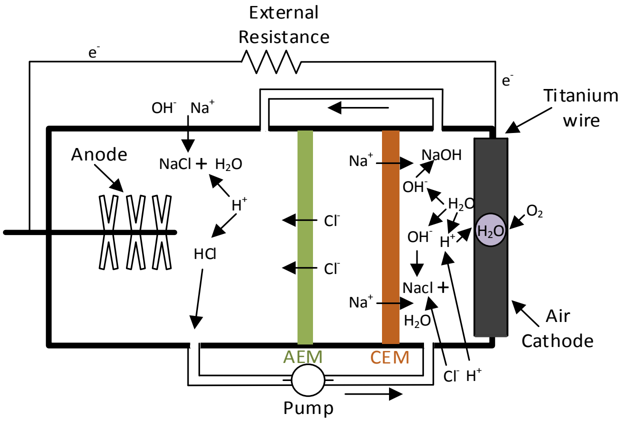
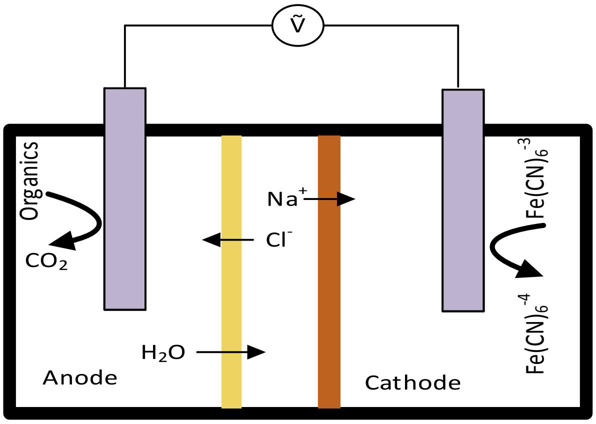
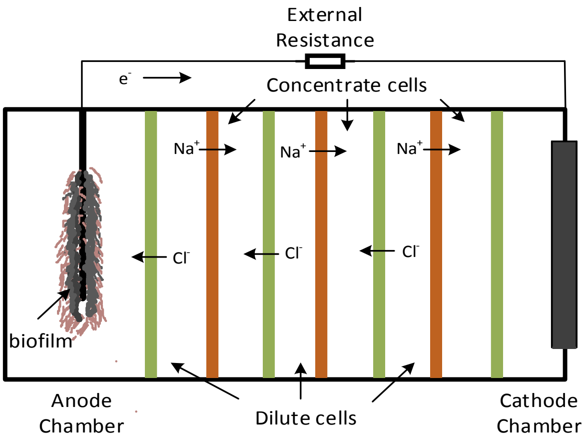
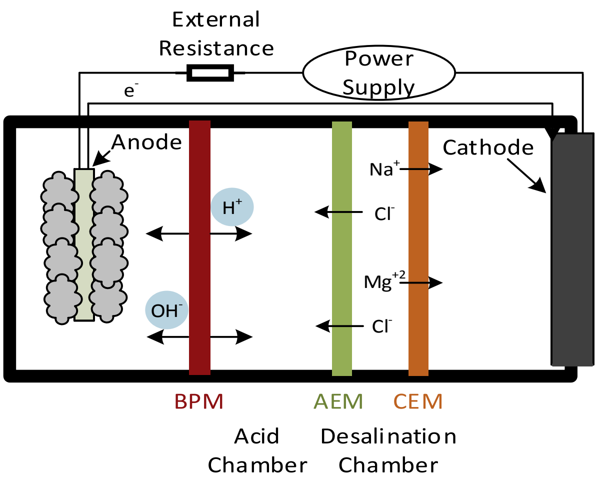
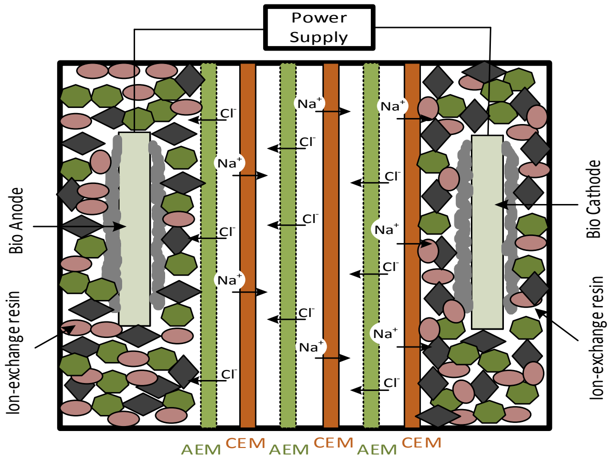
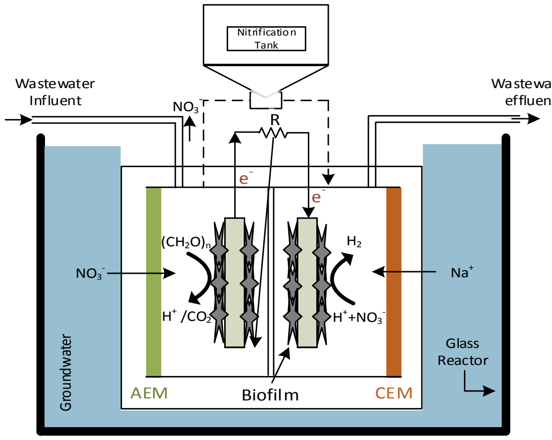
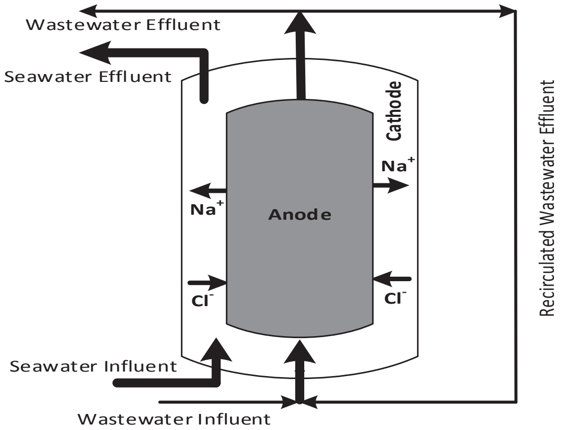
MDC configuration	Specific pros and cons	Reference
E. Recirculation MDC (rMDC)  	- Sequential recirculation and anolyte and catholyte through the cell - Utilization of low concentration of buffered solution - High desalination rate - High generated power - Effective pH control	(He et al., 2008; Kim and Logan, 2013a; Rozendal et al., 2008)
F. Osmotic MDC (OsMDC)  	- Replacement of AEM with FO - Increased saltwater dilution through osmosis water - Deploying potassium ferricyanide as catalyst - Improvement in overall desalination performance - Enhanced organic matter removal contained in wastewater - Cheap availability of FO than AEM - Lees fouling tendency - High water recovery - Low energy input	(McGinnis and Elimelech, 2007; Werner et al., 2013; Zhang et al., 2011)
G. Stacked MDC  	- Alternating AEM and CEM stacks - Increase in desalination rate by 40% compared to that in normal MDC reactor - Efficient charge transfer - Improved energy recovery - Enhanced ionic pair separation contained in salt water - High charge transfer efficiency	(Chen et al., 2011; Kim and Logan, 2013a)
H. Bipolar membrane MDC  	- Lamination of AEM and CEM to form BPM - Placement of BPM next to cathode, making four-chambered MDC - Increased semipermeability - Reduction in resistance and voltage drop - Enhanced desalination efficiency - Improved pH balance in anode - High coulombic efficiency value of 62–97%	(Chen et al., 2012a)

Table 1 (*continued*)

MDC configuration	Specific pros and cons	Reference
I. Ion-exchange resin packed MDC  	• Packing of desalination chamber with mixed cation and anion exchange resins • Reduced energy consumption • Enhanced desalination rate with high charge transfer efficiency • Fixed ohmic resistance	(Hatzell and Logan, 2013; Spoor et al., 2001)
J. Submerged microbial desalination-denitrification cell (S'MDC)  	• Incorporation of denitrification system into MDC • Electricity generation through ions removed from groundwater • No additional treatment of removed niterates • No escape of bacteria into groundwater	(Li et al., 2017)
K. Upflow MDC  	• Separation of two compartments with IEM contained in tubular reactor • Effective fluid-mixing within the chambers • Easier scale up • Enhanced generated power • Better desalination efficiency	(Jacobson et al., 2011a, 2011b)

redox kinetics at ambient conditions and high power input for the mechanical equipment, used to retain a specific level of dissolved oxygen in the catholyte. The former disadvantage required the use of expensive metals like platinum to minimize the activation over potential for oxygen reduction. The latera drawback was addressed in several studies, which attempted different approaches for minimizing the energy input. In previous MDC designs, the requirement of cathodic aeration offset the generated power by power required for aeration (Werner et al., 2013). As a result of investigation of several disadvantages related to air cathode MFC, which were also applicable to air cathode MDC, Logan (2010) proposed different strategies to enhance its performance (Logan, 2010). The upgradation offered to reduce these problems included exposing air cathode to atmosphere, the use of passive methods for optimal oxygen transfer in cathode, and using activated carbon with ultra-high surface area for achieving the desired levels of oxygen reduction without any need for an expensive catalyst (Biffinger et al., 2007; Freguia et al., 2008).

The Pt-catalyst coated on one side of the air cathode was not sustainable in terms of either economics or the environment, as it

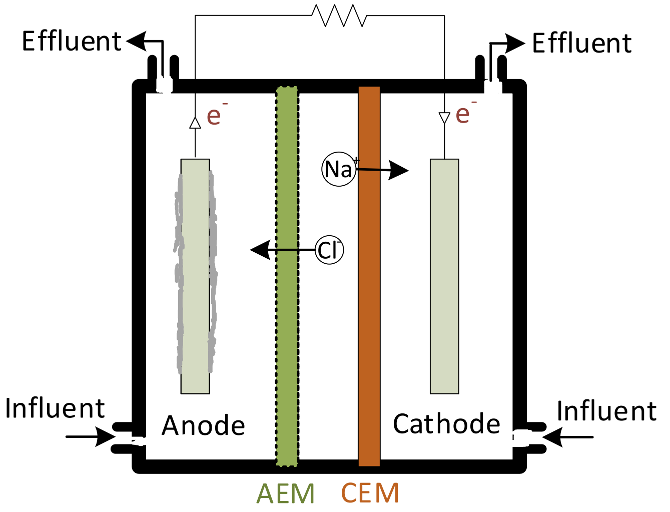


Fig. 1. The schematic diagram of three-chambered MDC used for desalination tests (Cao et al., 2009).

was expensive, required continuous replacement and contaminated the compounds in the bacterial solution (Lefebvre et al., 2009, 2010). In contrast, studies investigating other metals as an alternative to platinum have revealed pyrolyzed iron (II), phthalocyanine (FePc) and cobalt tetramethylphenylporphyrin (CoTMPP) as encouraging substitutes. Park and Zeikus (2003) impregnated the Fe(III) compounds on the cathode electrode to study the electron transfer process in the oxygen reduction reaction. The sequential reduction and oxidation of Fe from Fe(III) to Fe(II) and then back from Fe(II) to Fe(III) in redox reaction of oxygen, was observed. The iron compounds acted as mediators during the electron transfer process from cathode to terminal electron acceptor. Improved power output was observed for Fe(III)-cathode, better than that achieved with woven graphite cathode (Park and Zeikus, 2003). In another study, application of CoTMPP catalyst on cathode surface showed a similar performance as that of platinum impregnated cathode (Cheng et al., 2006; Zhao et al., 2005). However, none of those materials could sustainably be used as cathode catalysts because they required continuous replacement and there were high costs associated with their application on a large scale (Al-Mamun et al., 2016, 2017a, 2017b; Clauwaert et al., 2007b).

3.3. *Biocathode MDC*

Because of the above mentioned challenges associated with air cathode systems, studies related to biocathode have attained significant attention. Biocathodes constituted innovative sustainable electrodes and promoted the electrochemical reduction reactions in cathode chamber using microbes as catalyst. Biocathodes did not require expensive catalysts and represented as effective microbial catalytic electrodes due to their lower construction and operational cost, and their flexibility in the production of valuable chemicals (He and Angenent, 2006; Zhang et al., 2012a,b). Therefore, biocathodes appeared to be efficient alternatives due to their potential for self-regeneration, their ease of scale-up and their sustainability. The general illustration of biocathode MDC was presented as Figure B in Table 1. At the biocathode, microbial community catalyzed the reduction reactions taking place either at the electrode surface itself or in the catholyte (Croese et al., 2011; Lefebvre et al., 2008a, 2008b). The electroactive bacteria present in the cathode chamber acted as a catalyst to facilitate the oxidative-reduction reactions, which resulted in improving coulombic efficiency and enhanced water desalination (Wen et al., 2012). Thus, the spirit of the biocathode was to mediate the reduction reaction of an oxidant directly or indirectly by using microorganisms as biocatalysts (Huang et al., 2011; Lovley, 2011). Based upon the type of terminal electron acceptor utilized in cathode chamber, the biocathodes could be divided into two different types; aerobic and anaerobic cathodes. In aerobic biocathodes, oxygen was utilized as an oxidant due to its cheap availability and high redox potential. Bergel et al. (2005) utilized seawater biofilm-covered biocathode in proton exchange membrane (PEM) fuel cell, which led to efficient catalysis of oxygen reduction. This air-saturated biocathode resulted in power density and current density values of 0.32 W/m^2 and 1.34 A/m^2, respectively (Bergel et al., 2005). Meng et al. (2014) constructed a biocathode MDC for simultaneous desalination, power generation and anodic sludge stabilization. This achieved the desired parametric conditions of anodic pH value maintained between 6.6 and 7.6, and high stability over a long period of operation. The desalination rates achieved were 46.37± 1.14% and 40.74± 0.89% against initial NaCl concentrations of 5 and 10 g/L. This biocathode MDC configuration resulted in a maximum power output of 3.178 W/m^3 with open circuit voltage of 1.118 V. Moreover, a 3-day reduction in the startup period was observed (Meng et al., 2014). Wen et al. (2012) constructed a biocathode MDC with aerobic cathode containing carbon felt as cathode and aerobic consortia as biocatalyst. The maximum voltage produced with biocathode MDC was found to be 136 mV, which was higher than that produced in air cathode MDC. The acquired values of coulombic efficiency, salinity removal and total desalination rate were found to be 96.2± 3.8%, 92% and 2.83 mgh^{-1} respectively (Wen et al., 2012). The biocathode MDC process therefore appeared to be a promising approach for efficient desalination and current generation.

Kokabian and Gude (2013) evaluated the performance of an air cathode MDC and photosynthetic MDC with microalgae catalyzed biocathode in terms of power production and salt/COD removal. The PMDC operation produced a maximum power density of 84 mWm^{-3} and desalination rate of 40% (Kokabian and Gude, 2013).

In spite of the substantial attention focused on aerobic biocathodes in past few years, the main drawback associated with this approach was the level of the supply of dissolved oxygen that was required, because the insufficient availability of oxygen might reduce the system's performance. Because of the stated limitation and specific applications of aerobic biocathodes, extensive research efforts were focused on introducing anaerobic biocathodes. However, the start-up of anaerobic biocathodes and the growth of biocathode biofilm was a rather difficult and time-consuming process (Butler et al., 2010; Morita et al., 2011). A formal designation of electrotrophs was used to represent the microorganism responsible for direct or indirect acceptance of electrons from the cathode. A variety of terminal electron acceptors such as sulfate, nitrate, iron, manganese, fumarate, arsenate and carbon dioxide could be utilized (Clauwaert et al., 2007a; Cournet et al., 2010). One of the most transformative applications of electrotrophy was microbial electrosynthesis, which converted carbon dioxide and water into valuable multi-carbon organic compounds. Different approaches to generate anaerobic conditions at biocathode were reported in the literature. The addition of hydrogen/organic compounds at cathodes were one of the few approaches developed for establishing anaerobic biocathodes showed great potential (Jeremiasse et al., 2012; Villano et al., 2011). The first investigation by Rozendal et al. (2008) developed a novel anaerobic microbial biocathode system based on a three-phase biocathode startup procedure, using the concept of the reversibility of hydrogenases. Wherein, the acetate and hydrogen oxidizing bioanode was converted into hydrogen producing biocathode through reversing the electrode polarity (Rozendal et al., 2008). Improved hydrogen production of about 0.63 m^3 was observed, compared to 0.08 m^3 produced with controlled electrode. However, the use of non-renewable ferricyanite as the catholyte and anolyte made this approach unsustainable.

Another concept of the polarity inversion in BES was investigated, aiming to obtain a biocathode with improved characteristics of efficient oxygen reduction and minimum pH gradient. The polarity transposal in one-half cell was achieved through potentiostat and alternate feeding of acetate and dissolved oxygen to the biofilm, enabling the tested half-cell to change from anode to cathode and vice versa. Using the same concept, the polarity shift for biocathode in one-half disk-immersed cell was attained by rotating stack of conductive disks. The regular half rotations of 180^0 resulted in interconversions between anode and cathode leading to biofilm escalation, which catalyzed both anode as well as sscathode driven acetate oxidation and methanogenesis respectively (Cheng et al., 2010, 2011). In another research study, anaerobic biocathodes were established through enriching the anode in sediment microbial fuel cell with the help of two different marine sediments and the subsequent electric inversion of anode to function as cathode in BESs (Pisciotta et al., 2012).

However, all these approaches for building up aerobic biocathodes were convoluted and time-consuming due to their multi-step-procedures (Al-Mamun et al., 2017b). A new method related to heterotrophic pre-enrichment was established to accelerate the start-up of anaerobic facultatively autotrophic biocathodes. In this technique, the acetogenic bacteria convert CO_2 into organic compounds by replacing H_2 with cathode as source of energy and electron (Berg, 2011; Drake, 2008). At first, the heterotrophic enrichment of bacteria was conducted with glucose using a pre-enrichment procedure based on the facultative autotrophy of acetogens. Subsequently, the switch of microorganisms from heterotrophic to autotrophic metabolism was enabled by providing CO_2 as the sole source of electron acceptance and carbon.

3.4. *Stacked MDC*

The stacked MDC (SMDC) was constructed by inserting multiple IEM pairs between the anode and cathode that enhanced the desalination performance. This insertion improved the charge transfer efficiency (CTE) and salt removal due to flow of ions through the membrane pairs (Gude et al., 2013). The system configuration was presented in Table 1G. The system consisted of a series of dilute and concentrate cells created with the introduction of alternating AEMs and CEMs. The transfer of single electron across the electrodes was responsible for the migration of an ion pair in each chamber across the membranes, leading to increased CTE and total desalination rates (TDR) (Kim and Logan, 2013a). The SMDC was a cost-effective system to recover more energy than other MDC configurations. Chen et al. (2011) developed the very first prototype of stacked MDC to enhance the desalination rate by establishing two desalinated and one concentrate chambers using two pairs of CEM and AEM. A notable increased TDR was 1.4 times higher than that obtained with single desalination chambered MDC (Chen et al., 2011).

Given the versatile MDC configurations, variations in design and operating parameters, such as the assembly of stacked MDC electrodes connection and hydraulic flow method in parallel or series mode, might affect the desalination process. Choi and Ahn (2013) investigated the effect of varying the electrode connection and hydraulic flow mode on desalination performance of air cathode MFC. Hydraulic flow in series and parallel electrodes connection achieved higher power density of 420 mWm^{-2} with a COD removal of 44% (Choi and Ahn, 2013). Kim and Logan (2011) substantially improved the performance of stacked MDC and operated four stacked MDCs in series, each one containing five desalination chambers. The energy losses in electrodialysis due to high internal resistance were minimized by limiting the inter-membrane distances, which enabled the stacked MDC to generate power similar to that produced by single desalination chamber MDC. This configuration of stacked MDC reduced the salinity by 44% along with CTE of 430% and TDR of 77 mg/h (Kim and Logan, 2011).

The MDC configuration disscussed above possessed few shortcomings, such as, pH imbalance, increased water losses in dilute chambers and over potential. The shortcomings reduced its desalination and electricity generation efficiency. Anolyte acidification occurred due to high rate of proton release in anode chamber in response to exoelectrogenic oxidation of organic matter, compared to proton diffusion rate in cathode chamber. The proton transportation was hindered by AEMs in stack of membranes inserted between anode and cathode, causing protons accumulation in anode chamber and consequent decrease in anolyte pH. A reduction in anolyte pH below the neutral impeded the respiration of anodic bacteria, causing a decrease in microbial activity and growth. However, the pH variation in SMDC was less pronounced than that in single cell MDC due to the flow of organic medium in a series of MDCs in SMDC structure; thus acted to remove the pH fluctuations (Qu et al., 2013). In a similar way, the pH in a cathode chamber would increase due to placing the CEM next to the cathode. However, the disparity of pH in the anode as well as in the cathode chamber would lead to significant potential losses, which in turn would reduce the efficiency of the process efficiency. Various approaches were adopted to avoid the decrease in anodic pH, including the use of a large volume of electrolyte, electrolyte recirculation between anode and cathode chambers, and placing bipolar membrane (BPM) between anode and AEM. Davis (2013) alleviated the anolyte pH imbalance using non-buffered saline catholyte effluent of previous cycle in a large scale stacked MDC consisting of three desalination chambers and four anolyte brushes. A TDR of 0.1074 g/h with subsequent decrease in anodic substrate loss from 11% to 2.6% was achieved by increasing the anolyte conductivity (Davis, 2013).

Zuo et al. (2014) replaced the anolyte and catholyte every 24 h to maintain the stable solution pH, while operating the stacked MDC, packed with mixed ion-exchange resins, in batch mode. This achieved a desalination efficiency of 93.4% while treating the low saline (<10 g/L) water, and simultaneously produced maximum power and current of 11.8 W/m^3 and 202.1 mA respectively (Zuo et al., 2014). Qu et al. (2012) eliminated the pH variation in continuously operated and hydraulically connected MDCs by a cyclic flow of anodic solution from anode to cathode chamber in back-to-back linked MDCs. This achieved an increased removal of NaCl of approximately 97% at a hydraulic retention time (HRT) of two days, compared to a removal of 76% obtained at HRT of one day (Qu et al., 2013). Shehab et al. (2014) constructed a microbial electro deionization cell (MEDIC) stack using MDCs packed with IER to enhance water desalination. The MEDIC operation decreased the anolyte pH from 7.03 to 6.30 and increased the catholyte pH from 7.40 to 11.60. The desalination performance and generated power density were observed to be increased by 40 and 70% respectively, which was attributed to stacked MDC configuration and use of IER (Shehab et al., 2013). Ge et al. (2014) maintained the anolyte pH ~ 6.5 and catholyte pH < 8.0 in a desalination process using a MDC stack consisting of 10 pairs of desalination chambers. This stack configuration increased the CTE by 450% with a TDR of 90.8 mg/h (Ge et al., 2014).

An increase in the number of stacks placed between anode and cathode chambers in a single unit would lower the generated current and consequently increase the HRT, and achieve the desired level of desalination. The increased HRT would facilitate the water transport from dilute to concentrate cells due to osmosis. Kim and Logan (2011) proposed a strategy to overcome the water losses in dilute chamber through linking seawater flows to multiple MDCs in series. This approach would enhance the extent of desalination by maintaining the degree of ionic separation (Kim and Logan, 2011).

3.5. Recirculation MDC (rMDC)

In an MDC reactor, the placement of different chambers with an insertion of pair of IEM between electrodes was responsible for anolyte acidification (decrease of pH). As explained earlier, in the desalination process, protons and hydroxyl ions were produced due to bioelectrochemical oxidation and electrochemical reduction reactions taking place at anode and air cathode respectively. The potential gradient due to electrochemical reactions and the subsequent flow of electrons through the external circuit, developed the major flux through IEM that constituted salt ions instead of protons and hydroxyl ions. This situation might facilitate the accumulation of protons and hydroxyl ions in anode and cathode chambers, leading to a pH variation inside the cell. The most deleterious effects of this pH change have been observed on anode efficiency than that of cathode due to reduced microbial growth and activity in anode chamber. However, the pH imbalance in the cathode chamber would cause potential losses (Kim and Logan, 2013b; Zhao et al., 2006).

The pH span for most enzymes/microbes to function satisfactorily was 6–8 (Lagrega and Evans, 2001). He et al. (2008) investigated the performance of air-cathode MFC at varying electrolyte pH to observe the variation in generated current. The operated MFC was observed to withstand even with a solution with a pH of 10, without any prominent variation in performance. The measured open circuit potential revealed the optimal performance of anodic reaction at neutral pH while for cathodic reactions it was at increasing pH (He et al., 2008). It was therefore essential to reduce the pH variations in MDC in order to enhance the desalination performance and density of generated power.

Various studies aiming to eliminate the pH imbalance in MDC chambers were reported in the literature; these include the addition of different buffer solutions and the use of excess anolyte volumes (Jacobson et al., 2011a). However, these approaches were neither efficient nor sustainable due to the high operational and capital cost of the process: expensive materials, cost of pumping and storing large volumes of electrolytes. The recirculation of electrolytes in anodic and cathodic chambers of MDC emerged as a promising technique for reduced pH variations as well as increased power densities. Luo et al. (2010) developed a microbial electrolysis and desalination cell (MEDC) in which the pH alleviation acquired through anolyte recirculation that increased the desalination rate, current density and H_2 production by 80%, 61% and 30% respectively (Luo et al., 2010). In order to avoid the need for expensive chemicals in anode and cathode chambers to inhibit pH imbalance, a new and emerging technology related to recirculation of both electrolytes through the cell was now under investigation (Kim and Logan, 2013a; Luo et al., 2010). The MDC with this mode of operation is termed recirculation MDC (rMDC). The general configuration of rMDC is given in Figure E (Table 1). Qu et al. (2012) designed and operated rMDC by allowing the recirculation of electrolytes between anode and cathode chambers. They observed the positive effects of recirculation on MDC performance and obtained high power density values of $931 \pm 29\ \mathrm{mW/m^2}$ and $779 \pm 30\ \mathrm{mW/m^2}$ compared to $698 \pm 10\ \mathrm{mW/m^2}$ and $508 \pm 11\ \mathrm{mW/m^2}$ achieved without recirculation (Qu et al., 2012). They also found a decrease in coulombic efficiency from 60 to 20% due to aerobic degradation of recycled anodic substrate in cathode chamber. This showed that rMDC could be a promising approach for effective desalination when substrate losses due to microbial oxidation in the cathode chamber could be minimized through the optimization of recirculation.

3.6. Half cell coupled MDCs

The versatility of BESs in terms of reactor design and operation offers various applications. The system can be made more effective and adaptable using different combinations of complementary functions. The development of MDC suffered from various challenges including the placement of membranes, increased internal cell resistance over time with a resultant drop in voltage, reduction in osmatic pressure, substantial contamination and loss of valuable commodities (Call et al., 2009; Cheng et al., 2009). To improve the desalination rate with simultaneous production of useful byproducts while potentially treating wastewater, several integrated multi-chambered MDC configurations were proposed. In addition to desalination with concurrent generation of electricity, the coupling of MDC with microbial electrolysis cells (MECs) would lead to the production of valuable chemicals; the resultant reactor was termed as microbial electrolysis desalination cell (MEDC). The concept of MEDC was tested by Mehanna et al. (2010a, b) and Luo et al. (2010) for the first time. The constructed MEDCs were composed of three chambers; anode chamber, desalination chamber and cathode chamber. The chambers were produced by inserting AEM between desalination chamber and anode chamber, and CEM between desalination chamber and cathode chamber. Desalination efficiencies of 68% (20 g/L NaCl) and 98.8% (10 g/L NaCl) with simultaneous hydrogen production rate of $0.16\ \mathrm{m^3/m^3d}$ and $1.5\ \mathrm{m^3/m^3d}$ were reported in these studies (Luo et al., 2010; Mehanna et al., 2010a). However, this technique of MEDC possessed several limitations, such as, pH reduction in anode chamber due to placement of AEM that substantial transferred $\mathrm{Cl^-}$ from the desalination chamber to the anode chamber, and shipment of phosphate buffer containing phosphate groups from the cathode chamber to the desalination chamber (Harnisch et al., 2008; Torres et al., 2008). These drawbacks were responsible for decreased anodic performance due to the detrimental effects on the microbial metabolism and thicker deposits of $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$ in the desalination chamber. To overcome these challenges, a new device called a microbial electrolysis desalination and chemical-production cell (MEDCC) was proposed. This equipment was developed with the insertion of BPM between AEM and anode chamber in MEDC, creating another production chamber, termed an acid-production chamber. The MEDCC thus consisted of four chambers; an anode chamber, an acid-production chamber, a desalination chamber and a cathode/alkali-production chamber. The BPM showed potential applications in the field of environmental engineering, chemical production, energy sources and bioengineering due to its potential for energy saving and its lack of harm to the environment (Xu, 2001). Under the application of an electric field, BPM facilitated a water splitting reaction, maintaining almost neutral and low pHs in the anode and cathode chambers respectively (Heijne and Liu, 2010). In the case of MEDCC, the transportation of dissociated ions took place across the BPM; $\mathrm{H^+}$ ions migrated from anode chamber to the acid-production chamber, forming the acid, and $\mathrm{OH^-}$ ions moved from the acid-production chamber to the anode chamber, neutralizing the anolyte pH. At the cathode, oxygen reduction took place through the following reaction (Chen et al., 2012a):

$$2H_2O + 4e^- + O_2 \rightarrow 4OH^- \quad (1)$$

The movement of these dissociated ions generated junction potentials across the MEDCC chambers. Under the effect of these junction potentials, Na^+ and Cl^- ions in the desalination chamber moved to the cathode/alkali chamber and the acid-production chambers forming alkali and acid respectively. Thus, the use of BPM improved the desalination rate by inhibiting the undesired transfer of chlorides and phosphate ions. Chen et al. (2012a, b, c) devised a MEDCC and compared its performance with MEDC and electrolysis desalination and chemical-production cell (EDCC) in terms of desalination rate, coulombic efficiency and acid-alkali production rate. Higher coulombic efficiencies (62–97%) were obtained, compared to 32–65% obtained with MEDC. The achieved desalination rate of 0.078 mmol/h was also higher than the MEDC-generated rate of 0.048 mmol/h (Chen et al., 2012a). However, the desalination and chemical production performance of MEDCC was affected by several factors including stack structure, the number of desalination chambers, membrane spacing and the applied voltage. The effects of these factors were investigated by Chen et al. (2012a, b, c), using two different types of stacked MEDCCs in order to optimize the desalination rate and chemical-production rate. The first type of MEDCC was constructed by inserting one to four back-to-back concentrating and desalination chambers between the desalination and cathode chambers of MEDC. This configuration was designated as AEM-CEM structure or AC mode. In the second type of MEDCC, the stacked chambers in the first type were replaced by alkali-production, acid-production and desalination chambers using BPM in addition to AEMs and CEMs. It was labeled as BPM-AEM-CEM stack structure or BAC mode. The use of AC mode in MEDCC with membrane spacing of 1.5 mm resulted in significant increase in the desalination rate, which was 43% with estimated value of 0.58 mmol/h (Chen et al., 2012b).

Conventional methods for the separation of metals were energy-intensive and caused significant increase in environmental pollution. Besides the production of value-added chemicals, the MDC might be combined with metal reduction reaction for the removal of heavy metals contained in polluted water/wastewater. Using a four-chambered MDC was a novel approach proposed to treat Cu(II) containing synthetic wastewater in cathode chamber with simultaneous brine/seawater desalination. The peculiar aspect of this configuration was the placing of additional AEM between CEM and cathode chamber in order to avoid the contamination of other chambers through the transfer of Cu(II). This achieved a maximum current density of 2.0 A/m^2 with a simultaneous copper removal rate, salt removal rate and desalination rate of 94.1, 43.9 and 5.1% respectively (An et al., 2014a). In another study by the same group, Cr(VI) containing wastewater used as the catholyte was reduced with concurrent desalination of brine in a MDC reactor. An increase was observed in both the current density and the desalination rate, along with an increase in the concentration of Cr(VI) in the wastewater catholyte. The Cr_2O_3, the reduced form of Cr(VI) produced as a result of electrochemical reaction, was deposited on the cathode surface (An et al., 2014b). Another approach used to remove heavy metals involved hydroxide precipitation using alkaline solution produced by MDC. The metals were precipitated by mixing hydraulically connected MDCs-produced alkaline catholyte effluent and metals containing wastewater. This achieved an almost complete removal of copper metal (0.27 mg/L) as well as the efficient performance of the MDC stack in terms of acquired average power density, salt removal and COD removal rate of 737 mW/m^2, 53.6 kg/m^{3}d and 1.84 kg/m^{3}d respectively (Dong et al., 2017). Li et al. (2017) developed an energy-positive integrated MEDC for both nitrogen and Pb(II) removal in municipal and industrial wastewater respectively, while simultaneously desalinating seawater. The pH imbalance was alleviated through the integration of nitrification in the cathode and denitrification in the anode. This batch-operated reactor resulted in 99.5% of Pb(II) removal, while producing maximum electricity of 293.7 mW/m^2 with desalination and hydrogen removal efficiency of 63.7 and 95.1% respectively (Li et al., 2017).

3.7. Capacitive MDC (cMDC)

One major concern associated with the operation of MDC was the accumulation of positive (Na^+) and negative (Cl^-) ions inside the cathode and anode chambers, respectively. The accumulation of ions will change the pH of the anolyte and catholyte; this will lead to the inhibition of microbial growth, the need for frequent replacement of the anolyte and the catholyte, and the burden of regulating total dissolved solids (TDS) for water reuse (Xu et al., 2008). To address these issues, the microbial electrochemical desalination (MED) system was upgraded with a new concept of capacitive deionization (CDI). Yuan et al. (2012) developed an integrated technology comprising a CDI and an MFC for the treatment of low-concentration saline water. In this integrated system, the MFC generated electricity was utilized to drive the CDI module for desalination. Two different modes, discharging and short-circuiting, were investigated for desorption of ions that were adsorbed on electrodes. A higher desalination rate of 200.6 mg/(L h) was obtained in the discharging mode than that of 135.7 mg/(L h) achieved in short-circuiting mode (Yuan et al., 2012). Liang et al. investigated the influence of different arrangements and operating conditions of MFC-CDI system on salt removal. In the case of high resistive MFCs, higher salt removal was obtained by parallel-connected MFCs, whereas the MFCs with low internal resistance resulted in efficient salt removal while connected in series. The optimal arrangement of MFC-CDI circuit was seen to be based upon the electrical characteristics of selected MFCs and CDIs as well as on their operating conditions (Liang et al., 2015). Wen et al. constructed a MDC-MCDI system for complete desalination of MDC effluent by taking the advantage of low energy consumption of MCDI, driven by power source comprising of various assemblies of MDCs connected in series or parallel. A significant high desalination rate of 3.7 mg/h was observed with parallel connected MDCs configuration (Wen et al., 2014).

Instead of empowering the CDI from external sources for improved desalination, various approaches related to built-in CDI technology were investigated. Forrestal et al. (2012b) developed a sustainable MDC system with incorporated CDI, called a capacitive microbial desalination cell (cMDC). A CDI in the form of two membranes assembly comprising of CEM and activated carbon cloth (ACC) was inserted between the desalination and the anode chambers, and the desalination and the cathode chambers. The ions in the salty water were transferred and stored in electrical double layers of CEM and ACC, connected to the anode and the cathode respectively. This avoided the salinity of treated water and consequent anodic pH imbalance by preventing the movement of the salt ions towards the anode and cathode chambers. The adsorbed ions on ACC were separated by removing the electrical potential through disconnecting the anode and cathode. This configuration of cMDC achieved a desalination efficiency, which was 7–25 times higher than that obtained in conventional capacitive deionization processes (Forrestal et al., 2012b). A similar concept was investigated in another research study (Zhang and He, 2012a).

In another approach to avoid the increase in the salinity of both anolyte and catholyte due to the transfer of salt ions, Forrestal et al. (2012a) utilized the adsorptive activated carbon cloth (ACC) as electrodes to adsorb the ions by forming capacitive double layers.

This mechanism of electrochemical ion adsorption removed approximately 69.4% of salt without any increase in salinity in the anode and cathode chambers (Forrestal et al., 2012a). Stoll et al. treated shale gas produced water using a MCDC reactor with simultaneous degradation of organic matter contained in produced water and salt removal in saline water. The batch operation of this microbial reactor achieved an organic matter removal rate of 6.4 mg/h, together with a desalination rate of 0.036 g of salt per gram of carbon electrode (Stoll et al., 2015).

3.8. Osmotic MDC

In past decades, the concept of forward osmosis (FO) has attained significant attention in wastewater treatment due to its operating condition of low or no hydraulic pressure (Achilli et al., 2009; Cornelissen et al., 2008). FO is the transportation of water across the semipermeable membrane from a feed solution to a draw solution under the effect of a developed osmotic pressure gradient (McGinnis and Elimelech, 2007; Zou et al., 2017). In contrast to the draw solution, the feed solution has low water chemical potential or high osmotic pressure and this concentration gradient leads to the formation of water flux (Zhang et al., 2011). The FO has several potential advantages over other pressure driven processes of water treatment (reverse osmosis, nanofiltration, ultrafiltration etc.) due to its low energy input, high rejection of a wide range of contaminants, lower fouling tendency, easy fouling removal and high water recovery. Several research studies related to the incorporation of FO process in MDCs and MFCs reactors by replacing the IEM with FO membranes have been reported in the literature. This embedded form of FO-BES approaches to increase water recovery is referred to as osmotic MDC (OsMDC). The FO membrane permits the water flow from anode to desalination chamber with simultaneous reduction in the movement of salt ions across the desalination chamber. This water flux promotes the proton transportation from anode chamber to desalination/middle chamber, making the anodic pH lower than that in MDC. Very limited work has been conducted on integrating FO membrane in different BES for simultaneous wastewater treatment, clean water extraction and bioelectricity generation. Zhang and Angelidaki (2013) observed that treating wastewater in a FO integrated BES resulted in more electricity generation and water extraction than in CEM placed BES. The proposed potential applications of this constructed reactor included seawater desalination and water reuse using seawater as the draw solution. Using seawater as the catholyte would alleviate its need for recycling, as it would be diluted with FO membrane-transported extracted water. In terms of a combined operation, linking of this osmotic reactor with a MDC was suggested due to its capacity for extensive wastewater treatment, maximized bioelectricity generation and the reduction of required pressure in osmatic reactor (Zhang et al., 2011).

Zhang et al. (2012a,b) compared the performance of OsMDC with that of FO technology and MDC in terms of wastewater treatment, desalination and water recovery. The OsMDC reactor was found to be advantageous over the FO process by separating more salt ions and the greater production of electricity due to the oxidation of organics. OsMDC achieved higher quality water recovered from wastewater than that with MDC, as well as lower salinity through dilution. A significant desalination rate of 57.8% was achieved with a production of average current of 4.6 mA. An increase in water flux with an increase in salinity was observed, attributing to high difference in osmotic pressure, which developed because of concentration gradient (Zhang and He, 2012b). Werner et al. modified the previous designs of microbial osmotic reactors by incorporating the air-cathode in order to improve energy recovery through discarding the energy required for catholyte aeration. The configuration thus developed obtained an effective indirect desalination efficiency of 35% with high power generation of 43 W/m^3, compared to 40 W/m^3 and 23 W/m^3 obtained with reactor configurations with AEM and CEM respectively (Werner et al., 2013). Pardeshi and Mungray (2014) studied the performance of FO membrane consolidated in MFC using glucose as substrate and observed a power density of 27.38 W/m^3 (Pardeshi and Mungray, 2014). Ismail et al. used FO membrane embedded osmatic reactor for domestic wastewater treatment with concurrent bioenergy generation and desalination of oilfield produced water. The reactor operation resulted in COD removal efficiency, TDS removal efficiency, power density, current density and power yield of 92%, 80%, 48.52 mW/m^2, 136.30 mA/m^2 and 7.46 W/kg respectively (Ismail and Ibrahim, 2015). Zhang and Angelidaki (2013) developed a two-membrane based bioelectrochemical reactor consisting of a hydraulically connected osmotic microbial fuel cell (OsMFC) and an MDC. This combination showed a significantly better desalination performance of 95.9% and an energy production of 0.160 kWh/m^3 while taking effective advantage of the dilution and desalination potentials in OsMFC and MDC respectively (Zhang and He, 2013).

4. Critical evolution of recently investigated MDC configurations

The MDC configurations differ by their variation in functional application, electrodes material, electrolytes, IEM, concentration of saline water, size and number of chambers. These parameters affect the MDC's performance in terms of desalination efficiency, CE, COD removal, TDR and pollutant removal efficiency. The performance of various MDC configurations for desalination and power generation were summarized in Table 2. The first lab-scale prototype in the form of three-chambered cubic MDC was a simple structure and utilized for desalination of brine solutions. However, it showed the directions for constructing feasible MDCs capable for treating large volumes of different types of real wastewater. Moreover, this lab-demonstration suggested to explore the mechanisms of reducing internal resistance to achieve higher efficiency of desalination and energy recovery. Later on, the establishment of air cathode and bio-cathode MDCs improved the CEs, TDRs and desalination efficiencies through innovation in material and mechanism.

The subsequently developed stacked MDC attained considerable attraction due to its variety of functions. Table 2 illustrated that higher CODs, CE, TDR, power density and desalination efficiency were achieved by stacked MDCs. This was one of the configurations of MDC which was tested to be scaled-up for practical applications. The configuration utilized a number of IER stacks, this could lead to higher internal resistance at large scale. Since, the voltage produced by SMDC was limited, therefore the insertion of optimum number of stacks might achieve maximum desalination and power production. The UMDC, another important configuration also achieved higher desalination efficiency and power density. However, the higher resistance between the anode and cathode chambers limited the ions transfer and thereby declined its performance. Therefore, the optimization in configuration and operational parameters, such as, distance between the electrodes, selection of proper mediators and microbes is required. In addition, due to unavailability of cathode chamber, the outer surface of cathode was continuously rinsed with acid solution or treated water which might lead to a complex operation. The capacitive MDCs showed relatively low desalination rates as they were particularly developed for treating low conductive saline waters. Moreover, Table 3 illustrated the worthy

Table 2
Summary of the different MDC configurations and their bio-electrochemical performances.

Configuration	Anode material/ Chamber volume	Cathode material/ Chamber volume	Anion exchange membrane	Cation exchange membrane	Anolyte	Catholyte	Desalination chamber fed NaCl concentrations	External resistance, (Ω)	Coulombic efficiency (CE), %	Total desalination rate (TDR)	COD removal, (%)	Power density	Desalination efficiency, (%)	Ref.
Three-chamber MDC	Carbon Felt/11 mL	Carbon Felt/ 11 mL	DFI120/Tianwei Membrane	Ultrex CMI7000, Membrane International	Sodium Acetate (1.6 g/L)	Ferricyanide	5, 20 and 35 g/L	200	–	–	–	2000 mW/m^2	90	(Cao et al., 2009)
Three-chamber MDC	Carbon Cloth, (BASF, NJ)	30% Wet-proofed Carbon Cloth (0.5 $mgcm^{-2}$ Pt, 4 layers of PTFE), (type B-1B, E-TEK)	AMI-7001/ Membrane International + Experimental AEM/ Aminated Radel R-5500	CMI-7000/ Membrane International + Experimental CEM Sulfonated Radel R-5500	Sodium Acetate (1 or 2 g/L)	50 mM PBS Buffer	5 or g/L	50–1000	68 ± 11	–	–	480 mW/m^2	43–67	(Mehanna et al., 2010b)
Biocathode MDC	Carbon Felt/49 Ml	Carbon Felt/ 40 mL	AMI-7001 S/ Membranes International	CMI-7000 S/ Membranes International	Sodium Acetate (1.6 g/L)	Sodium Acetate	35 or g/L	200	96.2 ± 3.8	2.83 mg/h	56.2 ± 6.0	960 mW/m^2	92	(Wen et al., 2012)
Biocathode MDC	Graphite fiber brush/1400 mL	Graphite brush embedded in graphite granules/ 500 mL	Ultrex AMI-7001	CEM, Ultrex CMI-7000	Dewatered Sludge	Soil solution in deionized water	5, 10 and 35 g/L	1000	–	–	25.71 ± 0.15	3178 mW/m^3	–	(Meng et al., 2014)
Stacked MDC	Graphite fiber brush, (Mill-Rose Lab Inc., USA)/ 30 mL	Carbon cloth as air-cathode (30% wet-proofed, E-Tek, Type B)/18 mL	AMV/Asahi glass, Japan	Selemion CMV	Sodium Acetate (1 g/L)	Synthetic Seawater	35 g/L	10^6	–	–	–	1140 mW/m^2	98	(Kim and Logan, 2011)
Stacked MDC	Carbon graphite fiber brushes/28 mL	Carbon cloth as air-cathode (30% wet proofed, BASF, USA)/14 mL	DF120/Tianwei Membrane	Ultrex CMI7000/ Membrane International	Xylose (1 g/L) in 50 mM PBS	50 mM PBS buffer	20 g/L	10, 1000	49 ± 4 –35 ± 1	–	60 ± 2 –59 ± 2	860 ± 11 mW/ m^2	76 ± 1 –97 ± 1	(Qu et al., 2013)
Stacked MDC	Graphite fiber brush (Mill-Rose Lab Inc., USA)/ 160 mL	Carbon cloth as air-cathode (30% wet proofed)/53 mL	AMV/Asahi glass, Japan	Selemion CMV	Sodium Acetate (1 g/L) in 50 mM PBS	Synthetic Seawater (35 g/L NaCl)	Synthetic Seawater (35 g/L NaCl)	–	–		55.2 ± 1.7 –62.8 ± 0.4	685 mW/m^2	26 ± 0.5	(Davis, 2013)
Stacked MDC	Carbon felt as bioanode/21.2 mL	Carbon cloth as air-cathode (30% wet-proofed, E-Tek, Type B, BASF)/ 7.1 mL	DF120/Tianwei Membrane	Ultrex CMI7000/ Membrane International	Sodium Acetate (1.64 g/L)	Potassium phosphate salts solutions	20 g/L	1–1000	–	25.2 mg/h	–	–	99.4	(Chen et al., 2011)
Stacked MDC	Carbon brushes (Gordon Brush Mfg. Co. Inc., Commerce, CA, USA)	Carbon cloth	–	–	Phosphate-buffered Sodium Acetate (2 g/L)	Phosphate buffer solution (100 mM)	5 g/L	10	–	90.8 ± 8.3 mg/ h	–	–	–	(Ge et al., 2014)
rMDC	Carbon graphite fiber brushes/28 mL	Carbon cloth as air-cathode (30% wet proofed, BASF, US)/14 mL	DF120/Tianwei Membrane	Ultrex CMI7000/ Membrane International	Xylose (1 g/L) in 25 or 50 mM PBS	25 or 50 mM PBS	20 g/L	1000	22 ± 2, 25 ± 1	–	79 ± 4, 78 ± 3	931 ± 29 mW/ m^2	34 ± 1, 37 ± 2	(Qu et al., 2012)

(*continued on next page*)

Table 2 (*continued*)

Configuration	Anode material/ Chamber volume	Cathode material/ Chamber volume	Anion exchange membrane	Cation exchange membrane	Anolyte	Catholyte	Desalination chamber fed NaCl concentrations	External resistance, (Ω)	Coulombic efficiency (CE), %	Total desalination rate (TDR)	COD removal, (%)	Power density	Desalination efficiency, (%)	Ref.
rMDC	Activated carbon granules Weishimei Environmental Technology Co., Ltd., China/675 mL	Activated carbon granules as biocathode (Weishimei Environmental Technology Co., Ltd., China)/ 338 mL	1.8 mol/kg, Shanghua, China	2.0 mol/kg, Shanghua, China	Phosphate-buffered Sodium Acetate (1.64 g/L)	Phosphate-buffered sodium bicarbobate + ammonium chloride +	10 g/L	150, 100, 50 and 10	124.4	95.4 mg/h	–	11,800 mW/ m^3	93.4	(Zuo et al., 2014)
IER-MDC	Carbon fiber felt/ 100 mL	Same as anode electrode/ 100 mL	AMI-7001/ Membranes International Inc., New Jersey	CMI-7000/ Membranes International Inc., New Jersey	Acetate-laden synthetic wastewater with phosphate buffer (90 mL)	50 mM potassium ferricyanide	700 and 100 g/L	10–1000	>10	–	–	360 mW/m^2	95–98	(Zhang. et al., 2012a,b)
IER-MDC	Graphite fiber brush (Mill-Rose Lab Inc., USA)/ 30 mL	Platinum nanoparticles used as air-cathode/18 mL	AMV/Asahi glass, Japan	Selemion CMV	Phosphate-buffered Sodium Acetate (1 g/L)	Brackish water	13.6 g/L	10	54 ± 7	–	78 ± 2	650 ± 40 mW/ m^3	93–100	(Shehab et al., 2013)
IER-MDC	Carbon felt as bioanode/300 mL	Same as anode electrode functioning as biocathode/ 300 mL	AMI-7001/ Membrane International, Inc.	CMI-7000/ Membrane International, Inc.	Phosphate-buffered Sodium Acetate (1.64 g/L)	Phosphate-buffered Sodium bicarbonate (1.9 g/L)	2, 5 and 10 g/ L + mixed-bed ion-exchange resin	0.1 –99,999	–	–	–	–	36 (desalination ratio)	(Morel et al., 2012)
PMDC	Graphite paper/ 180 mL	Graphite paper/ 180 mL	AMI 7001/ Membranes international	CMI 7000/ Membranes international	Synthetic wastewater with aerobic sludge	Mineral solution with microalgae as biocatalyst	10 g/L	10,000	–	6.7 mg/h	65.6	84 mW/m^3	40	(Kokabian and Gude, 2013)
UMDC	Graphite granules (Carbon Activated Corp., Compton, CA, USA)/500 mL	Carbon cloth (Zoltek Companies, Inc., St. Louis, MO, USA)/350 mL	AMI-7001/ Membrane International, Inc., Glen Rock, NJ, USA	CMI-7000/ Membrane International, Inc.	Synthetic wastewater (Phosphate-buffered Sodium Acetate)	Acidified water	30 g/L	1	–	–	–	30,800 mW/ m^3	>99	(Jacobson et al., 2011a)
UMDC	Carbon brushes (Gordon Brush Mfg. Co., Inc., Commerce, CA)/1.9 L	Outer surface of CEM coated with layers of Pt and Nafoin solution, and covered by two layers of carbon cloth	AMI-7001/ Membrane International, Inc., Glen Rock, NJ	CMI-7000/ Membrane International, Inc.	Synthetic wastewater containing acetate (35 g/L)	Acidified water	Salt solution/ Artificial seawater	0.1 and 6	–	–	–	28,900 mW/ m^3	94.3 ± 2.7 and 73.8 ± 2.1	(Jacobson et al., 2011b)
MDC-MCDI	Carbon felt	Carbon felt	AMI-7001 S/ Membranes International, USA	CMI-7000 S/ Membranes International, USA	Phosphate-buffered Sodium Acetate (1.6 g/L)	Phosphate-buffered Sodium Acetate (1.6 g/L)	10 g/L	200	–	3.7 mg/h	–	–	74.4	(Wen et al., 2014)
cMDC	Graphite brush (Golden Brush, CA)/ 23 mL	Carbon cloth as air-cathode (30% wet proofed)/27 mL	Assembly: CEM/ ACC/Ni or Cu (CMXSB, Astom Corporation, Japan/	Assembly: Ni or Cu/ACC/CEM (Ni or Cu mesh current/	Phosphate-buffered Sodium Acetate (1.6 g/L)	Phosphate-buffered Potassium	Salt solution comprising of Sodium Chloride,	–	–	–	–	–	88	(Forrestal et al., 2012b)

			activated carbon cloth (McMaster Carr, IL)/Ni or Cu mesh current)	activated carbon cloth/CMXSB, Astom Corporation, Japan)		Chloride (10 g/L)	Sodium Phosphate and Sodium Biphosphate							
cMDC	Activated Carbon Cloth (ACC) (Chemviron Carbon, UK)/23 mL	Same as anode electrode/27 mL	Assembly: AEM/Ni or Cu/ACC (AMX, Astom Corporation, Japan)/Ni or Cu mesh current collector/activated carbon cloth	Assembly: CEM/Ni or Cu/ACC (CMX, Astom Corporation, Japan)/Ni or Cu mesh current collector/activated carbon cloth	Phosphate-buffered Sodium Acetate (1.6 g/L)	50 mM Ferricyanide solution	10 g/L	1	–	–	–	–	69.4	(Forrestal et al., 2012a)
MCDC with CDI module inside DC	Carbon fiber brush as bioanode (Gordon Brush, CA)/23 mL	Carbon cloth as air-cathode (30% Teflon coated)	No AEM used. Another CEM was inserted at place of AEM.	CMX-SB, Astom Corporation, Japan	Phosphate-buffered Sodium Acetate (1.6 g/L)	Sodium phosphate buffer	Produced water	–	–	–	–	–	70	(Stoll et al., 2015)
OsMDC	Carbon brush as bioanode (Gordon Brush Mfg. Co. Inc., Commerce, CA)	Carbon cloth as air-cathode (Zoltek Corporation, St. Louis, MO)	FO membrane in place of AEM (Hydration Technology Innovations, LLC, Albany, OR)	Membrane International Inc., Ringwood, NJ	Sodium acetate + Sodium bicarbonate, Sodium chloride	Potassium ferricyanide	10 g/L	1	–	–	–	–	57.8	(Zhang and He, 2012b)
MDC	Graphite brush/150 mL	Carbon cloth as air-cathode/50 mL	AR204-SZRA-412	CR67-HMR-412	Phosphate-buffered Sodium Acetate (2 g/L)	100 mM PBS	Mixed ion solution (Ca^{+2}, Mg^{+2}, Na^{+}, Cl^{-}, Br^{-}, SO_4^{-2})	1.5	–	–	–	–	13 and 29	(Luo et al., 2012a)
MDC	Graphite brushes/140 mL	Carbon cloth/140 mL	AMI 7001/Membranes international, NJ	CMI 7000/Membranes international, NJ	Domestic wastewater	Phosphate (50 mM) buffered ferricyanide	100 mM NaCl + 100 mM $NaHCO_3$	1000	131	–	52	8010 mW/m^3	66	(Luo et al., 2012c)

Table 3

Diversified applications of MDCs instead of desalination.

Remediation of contaminated water

Particular application	MDC Configuration	Anode Material/ Chamber Volume	Cathode/Cathode Chamber Volume	Anion Exchange Membrane (AEM)	Cation Exchange Membrane (CEM)	Anolyte	Catholyte	Treated fluid in which S'MDC to be immersed	Removed Ions/ Component	External Resistance, (Ω)	COD Removal, %	Coulombic Efficiency (CE), %	Power Density, (mW/m^2)	Ions/ component removal Efficiency, %	Ref.
Remediation of polluted groundwater	SMDDC	Carbon paper (Toray carbon paper, E-TEK division, USA)	Carbon paper (Toray carbon paper, E-TEK division, USA)	AMI 7001/ Membrane international, NJ	CMI 7000/ Membrane international, NJ	Synthetic wastewater	Anodic effluent	Nitrated tap water as synthetic groundwate	NO_3^-	5, 50 and 100	87.7	66.4	101.1 mW/m^2	90.5	(Zhang and Angelidaki, 2013)
Ammonia inhibition	SMDC with CSTs	Carbon paper	Carbon cloth	AMI 7001/ Membrane international,	CMI 7000/ Membrane international, Ringwood, New Jersey	Phosphate-buffered Sodium Acetate (1.6 g/L)	Synthetic ammonia-rich wastewater	Thermophilic digested manure	NH_4^+-N	10	–	–	4.33 A/m^2	86 g-N/m^2/ day	(Zhang and Angelidaki, 2015a)
Ammonia removal	SMDC	Carbon paper (E-TEK division, USA)	Outer surface of CEM coated with layers of Pt and Nafoin solution, and covered by two layers of carbon cloth	AMI 7001/ Membrane international, NJ	CMI 7000/ Membrane international, NJ	Acetate modified nutrient buffer solution	Neutral NaCl (0.02, 0.29 or 2 M) or KCl (0.02 M) solution	Synthetic ammonia-rich wastewater in CST	NH_4^+ -N	1–10	–	–	0.71 ± 0.5 W/m^2	88	(Zhang and Angelidaki, 2015b)
Cu containing wastewater treatment	FMDC	Carbon felt/49 mL	Graphite plate/49 mL	AMI-7001, Membranes International Inc., NJ	CMI-7001, Membranes International Inc., NJ	Sodium Acetate (1.64 g/L)	$CuCl_2$ solution + 5 g/L NaCl solution	–	Cu^{+2}	10 and 1000	–	–	226.2 mW/m^2	99.4 ± 0.4	(An et al., 2014a)
Removal of Cr (VI)	Three chamber MDC	Carbon felt/45 mL	Graphite plate/45 mL	AMI-7001/ Membranes International Inc., NJ	CMI-7001/ Membranes International Inc., NJ	Phosphate-buffered Sodium Acetate (45 mL/L)	45 mL potassium phosphate + different conc. of $K_2Cr_2O_7$	–	Cr (VI)	200	–	–	–	72.5 ± 11.8	(An et al., 2014b)

Nutrients Recovery

Particular application	MDC Configuration	Anode Material/ Chamber Volume	Cathode/Cathode Chamber Volume	Anion Exchange Membrane	Cation Exchange Membrane	Anolyte	Catholyte	Middle Chamber	Removed Nutrients	External Resistance, (Ω)	COD Removal, %	Coulombic Efficiency (CE), %	Power Density, (mW/m^2)	Nutrients removal Efficiency, %	Ref.
Removal of ammonium and phosphate ions	MNRC	Granular activated carbon/ 21.2 m/L	Carbon cloth as air-cathode (30% wet proofed)/3.6 mL	Ultrex AMI-7001/ Membrane International Inc.	Ultrex CMI7000/ Membrane International Inc	Synthetic wastewater (NH_4Cl, Na_2HPO_4, Na_2SO_4, NaH_2PO_4, glucose)	Synthetic wastewater	0.164 g/L NaCl solution	NH_4^+-N, PO_4^{-3}-P	5–1000	>82	7–15	–	>97 for HH_4^+-N and >64 for PO_4^{-3}-P	(Chen et al., 2015)

Water Softening

Particular application	MDC Configuration	Anode Material/ Chamber Volume	Cathode/Cathode Chamber Volume	Anion Exchange Membrane	Cation Exchange Membrane	Anolyte	Catholyte	Middle Chamber Electrolyte	Removed metals	External Resistance, (Ω)	COD Removal, %	Coulombic Efficiency (CE), %	Power Density, (mW/m^2)	Metals removal Efficiency	Ref.

Removal of water hardness	Three-chamber MDC	Carbon fiber brush as bioanode 60 mL	Same as anode electrode/60 mL	AMI-7001/ Membrane International, Inc.	CMI-7000/ Membrane International, Inc.	Sodium Acetate (3 g/L)	Potassium ferricyanide	Hard Water	As, Cu (II), Ni (II), Hg	1	–	–	–	95 [As (89 ± 6), Cu (97 ± 0), Ni (95 ± 1), Hg (99 ± 2)]	(Brastad and He, 2013)
Water hardness removal	Enzymes inoculated MDC	Carbon cloth with	Carbon cloth with Pt catalyst as air-cathode/25 mL	AMI-7001/ Membrane International, Inc.	CMI-7000/ Membrane International, Inc.	50 mM glucose	2 mM phosphate buffer	Synthetic and actual hard waters	Ca and Mg	100	–	–	–	46 (synthetic hard water), 74, 86 ± 1.7, 82.3 ± 3.7 (actual hard waters)	(Arugula et al., 2012)
Removal of water hardness	Three-chamber MDC	Carbon cloth/ 60 mL	Non-catalyzed carbon cloth as abiotic cathode/60 mL	AMI-Membranes International Inc., USA	CMI-7000/ Membranes International Inc., USA	3 g/L glucose	Deionized distilled water	Synthetic groundwater	Ca and Mg	5–3000	70	–	348 mW/m^2	80.7	(Hemalatha et al., 2017)

Production of Chemicals and Gases

MDC Configuration	Anode Material/ Chamber Volume	Cathode/ Cathode Chamber Volume	Anion Exchange Membrane/Cation Exchange Membrane	Acid production/ Alkali production Chamber Electrolyte	Anolyte	Catholyte	Desalination Chamber NaCl tested Concentrations	Produced Chemicals/ Gases	Production Volume/ % Recovery	External Resistance, (Ω)	COD Removal, %	Coulombic Efficiency (CE), %	Power Density, (mW/m^2)	Desalination Efficiency, %	Ref.
MEDC	Carbon cloth (type A; E-TEK)	Carbon cloth (type B-1B; E-TEK)	AMI-7001 (Membrane International, Inc.)/ CMI-7000 (Membrane International, Inc.)	–	50 mM phosphate buffer solution	50 mM PBS buffer	5 or 20 g/L	H$_2$	(6.5 ± 1.4)mL/ 44 ± 10, (2.7 ± 1.0) mL/15 ± 4	10	38 ± 3, 54 ± 4	48 ± 4, 38 ± 3		–	(Mehanna et al., 2010a)
MEDC	Graphite brushes (Golden brush, CA)/ 25 mL	Stainless steel mesh (Type 304, McMaster, IL)/36 mL	AMI-7001 (Membrane International, Inc.)/ CMI-7000 (Membrane International, Inc.)	–	Phosphate-buffered Sodium Acetate (1 g/L)	50 mM phosphate buffer	10 g/L	H$_2$	48.7 mL/72	10	–	–	–	98	(Luo et al., 2010)
MEDCC	Graphite brush/30 mL	Carbon cloth with Pt (30% wet proofed)/ 30 mL	Ultrex AMI-7001/ Ultrex CMI-7000	10 mL of 10 g/L NaCl	Phosphate-buffered Sodium Acetate (1 g/L)	30 mL of 10 g/L NaCl	10 g/L (10 mL)	Acid and Alkali	2.1 ± 0.7 mmol (AP)/ 75, 206 ± 0.9 mmol (A'P)/96	10	–	62–97	–	–	(Chen et al., 2012a)
MEDCC	Graphite brush/30 mL	Carbon cloth (30% wet proofed)/ 15 mL	Ultrex AMI7001(Membranes International)/Ultrex CMI7000(Membranes International)	14 g L^{-1} of NaCl solution	Phosphate-buffered Sodium Acetate (1 g/L)	Deionized water	35 g/L	Acid and Alkali	0.079 ± 0.006 mmol/ h (AP), 0.13 ± 0.02 mmol/h (A'P)	10	–	>95	–	63	(Chen et al., 2012b)
MEDCC	Carbon brush/ 336 mL	Fabricated using Dong et al. method (Dong et al., 2012)/1 mL	Ultrex AMI-7001, MI, USA/Ultrex CMI-7000, MI, USA	1 g/L of NaCl solution	Sodium Acetate (1 g/L) in 50 Mm PBS	1 g/L of NaCl solution	35 g/L	Acid	–	10	–	113 ± 9	–	–	(Ye et al., 2017)

applications of MDC reactors coupled with other functions (MEDC and MEDCC). These configurations were beneficial due to the production of valuable commodities. However, these configurations experienced different operational challenges such as pH imbalance, increased internal resistance, potential losses and lower water recovery. The investigation for potential loss in a stacked MDC revealed that the junctional potential, developed across an IEM due to concentration difference between dilute and concentrate chambers, increased rapidly with progression in desalination (Kim and Logan, 2011). To minimize these issues different approaches such as recirculation of electrolyte, addition of acidic/basic buffer, and increase of anodic volume were adopted. However, these configurations were still suffering from pH imbalance and thereby producing less value-added products and salt removal. Therefore, an efficient technique is required to establish the pH neutrality across these MDCs in order to achieve the maximum production of value-added commodities for compensating the energy input. A novel approach integrating the externally installed electrodialysis module with these MDCs can present a promising solution in eliminating the pH variation. The schematic description for this combined process in given below in Fig. 2. The ED module can comprise a number of dilute and concentrate cells which can be filled with low and high concentrated brine solutions. The recirculation of electrolytes between this ED module and MEDC/MEDCC will improve the performance of these MDC configuration in two ways. First, it will reduce the pH imbalance both in anode and cathode chambers. Secondly, it will reduce the potential and water losses by eliminating the water concentration gradient across the chambers. Moreover, the operation of ED module will produce desalination as well as production of H_2 gas at cathode. Therefore, the overall improvement in the form of increased performance of MEDC/MEDCC and production of H_2 gas as well as achieved desalination from electrdialysis module will compensate the energy input.

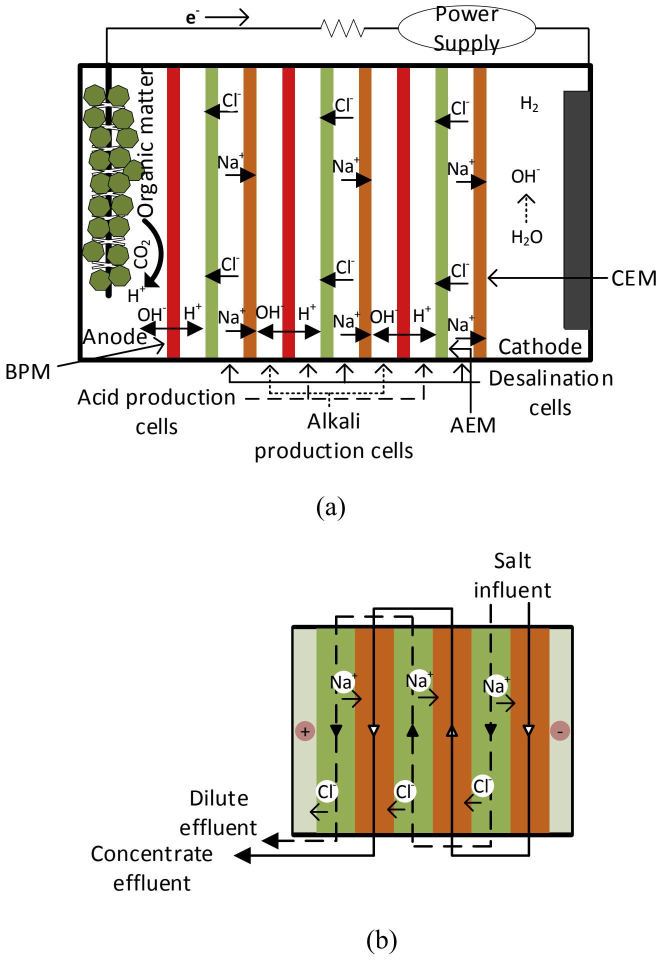


Fig. 2. . Schematic illustration for combined operation of MEDCC and ED module, (a) the MEDCC reactor (b) the ED module.

5. MDC efficiency optimization

The transportation of Na^+ and Cl^- ions across the desalination chamber in a process of desalination is influenced by the electric field, which is developed by the flow of electrons and protons through the external electric circuit and electrolyte chamber respectively. Therefore, the desalination efficiency in terms of ions transfer depends greatly upon the density of the generated current. However, effective desalination is achieved with an increase in current density, which in turn is enhanced by minimizing internal resistance through utilizing most of the MDC generated energy in driving the ions across the membranes. In this context, there is still a need to technically address the different factors offering resistance in the desalination process and generated electricity.

5.1. Effect of intermembrane distance

The inter-membrane distance has significant influence on the MDC process in terms of desalination efficiency and produced power density. Small inter-membrane distances would cause lower internal resistance than large spaced chambers offering high internal resistance. However, large volume chambers can enhance salt removal through an increase in HRT. Ping and He (2014) investigated the effect of inter-membrane distance (0.3–2.5 cm) on desalination efficiency of a bench-scale MDC, under constant operating conditions of HRT and influent flow rate. Using an inter-membrane distance of 0.3 cm, the desalination rates achieved were twelve and seven times higher than those with 2.5 cm for initial salt concentrations of 10 and 30 g/L respectively (Ping and He, 2014). In the initial stage of MDC studies, a series of MDC processes were conducted with intermembrane distances of 3, 10 and 20 mm at initial resistance of 25, 21 and 449 Ω respectively. At the end of the cycle due to a decrease in electrolytic conductivity over the process of desalination, a significant increase in ohmic resistances approximately equivalent to 30 times of initial values was observed. This increase could be correlated to varying spaced chambers and various concentrations of salt solution (Cao et al., 2009; Mehanna et al., 2010b). In later studies, the reduced intermembrane distance of 1.3 mm resulted in high power density, enhanced desalination and high recovery of freshwater (Davis, 2013; Kim and Logan, 2011).

5.2. Effect of resin packing

The stacked MDC operated with higher initial salt concentrations showed a promising option to reduce internal resistance by minimizing the depth of electrolytes between membrane pairs. However, at lower initial salt concentrations, the internal resistance was increased due to low conductivity of electrolytes. In addition to variations in salt concentrations, the presence of spacer media also contributed to internal resistance of a MDC. The removal of spacer media can reduce internal resistance of the MDC. However, the removal will lead to membrane deformation in case of continuous operation, which will affect the flow through chambers (Hatzell and Logan, 2013). Thus, the recent studies have investigated the internal resistance of MDC by filling the intermembrane gap with IER. The IER filling reduced internal resistance by increasing the solution's conductivity through accelerated migration of ions across the desalination chamber (Spoor et al., 2001; Tanaka, 2007; Xu and Huang, 2008).

An IER packed MDC reactor was developed using an electrodeionization (EDI) process in order to increase the desalination rate. In a desalination study of artificial salty water with NaCl concentrations of 5 and 10 g/L, R-MDC showed an ohmic resistance in the range of 3–4.7 Ω, which was 55–272% lower than that observed in controlled non-filled MDC (Morel et al., 2012). The desalination rate obtained with this R-MDC configuration was 1.5–8 times higher than that achieved with controlled MDC. In another study, the concept of IER coupled MDC was investigated to evaluate the desalination performance and electricity production. In such coupled MDCs, reduction in salinities (720 mg/L to 40 mg/L within 30 h, 100 mg/L to 10 mg/L within 10 h) were achieved compared to that (720 mg/L to 50 mg/L within 80 h, 100 mg/L to 30 mg/L within 40 h) by controlled MDC. A notable decrease in internal resistance was observed with the IER packed MDC (7383 ± 69 to 1590 ± 58 Ω and 641 ± 1 to 277 ± 6 Ω for salt concentrations of 50 mg/L and 700 mg/L, respectively) was observed with the IER packed MDC (Zhang et al., 2012a, b).

Another study attempted to enhance the performance of stacked MDC by using an IER embedded microbial electrodeionization cell (SMEDIC). The study developed two configurations of SMEDIC, one with spacers (SMEDIC + S), and another without spacers (SMEDIC-S). The study then compared the efficiency of desalination, power generation, and the reduction of internal resistance using higher to moderate concentrations of salt (35 g/L and 13 g/L). The SMEDIC + S and SMEDIC-S reactors achieved higher desalination efficiencies of 90–94% and 61–72% than the 60% and 43% that were obtained with SMDC using 13 g/L and 35 g/L of salt concentrations (Shehab et al., 2014).

Zuo et al. studied the impact of multiple cations and anions ($SO4^{-2}$, NO_3^-, Cl^-, Ca^{+2}, Mg^{+2}, Na^+, etc) contained in saline water on the performance of IER packed MDC by analyzing the variations in resin property and membrane fouling. Both additional cations-fed resin packed MDC (CR-MDC) and additional anions-fed resin packed MDC (AR-MDC) reactors were operated to analyze the transfer behavior of multiple ions and also their removability. The observed order for the migration of ions was $SO4^{-2} > NO_3^- > Cl^-$ while for cations it was $Ca^{+2} \approx Mg^{+2} > NH_4^+$. After long-term operation, the conductive properties of both membrane and IER decreased due to cation fouling/scaling and exchange between sulphonic acid groups respectively. The AR-MDC operation removed more multiple anions than the multiple cations removed in the CR-MDC operation, achieving a desalination efficiency of 99% at a hydraulic retention time of 50 h. The predicted performance of R-MDC revealed that it was not suitable for sea/brackish water treatment due to their higher level of hardness (Zuo et al., 2013). In a similar study, the performance of fabricated stacked resin-packed MDC (SR-MDC) with a capacity of more than 10 L was investigated to treat the municipal wastewater with salt concentration of 0.5 g/L NaCl. The batch operation of this MDC configuration achieved a high desalination efficiency of 94.8% with an internal resistance of 3.2 Ω and generated power density of 11.8 W/m^3 (Zuo et al., 2014). These studies showed that IER offered a promising approach to enhance the performance of SDMC reactors by reducing internal resistance. To make the use of IER more effective, limitations related to resin contamination and membrane fouling should be investigated.

5.3. pH control

The insertion of AEM and CEM in a MDC to produce a desalination chamber guided the directional transport of salt ions. This chamber presents a barrier in the flow of ions produced due to oxidation/reduction reactions. Because of the hindrance to the transfer of these ions, protons and hydroxyl ions, produced by microbial respiration and oxygen reduction, continued to accumulate in the anode and cathode chambers respectively. This build-up of ions would create a pH imbalance, which will affect the anodic and cathodic reactions. As explained in the recirculation MDC section, this pH variation could be reduced by increasing the volume of the anodic solution, the addition of acid/base/buffer solutions, and the recirculation of anolyte and catholyte (Luo et al., 2012c). However, these techniques were neither sustainable nor economical due to wastage of chemicals and materials they involve. Later studies investigated different routes of proton and hydroxyl ions transfer using electrolyte circulation through the chambers, and the addition of cathode effluent in the anode chamber in order to achieve self-balanced electrolyte pH conditions.

The technique of electrolyte recirculation between the chambers would eliminate the pH imbalance through mixing the anodic acidic solution with the catholic alkaline solution. However, the organic matter and microbes transferred during recirculation might stimulate the growth of biofilm on the cathode, reducing the catalytic activity. In order to enhance desalination performance and avoid the biofilm growth in the cathode chamber, a new concept of circulation MDC was developed, and called the separator coupled circulation stacked microbial desalination cell (c-SMDC-S). This MDC configuration was compared with the non-separator coupled circulation stacked microbial desalination cell (c-SMDC) and the regular SMDC to investigate the effects of buffer free electrolyte circulation on pH change, electricity production and the operating period of the reactor. In comparison to other MDC configurations tested, c-SMDC-S stable operation lasted for 2 months with slight anodic pH variation of 6.8–7.9, achieving a desalination ratio of 65–37% (Chen et al., 2012a, b, c). In another study related to microbial nutrient recovery cell (MNRC), the electrolyte circulation technique promoted the satisfactory removal and recovery of nutrients by adjusting the pH (Chen et al., 2015). In a stacked MDC operation, the addition of catholyte effluent to the anode chamber reduced the pH imbalance and enhanced the salinity removal by 26% compared to 18% achieved without the addition of catholyte (Davis, 2013).

Another feasible approach proposed to remove the pH imbalance was the establishment of ionic traffic through the membranes. In cMDC, the insertion of CEM next to the anode facilitated the transfer of proton from the anode chamber to the desalination chamber and from there to the cathode chamber, eliminating the pH variation (Forrestal et al., 2012b). cMDC thus also addresses not only the accumulation of salt ions in adjacent chambers during the desalination process, but also the control of pH fluctuation. In another study, a direct ion transfer pathway was constructed by dividing the desalination chamber into upper and lower compartments. The upper part was operated for desalination while the lower part served as a medium for proton transfer. Different types of separators (AEM, CEM and Ultrafiltration membrane) were utilized as separators in the lower chamber to test their protons transfer ability in reducing the pH gradient. AEM showed the best performance and decreased the pH variation by 54% (Yang et al., 2013).

However, if used on a large scale, the electrolytes recirculation approach for pH mitigation would facilitate the growth of biofilm and heavy deposits in the cathode chamber. For effective application of this method, these issues, along with the high cost of pumping, need to be investigated in future.

5.4. *Operating conditions*

The MDC performance in terms of desalination efficiency and generated power density is greatly affected by operating parameters. Various factors influencing the MDC functioning include the electrolyte circulation rate (ECR), the substrate concentration, the mode of operation, ratios of concentration/dilution solution volume, the salt concentration and HRT.

ECR parameter affected the mass transfer resistance and consequently the desalination rate through variations in the thickness of the solution boundary layer. Qu et al. investigated the influence of ECR in reducing pH fluctuation, enhancing salt removal and increasing power density in a MDC operation. Higher reduced salinity levels of 34± 1% (50 mM) and 37± 2% (25 mM) were achieved with electrolyte recirculation, compared to 39± 1% (50 mM) and 25± 3% (25 mM) obtained without recirculation.

In an investigation of air-cathode MDC as a pre-treatment step of RO, two different concentrations (1 g/L and 2 g/L) of acetate solution as an anodic substrate were utilized to analyze their effects on solution conductivity, generated power density and coulombic efficiency (CE). At higher concentration of substrate, higher values of CE and power density (68± 11% and 424± 57%) were achieved, compared to values (66± 11% and 159± 34%) obtained with low substrate concentration (Mehanna et al., 2010b). Generally, the desalination performance of a wastewater treating process increases with an increase in the salinity of the saline water. Whereas, low salt concentration leads to lower desalination rate due to increased internal resistance and the resultant lower electrolyte conductivity. In a research study, the effect of three different salinities (5 g/L, 10 g/L and 20 g/L) was investigated on the performance of both OsMDC and controlled MDC in terms of desalination efficiency and generated current. In the MDC process, a reduction in the salinity of the saline water decreased the produced current, which could be due to a reduction in the electrolyte conductivity. However, in comparison to OsMDC, lower salt removal rates were observed at all investigated salinities, which can be attributed to water inclusion due to osmotic pressure (Mehanna et al., 2010b).

Mode of operation was another significant factor contributing to MDC performance. Three different operating modes of MDC such as batch, cyclic batch and continuous were frequently reported in the literature. At the beginning of the batch cycle, maximum output voltage and power density were achieved together. While, with the lapse of time, the MDC performance decreased due to increased internal resistance and low electrolytic conductivity (Ping et al., 2013). The MDC operated in cyclic batch mode showed better performance than the MDC operated in batch mode. This could be ascribed to stable pH and lag phase time reduction because of MDC feeding at regular intervals (Forrestal et al., 2012a; Pradhan and Ghangrekar, 2015). However, the continuous circulation of electrolyte was best at improving the MDC performance because it removed the pH fluctuations through homogeneous distribution of the substrate, causing an increase in desalination efficiency and produced power density (Jacobson et al., 2011a).

HRT was another important parameter in the wastewater treatment process, which greatly effects the operational and capital cost of a MDC process (Akman et al., 2013). Longer HRT would facilitate less salt influent into the middle chamber causing less water and salt ions diffusion in desalination and anode/cathode chambers respectively. Whereas, more transfer of water and salt ions would take place at shorter HRT due to the high concentration gradient. Therefore, varying the HRT would significantly influence the generated power density and the desalination performance of MDC. Ping and He (2014) investigated the effect of HRT variation on the desalination performance of bench-scale MDC. Higher desalination of 35% was achieved at HRT of 20 h, compared to 12% obtained with HRT of 6 h (Ping and He, 2014). In another study, a numerical approach was utilized to simulate the specific relationship between the biological, electrochemical and engineering factors of MDC reactor. The model developed was based on Nernst-Monod equation to optimize large-scale MDC configuration and operation. The model calibration was conducted using the experimental data generated with variation in substrate flow rates. In addition, the model was validated by the data obtained with different concentrations of salt and substrate, and varying external resistances. The model predicted well the generated current, desalination rate and organic concentration close to their corresponding experimental values. However, in model development, a number of parameters were not considered; in particular, the variation in substrate concentration and heterogeneous spatial distribution of microbial film across anode over the process of desalination. This limited the model's ability to simulate the reliable desalination process of MDC with deviation in predefined values of external resistance and salt concentrations (Ping et al., 2014). In order to interpret the MDC experimental data and guide the operating system well, extensive research efforts further improved the model for MDC operation in treating brackish water. The model was modified by considering various external resistances, subsequent variations in generated current, differences in salt concentration between different compartments and resultant water osmosis, and salt diffusion. The improved model estimated the experimental data well and was highly able to provide enough supportive information on the optimization of the process (Ping et al., 2015).

5.5. *Desalinated water contamination*

In the course of MDC desalination process, different charged ions (PO_4^{-2}, Cl^-, HPO_4^-, K^+, NH_4^+) in cathode buffer solution can be transferred to the desalination chamber under the effect of electric potential and concentration gradient. Therefore, the treatment of real wastewater containing complex components ($CaCO_3$, $CaSO_4$, $Ca(NO_3)_2$, $MgCO_3$, $MgSO_4$, $Mg(NO_3)_2$) may be accompanied by transfer of these ions into the desalination chamber. The diffusion of these ions in the middle chamber will contaminate the IEM as well as the treated water, causing further processing for water reuse. Spectroscopic techniques revealed AEM to be fouled more by the organic compounds than by CEM in a long-term MDC process for treating complex compounds containing domestic wastewater. (Luo et al., 2012b). In another study, phosphate buffer solutions used in MDC or MEDC caused the transfer of phosphate groups through AEM to desalination chamber. These transported groups resulted in heavy deposits of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ in the desalination chamber (Luo et al., 2010; Mehanna et al., 2010a). A cMDC was developed in order to avoid the transfer of these undesired groups and to facilitate their removal. This can be an efficient pre-treatment process for membrane and RO systems in reducing the loading of organics and salinity to avoid membrane fouling and additional processing cost (Forrestal et al., 2015). However, more research efforts need to be directed towards establishing the MDC operation as the sole process for complete removal of organic and salt components while producing deionized freshwater.

5.6. Membrane scaling and fouling

Over the desalination cycle of MDC, changes in membrane properties occur due to their biofouling/scaling because of the transfer of wastewater contained complex compounds through them. This characteristic membrane scaling would reduce the desalination performance by inhibiting the mass transport of ions through them and consequently inducing the pH imbalance. Luo et al. investigated the transport mechanisms of ions as well as membrane fouling/scaling in a MDC process in order to understand the fundamentals for their removal from wastewater. The presence of cations (Ca^{+2}, Mg^{+2}) with Cl^- as a common counter ion in treated saline water adversely affected both power output and desalination rate in batch MDC. It was due to the fact that only 0.4% and 0.1% of Ca^{+2} and Mg^{+2} were transported to cathode chamber while most of the unrecovered content of these ions precipitated on membranes, causing pH imbalance. Due to membrane scaling, the ohmic resistance of MDC increased from 37 Ω to 140 Ω while the produced current density and the desalination efficiency ranged 660 - 210 mA/m^2 and 29–13% through five cycles respectively. The recirculation approach used to eliminate the pH variation increased the mixed salt removal rate by 90%, which was 152% higher than that achieved in fed-batch operation (Luo et al., 2012a). In an investigation related to identifying the key factors influencing the MDC performance over long-term operation, membrane fouling was the sole contributor in increasing the system internal resistance and subsequent ionic transfer across the chambers. A significant decrease of 47% in current density, 46% in coulombic efficiency, and 27% in desalination efficiency was observed with an increase in reactor resistance from 98 Ω to 460 Ω (Luo et al., 2012b). Ping et al. also studied the membrane behavior by investigating their fouling/scaling over the long-term operation of MDC treating actual or synthetic wastewater. The CEM showed a significant increase in offered resistance over the desalination period when compared to the resistance presented by AEM. The increased resistance of CEM was due to the precipitation of various inorganic compounds [$CaCO_3$, $Ca(OH)_2$], which would intensify the need for reactor maintenance, membrane replacement and other associated expenses (Ping et al., 2013). Scaling of CEM has revealed a decrease in MDC performance in treating hard water (Brastad and He, 2013). In a study related to the long-term operation of mixed IER-MDC, various parameters like competitive migration behavior of multiple ions, conductivity changes in mixed resin and membrane fouling were investigated. It was found that the depositing of Ca and Mg compounds on CEM and their exchange of sulphonic or carbonate groups reduces desalination efficiency (Zuo et al., 2013).

6. Current challenges and future prospects

Comparing to other energy intensive BESs for wastewater treatment, MDC became more significant technology for sustainable desalination and renewable energy production. MDC development went through innovations in reactor design, selection of feasible materials and identification of bio-chemical mechanisms to amplify the power output and reduce capital cost. However, certain challenges should be addressed in order to construct an optimized MDC for sustainable operation.

Desalination efficiency is a key parameter that determines the performance of a MDC reactor. The parameter is influenced by microbial oxidation and system internal resistance. The impact of internal resistance on MDC efficiency can be understood by investigating the mechanism of ions transfer and membrane properties. Especially, the investigation of internal resistance behavior will be more essential in treating real wastewater with complex compounds. Whereas, the microbial oxidation can be monitored in two ways. First, the anolyte as wastewater that acts as sole driver for desalination can be properly monitored to achieve maximum energy. Secondly, different effective routes for ions transfer can be investigated to prevent possible pH imbalance and electrolytes contamination. However, optimization of MDC configuration as well as its operational parameters can enhance its efficiency enabling its operation at large scale.

Membrane scaling/fouling is one of the major issues affecting the sustainable operation of MDC. Fouling control mechanisms were required in MDC for effective desalination and resource recovery. The cost analysis of MDC technology is essential to ensure its economic feasibility. The research efforts can be directed towards testing the inexpensive materials with low resistance and large surfaces. The currently utilized expensive catalysts are also required to be replaced with low cost durable ones. The effluent from the MDC operation can be carefully inspected as it may contain hazardous formations requiring special procedure for disposal. An understanding of microbial functioning and its compact on environment can avoid any obvious risk.

Moreover, the optimization of aforementioned key parameters greatly contributes in scale-up of MDC reactor performing the long-term feasible operations and practical applications. Recently developed mathematical model for guiding a MDC operation can be revised with supplementary modifications in order to lead the sustainable operation of large-scale MDC. The application of this modified model can be useful in understanding the effect of different parameters such as organic and salt content in wastewater and brine solution on desalination rate and generated current. A techno-economic study for the recently generated largest MDC system can also be conducted in order to investigate its feasibility in terms of reactor performance and stability.

7. Conclusion

MDC has emerged as a promising sustainable technology to meet increasing energy demands with simultaneous seawater desalination, wastewater treatment and renewable energy production. A comprehensive review of different MDC modifications including their desalination performance and generated power has been presented. Various operational parameters affecting the MDC performance in terms of desalination and generated coulombic efficiencies have been critically analyzed.

Based on literature survey, it has been suggested that the installation of ED module, comprising of consecutive concentrate and dilute cells, with MEDC/MEDCC reactor will improve their performance. The integral operation will lead to higher desalination performance as well as production of valuable commodities under controlled pH condition through the electrolytes recirculation across the chambers. Moreover, the practical applications of a MDC reactor require operational parametric optimization for efficient use of produced energy in improving the treatment efficiency. However, meticulous future investigations concerning to membrane scaling/fouling, materials compatibility, electron transfer kinetics, microbial growth and catalyst durability are needed in order to improve the sustainable/feasible MDC operation.

Acknowledgement

The authors appreciate the financial support of Sultan Qaboos University, Muscat, Oman through His Majesty's Trust Fund (SR/ENG/CAED/17/01).

Abbreviations

AC	Anode chamber
AEM	Anion exchange membrane
AP	Acid production
A'P	Alkali production
APC	Acid production chamber
A'PC	Alkali production chamber
BES	Bio-electrochemical systems
BPM	Bipolar membrane
CC	Cathode chamber
CC′	Concentrate Chamber
CEM	Cation exchange membrane
cMDC	Capacitive microbial desalination cell
CoTMPP	Cobalt tetramethylphenylporphyrin
CSTs	Continuous stirred tanks
CTE	Charge transfer efficiency
DC	Desalination chamber
DC′	Dilute Chamber
ED	Electro dialysis
FMDC	Four-chamber microbial desalination cell
FO	Forward osmosis
HRT	Hydraulic retention time
IEM	Ion-exchange membrane
IER	Ion-exchange resin
IER-MDC	Ion-exchange resin packed MDC
MCDC	Microbial capacitive desalination cell
MDC-MCDI	MDC powered membrane capacitive deionization
MEDC	Microbial electrodialysis cell
MEDCC	Microbial electrolysis desalination and chemical-production cell
MEDIC	Microbial electro deionization cell
MNRC	Microbial nutrient recovery cell
OsMDC	Osmotic microbial desalination cell
PBS	Phosphate buffered solution
PMDC	Photosynthetic MDC
rMDC	Recirculation MDC
RO	Reverse osmosis
S'MDC	Submersible microbial desalination cell
SMDC	Stacked microbial desalination cell
SMDDC	Submerged microbial desalination-denitrification cell
SR-MDC	Stacked ion-exchange resin packed MDC
TDR	Total desalination rates
UMDC	Upflow microbial desalination cell

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