

Recent Progress in the Use of Capacitive Deionization and Microbial Desalination Cell for Water Treatment - A Critical Review

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ABSTRACT. *The increasing depletion of water resources is a severe obstacle to the sustainable development. Finding new ways to provide clean water is one of the many collaborative activities that will be obligatory to resolve this worldwide issue. In this regard, among various methods, electrochemical methods have been used for water treatment. For instance, capacitive deionization (CDI) and microbial desalination cells (MDCs) are capable technologies that can overcome the aforementioned issue. In this regard, current study examines recent advancements in MDC and CDI technologies along with the ongoing research in this field. Moreover, it discusses different configurations of these technologies constructed in the past with different materials and methods to present a better understanding of systems' efficiencies, along with their contribution towards research and development. It further presents the unexplored prospects of MDCs and CDI for future work.*

Keywords: Capacitive deionization, Energy production, Desalination, Microbial Desalination Cell (MDC), Water Treatment

1. INTRODUCTION

The world is facing an extreme water shortage. It has been estimated that less than 0.5% surface of earth is consists of fresh water which is acceptable for human utilization, whereas, 97% of the water is in seas and oceans [1]. Around 25% of the population around the world does not have access to drinkable water in a sufficient quantity and quality and more than 80 nations are experiencing a water shortage.

More than 75% of Asia lacks access to clean water, and countries that contain than 90% of the population in that region are already under a serious water crisis. The gap between water demand and water supply will be 40% by 2030. There is a significant "water stress" issue in Pakistan and this situation is rapidly transitioning to "water shortage" situation and yearly water availability has fallen below 1000m³ [2]. Thus, there is a need of planning an effective water management approach. Previously, the solutions proposed to manage the water scarcity include construction of massive infrastructure, providing alternative source of water, increasing the supply of water, reducing water usage, revolutionizing water and wastewater treatment [3, 4]. Apart from water saving structures, various methods like electrodialysis (ED), multistage flash distillation (MSF), reverse osmosis (RO) and nanofiltration (NF) have also been used in spite of high-energy consumption to treat saline water sources (e.g., brackish water and seawater). However, these techniques are not a suitable substitute for the desalination of saline water due to high energy consumption, brine production and greenhouse gas emissions [5].

Capacitive deionization (CDI) is one of the latest technology for saline water treatment [6]. Compared to conventional processes, its advantages include greater safety, an ability to operate at minimal voltage, no requirement of high-pressure pump and chemical regeneration, quick system cleaning, cost and energy efficiency, and environmentally friendliness [7]. Microbial desalination cell (MDC) is an evolving concept which is constructed through a modification of microbial fuel cell (MFC). MDC not only performs desalination but also treats wastewater and generates renewable energy at the same time. It may be integrated with other methods like electrodialysis and reverse osmosis (RO), and it can also be used as an independent desalination method. Keeping

in view the importance of these technologies, this study represents a critical review on the recent researches conducted on both CDI and MDCs.

2. USE OF CAPACITIVE DESALINATION CELL FOR WATER TREATMENT

CDI has been considered as an innovative, environment friendly, energy efficient and cost-effective technology with a high recovery rate ($0.5\text{--}1\text{ kWh/m}^3$) [8]. Electro-sorption and desorption of ion are the two stages for desalination of water by conventional CDI. The two common CDI configurations are flow-by CDI and flow-through CDI [9]. When these two configurations were compared in a study with regards to their long term efficiency, it was found that the stability of CDI is enhanced up to 360% by using flow-by configuration which has a lifetime of 18 days while flow-through configuration had a lifespan of 5 days [10]. Moreover, flow by configuration is also considered better because it contains a hydrodynamic diffuse boundary layer that inhibits dissolved oxygen's transportation to the cathode surface. This can also cause reduction in unequal potential distribution in flow-by configuration.

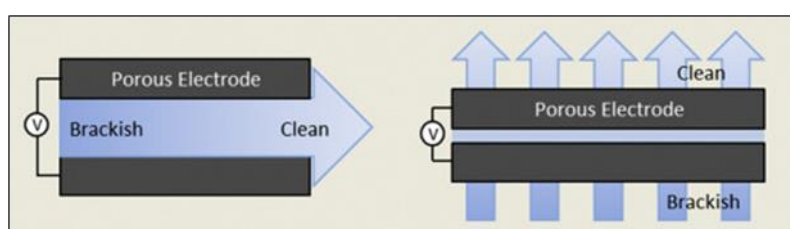


Fig-1: Flow-by vs. flow-through CDI mechanisms

Flow electrode capacitive Deionization (FCDI) is a sustainable saltwater desalination technology with simpler system design and operation, optimized system performance, energy efficient and lower cost with greater ion transport efficiency and adsorption within the electric double layers (EDLs). Unlike other structures, the contact between the adsorbent, dissolved ions and the electrodes is increased by passing the solution in the system directly through macropores of the electrode [11].

Various components are used in the fabrication of lab-scale FCDI cell. These components and their explanation are provided in Table 1.

Table -1: Components of FCDI system

Components	Details
Current collectors	Graphite, stainless steel, titanium plates, and composite current collectors (comprised of acrylic sheets and graphite paper).
Ion exchange membranes (IEMs)	IEMs can improve the effectiveness of desalination.
Gaskets and spacers	Its job is to not let short circuit happen in the middle of the two current collectors. Some of the gaskets are Silicone, Rubber, Latex [14-16].
Peristaltic pumps	Reducing the flow rate of water feed (increasing the residence time of water feed) improves salt removal efficiency.
End plates	PVC, Polyethylene, Polycarbonates, Rigid plates of high-density polyethylene (HDPE), Acrylic and Stainless steel.
Power supply	DC power supply is used. FTCDI uses the zero-voltage method, but overtime it decreases the electrode's capacity [17].
Activated carbon (AC) content	5% by weight, 7.5% by weight, 10% by weight, and 12.5% by weight. Desalination performance and charge efficiency improves over time when the AC content is raised (i.e., at 12.5% by weight) [18].
Electrode material	Anode and cathode can be in the form of mesh, graphite plate-based, titanium mesh-membrane, activated carbon and stainless steel.
Faradaic reactions	Influences electrode performance and lifespan, energy efficiency, pH variations in product water and production of chemical [19].

Components	Details
Hydrodynamic voltammetry	Important for carbon slurries' electro-chemical behavior and to accelerate the speed of transport of mass towards the electrode in a specified way.

3. USE OF MICROBIAL DESALINATION CELL FOR WATER TREATMENT

Microbial desalination systems come from the root of microbial electrochemical systems in which biological reaction helps to remove salt from saline water and generate electricity, it consists of three chambers i.e., anode, cathode and desalination chamber. The microbes are facilitated by anode chamber for energy generation and wastewater treatment, while desalination chamber treats saline water [20].

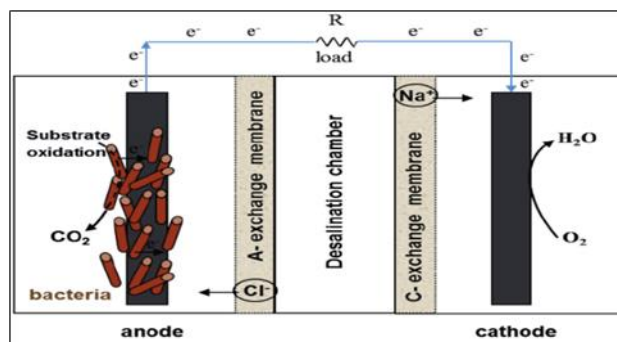


Fig-2: Schematic of microbial desalination cell

3.1. Design Configurations of Microbial Desalination Cell

Various design configurations of MDC have been developed by previous researchers including (a) air cathode MDC, (b) bio-cathode MDC, (c) stack structure MDC, (d) recirculation MDC, (e) microbial-electrolysis desalination and chemical-production cell, (f) capacitive MDC, (g) up-flow MDC, (h) osmotic MDC, (i) bipolar membrane MDC, (j) decoupled MDC, (k) separator-coupled stacked-circulation MDC, (l) ion-exchange resin coupled MDC, as explained below.

3.1.1. Air-Cathode Microbial Desalination Cell

An air-cathode MDC is made up of three chambers i.e., cathode chamber, anode chamber, and desalination chamber. The cathode chamber contains a cathode that has its external side exposed to the atmosphere for oxygen which serves as terminal acceptor of electron. Platinum and cobalt tetra-methoxy-phenyl-porphyrin has been broadly used as catalyst in air cathode MDC [21].

3.1.2. Bio-cathode MDC

The bio-cathode MDC is made up with a cathode that can utilize microbial biofilm attached onto the cathode that function as a catalyzing agent to aid the reduction of oxidant. Bio-cathode has been categorized into two domains i.e., aerobic and anaerobic bio-cathodes. In aerobic bio-cathodes, oxygen acts as an acceptor of electron. While, terminal electron acceptor can be of different catholytes in anaerobic bio-cathode [22].

3.1.3. Stack Structure MDC

It is built with two desalination chambers with anode exchange membranes (AEMs) and cathode exchange membranes (CEMs) between them. Incorporating several ion exchange membranes (IEMs) in arrangement of series results in the enhancement of charge transfer efficiency (CTE) which leads to greater rate of desalination. This configuration permits the transfer of anions and cations produced within the desalination compartment per number of electron pulse in the external circuit. This mechanism results in improved desalination rate and better CTE [23].

3.1.4. Recirculation MDC

In this type, catholyte and anolyte are recirculated to resolve the problem of pH. For this purpose, both electrolytes are flown via an exterior channel or conduit between the cathode and anode compartments [24].

3.1.5. Microbial-electrolysis desalination and chemical-production cell (MEDCC)

It is a modification of microbial electrolysis desalination cell (MEDC) in which a bipolar membrane (BPM) is positioned in-between AEM/CEM and anode/cathode chamber for production of acid/alkali [25]. In a recent study,

alkali and acid production chambers were used for dissolving serpentine and absorbing atmospheric carbon dioxide, respectively [26].

3.1.6. Capacitive MDC (cMDC)

This design uses the combination of CDI and MFC to overcome pH problem of electrolytes. In this configuration, a double layer capacitor is used to stop the migration of anion and cations to cathode and anode chambers through absorption. Later, a novel configuration of cMDC was developed in which the capacitive deionization was used within the MDC. Generally, it consists of two elements i.e., ion-exchange membrane (IEM) and carbon cloth (as the double capacitive layer) which is inserted between electrode chambers and desalination chamber [27].

3.1.7. Up-Flow MDC (UMDC)

It is a battery-cell like structure that consists of two chambers in co-axial formation. The desalination occurs in the external chamber, and the internal chamber acts as the anode, which are separated by IEMs. Meanwhile, the external layer of UMDC performs the function of cathode, the AEM is wrapped across the anode chamber's external face and the CEM is located outside the desalination chamber [28].

3.1.8. Osmotic MDC (OsMDC)

In this configuration, the AEM of conventional MDC is replaced with a forward osmosis membrane to get more effective water recovery. The intent of this set-up is to make the water from anode section move to desalination section and restrict the transfer of ions to the anode and cathode compartment from the desalination section. This in turn increases efficiency of the system [29].

3.1.9. Bipolar membrane MDC (BMP-MDC)

The Bipolar membrane in an MDC is made up of CEM and AEM, which are pasted together by a physical operation like pressing which serves as a transitional layer that dissociates the saline water when a voltage is applied. Unlike the conventional MDC, it contains four sections, where the unit which converts salt into base and acid is situated adjacent to the anode compartment [30].

3.1.10. Decoupled MDC

It is made up of anode and cathode units situated between separate containers that are placed in a salt solution. The cathode and anode chambers are constructed in plate configuration with CEMs and AEMs on every side of the chambers. The support structure is a stainless-steel mesh enclosed with a carbon cloth to function as current collector. Moreover, a decoupled MDC can also be fabricated with many cathode and anode units connected in series. The catalyst used in decoupled MDC is a combination of three materials i.e. carbon, powder, Nafion layered carbon cloth and platinum [31].

3.1.11. Separator-coupled stacked-circulation MDC (c-SMDC-S)

A total of five chambers are fitted in this configuration including a concentrate, two desalination, an anode and a cathode chamber. The anode chamber has activated carbon particles that enhance the growth of bacteria, and a graphite rod [32]. In this set-up, an air cathode is used which consists of a carbon cloth having one side exposed to air and the other attached with a piece of glass, acting as a separator. It also connects the anode and cathode chamber through a channel for recirculation of electrolyte which is facilitated by an external electrolyte chamber providing buffer free electrolyte [33].

3.1.12. Ion-exchange resin coupled MDC (R-MDC)

In this type, traditional MDC's desalination chamber is packed with anion and cation exchange resins. Generally, the electrodes used in its designing are graphite rods that contain carbon for better electrical conductivity [34].

The power density, removal of chemical oxygen demand (COD), columbic efficiency, and desalination efficiency of above-mentioned configurations are shown in Table 3.

Table-2: Technical efficiencies of different MDC configurations

Configuration	Power Density	COD Removal	Columbic Efficiency	Desalination Efficiency	Reference
Air-Cathode MDC	480 mW/m ²	-	-	43% to 67%	[21]
Bio-Cathode MDC	-	-	96.2%	92 %	[35]
Stack Structure MDC	11.8 W/m ³	-	450%	93.4%	[36]

Configuration	Power Density	COD Removal	Columbic Efficiency	Desalination Efficiency	Reference
Recirculation MDC	931 mW/m ²	-	-	55 ± 2%	[24]
MEDCC	-	94%	-	22%	[26]
cMDC	-	-	-	88%	[27]
Upflow MDC	38.9W/m ³	-	-	73.8% - 99%	[28]
OsMDC	160W/m ³	-	-	57.8% - 95.9%	[37]
BMP- MDC	-	-	62% - 97%	50% - 63%	[23]
Decoupled MDC	360 mW/m ²	-	78%	95% - 98%	[34]
c-SMDC-S	-	89%	28%	40% - 81%	[38]
R-MDC	650 mW/m ³	78%	58%	93% - 100%	[32]

Table 3 shows that since different configurations of MDCs exhibit variable efficiencies, therefore, it is pertinent to comparatively analyze them. For this purpose, strengths and limitations of these configurations are provided in Table 4.

Table-3: Strengths and limitations of different configurations of MDCs

Configuration	Strengths	Limitations	Reference
Air-Cathode MDC	✓ High reduction potential and minimal toxic effects of oxygen.	Redox kinetics are slow, high power input and costly.	[25]
Bio-Cathode MDC	Low-cost, no requirement of expensive catalyst, generation of chemicals, concentration of oxygen, and electron received are increased.	-	[25]
Stack Structure MDC	Increase in internal resistance enhances desalination, requires less voltage and produces more energy.	pH imbalance, acidification of anolyte, higher HRT and water losses.	[25]
Recirculation MDC	Balances pH and improves capacity of power density.	Four-fold decrease in the columbic efficiency (CE).	[25, 39]
MEDCC	Better energy recovery, greater CTE, better power density.	High internal resistance and pH imbalance.	[24]
cMDC	pH balance of catholyte and anolyte.	-	[24]
Up-flow MDC	Scaling up is easier, requires no external mixing and makes oxidation more efficient.	-	[25, 40]
OsMDC	High electricity generation, saline water dilution and high treatment capacity.	Membrane biofouling, low columbic efficiency and reduction in separation.	[40, 41]
Bipolar Membrane MDC	Minimal drop in voltage, efficient membrane selection, low resistance, extended life period, produces chemical, and pH balance.	Requires external energy and is costly.	[29]
Decoupled MDC	Configured electrodes are efficient, varying liquid volume ration is simpler, and easier to control and dismantle, repair, replace and scaling up.	-	[25, 40]

Configuration	Strengths	Limitations	Reference
c-SMDC-S	Better CE, avoids pH imbalance, prevents biofouling on the cathode and runs for extended time periods.	-	[38]
Ion-exchange resin coupled MDC	Better charge transfer, less energy consumption and ohmic resistance	Scaling on IEMs, high internal resistance and columbic efficiency drop.	[40]

4. WAY FORWARD TO FUTURE STUDIES

Future studies on CDI can be conducted on multi-salt composition saline water to understand CDI practicability on real sea water, further studies on characterization of high concentrate wastewater, optimum electrode pore size for effective removal of salts, energy recovery from electrodes, exploring different type of materials for flow-electrodes with high conductivity and greater suspension, selective ion removal from FCDI, removal of negatively charged contaminants (e.g., bacteria), positively charged contaminants (e.g., cationic dyes) and nano-plastics need to be explored. The FCDI is better in large scale applications than CDI and can be explored for more economical full-scale studies. Moreover, in full-scale design, there is a need for pre and post treatment and of the wastewater. Therefore, full-scale setup of CDI need to be studied to utilize this technology to its full capacity.

Similarly, studies regarding MDCs should be focused on the development of ion-exchange membranes with better resistance to biofouling. Moreover, materials like carbon nanotubes, activated carbon, graphite and other carbonations should be tested for the construction of anode to provide greater surface area and superior bonding of exoelectrogenic bacteria. Various microbial species can also be used in the process of bio-cathode. In addition, finding an effective and sustainable approach for the stabilization of pH in the anode compartment to promote the growth of microbes, and genetic modification of the exoelectrogenic bacteria to enhance their columbic efficiency can be tested in future. Alongside, various types of wastewaters can be explored to assess their treatment and columbic efficiencies. This aspect implies that there is a need of a full-scale set-up design to deeply understand the feasibility and applicability of MDCs.

5. CONCLUSIONS

Studies conducted on CDI and MDCs have been reviewed, which are two advanced water desalination technologies that have been the subject of research and development in recent years. Major parameters influencing CDI are capacitance, cell volume, applied voltage, and flow rate. FCDI is the advanced version of CDI, and its most important parameters are conductivity and inter-particle connectivity of the flow electrode material. The literature shows that the MDC is significantly affected by the exoelectrogens on the biofilm and the electrode material (anode and cathode). In summary, the integration of CDI and MDC has the potential to revolutionize the field of water desalination, thereby providing an efficient and effective solution for producing fresh water. However, further research and developments are needed to fully realize the potential of this technology.

REFERENCES

- [1] Zou, M.M.a.L., *A study of the capacitive deionisation performance under various operational conditions*. 2012.
- [2] Parry, J., et al. . *Making Every Drop Count: Pakistan's growing water scarcity challenge*. September 29, 2016 [cited 2022 27 Nov]; Available from: <https://www.iisd.org/articles/insight/making-every-drop-count-pakistans-growing-water-scarcity-challenge>.
- [3] Hashim, H.Q. and K.N. Sayl, *Detection of suitable sites for rainwater harvesting planning in an arid region using geographic information system*. Applied Geomatics, 2021. **13**(2): p. 235-248.
- [4] Zhou, L., et al., *Novel perspective for urban water resource management: 5R generation*. Frontiers of Environmental Science & Engineering, 2021. **15**(1): p. 1-13.
- [5] Ihsanullah, I., et al., *Desalination and environment: A critical analysis of impacts, mitigation strategies, and greener desalination technologies*. Science of the Total Environment, 2021. **780**: p. 146585.
- [6] Xing, W., et al., *Versatile applications of capacitive deionization (CDI)-based technologies*. Desalination, 2020. **482**: p. 114390.
- [7] Choi, J., et al., *Applications of capacitive deionization: Desalination, softening, selective removal, and energy efficiency*. Desalination, 2019. **449**: p. 118-130.
- [8] He, D., et al., *Faradaic reactions in water desalination by batch-mode capacitive deionization*. Environmental Science & Technology Letters, 2016. **3**(5): p. 222-226.

- [9] Guyes, E.N., A. Simanovski, and M.E. Suss, *Several orders of magnitude increase in the hydraulic permeability of flow-through capacitive deionization electrodes via laser perforations*. RSC advances, 2017. **7**(34): p. 21308-21313.
- [10] Cohen, I., et al., *The effect of the flow-regime, reversal of polarization, and oxygen on the long term stability in capacitive de-ionization processes*. Electrochimica Acta, 2015. **153**: p. 106-114.
- [11] Son, M., et al., *Improving the thermodynamic energy efficiency of battery electrode deionization using flow-through electrodes*. Environmental Science & Technology, 2020. **54**(6): p. 3628-3635.
- [12] Choo, K.Y., et al., *Study on the electrochemical characteristics of porous ceramic spacers in a capacitive deionization cell using slurry electrodes*. Journal of Electroanalytical Chemistry, 2019. **835**: p. 262-272.
- [13] Nativ, P., Y. Badash, and Y. Gendel, *New insights into the mechanism of flow-electrode capacitive deionization*. Electrochemistry Communications, 2017. **76**: p. 24-28.
- [14] Ma, J., et al., *Analysis of capacitive and electrodialytic contributions to water desalination bflow-electrode CDI*. Water research, 2018. **144**: p. 296-303.
- [15] Ma, J., et al., *Energy recovery from the flow-electrode capacitive deionization*. Journal of Power Sources, 2019. **421**: p. 50-55.
- [16] Hatzell, K.B. and Y. Gogotsi, *Suspension electrodes for flow-assisted electrochemical systems*, in *Nanomaterials in Advanced Batteries and Supercapacitors*. 2016, Springer. p. 377-416.
- [17] Zhang, X., et al., *Flow-electrode capacitive deionization utilizing three-dimensional foam current collector for real seawater desalination*. 2022. **220**: p. 118642.
- [18] Chen, T.-H., et al., *Cation selectivity of activated carbon and nickel hexacyanoferrate electrode materials in capacitive deionization: A comparison study*. 2022. **307**: p. 135613.
- [19] Zhang, C., et al., *Faradaic reactions in capacitive deionization (CDI)-problems and possibilities: A review*. 2018. **128**: p. 314-330.
- [20] Liu, Q., B. Xie, and D. Xiao, *High efficient and continuous recovery of iodine in saline wastewater by flow-electrode capacitive deionization*. Separation and Purification Technology, 2022: p. 121419.
- [21] Mehanna, M., et al., *Microbial electrodialysis cell for simultaneous water desalination and hydrogen gas production*. Environmental science & technology, 2010. **44**(24): p. 9578-9583.
- [22] Huang, L., J.M. Regan, and X. Quan, *Electron transfer mechanisms, new applications, and performance of biocathode microbial fuel cells*. Bioresource technology, 2011. **102**(1): p. 316-323.
- [23] Kim, Y. and B.E. Logan, *Microbial desalination cells for energy production and desalination*. Desalination, 2013. **308**: p. 122-130.
- [24] Qu, Y., et al., *Simultaneous water desalination and electricity generation in a microbial desalination cell with electrolyte recirculation for pH control*. Bioresource technology, 2012. **106**: p. 89-94.
- [25] Al-Mamun, A., et al., *A review of microbial desalination cell technology: configurations, optimization and applications*. Journal of Cleaner Production, 2018. **183**: p. 458-480.
- [26] Zhu, X. and B.E. Logan, *Microbial electrolysis desalination and chemical-production cell for CO₂ sequestration*. Bioresource technology, 2014. **159**: p. 24-29.
- [27] Forrester, C., P. Xu, and Z. Ren, *Sustainable desalination using a microbial capacitive desalination cell*. Energy & Environmental Science, 2012. **5**(5): p. 7161-7167.
- [28] Jacobson, K.S., D.M. Drew, and Z. He, *Efficient salt removal in a continuously operated upflow microbial desalination cell with an air cathode*. Bioresource technology, 2011. **102**(1): p. 376-380.
- [29] Chen, X., et al., *Optimization of membrane stack configuration in enlarged microbial desalination cells for efficient water desalination*. Journal of Power Sources, 2016. **324**: p. 79-85.
- [30] Buck, R., *Ion-selective membranes and electrodes*, Access Science. 2014, McGraw-Hill Education.
- [31] Ping, Q. and Z. He, *Improving the flexibility of microbial desalination cells through spatially decoupling anode and cathode*. Bioresource technology, 2013. **144**: p. 304-310.
- [32] Morel, A., et al., *Microbial desalination cells packed with ion-exchange resin to enhance water desalination rate*. Bioresource technology, 2012. **118**: p. 43-48.
- [33] Chen, S., et al., *Improved performance of the microbial electrolysis desalination and chemical-production cell using the stack structure*. Bioresource technology, 2012. **116**: p. 507-511.
- [34] Zhang, F., et al., *Microbial desalination cells with ion exchange resin packed to enhance desalination at low salt concentration*. Journal of membrane science, 2012. **417**: p. 28-33.
- [35] Wen, Q., et al., *Using bacterial catalyst in the cathode of microbial desalination cell to improve wastewater treatment and desalination*. Bioresource Technology, 2012. **125**: p. 108-113.
- [36] Ge, Z., C.G. Dosoretz, and Z. He, *Effects of number of cell pairs on the performance of microbial desalination cells*. Desalination, 2014. **341**: p. 101-106.
- [37] Zhang, B. and Z. He, *Improving water desalination by hydraulically coupling an osmotic microbial fuel cell with a microbial desalination cell*. Journal of membrane science, 2013. **441**: p. 18-24.

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- [38] Chen, X., et al., *Sustainable water desalination and electricity generation in a separator coupled stacked microbial desalination cell with buffer free electrolyte circulation*. *Bioresource Technology*, 2012. **119**: p. 88-93.
- [39] Shehab, N.A., et al., *Microbial electrodeionization cell stack for sustainable desalination, wastewater treatment and energy recovery*. *Proceedings of the Water Environment Federation*, 2013. **2013**(19): p. 222-227.
- [40] Saeed, H.M., et al., *Microbial desalination cell technology: a review and a case study*. *Desalination*, 2015. **359**: p. 1-13.
- [41] Tawalbeh, M., et al., *Microbial desalination cells for water purification and power generation: A critical review*. *Energy*, 2020. **209**: p. 118493.