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Green energy production utilizing Microbial Desalination Cells (MDCs) focuses on electrode type and cell configuration

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Abstract
The global water crisis and challenges associated with remote drinking water sourcing have escalated concerns about pervasive water scarcity. In the realm of sustainable development, prioritizing research into renewable and environmentally friendly alternative energy sources is imperative. Seawater and brackish water are being explored as prospective drinking water resources. Research indicates that current seawater desalination methods, employing thermal and membrane technologies, incur substantial energy costs and lack long-term sustainability. Microbial Desalination Cells (MDCs) have emerged as a green and dependable technology for wastewater treatment and brackish water desalination. This review delves into pivotal operational challenges encountered in MDC development, encompassing electrode type, pH imbalance, and stack structure, with the primary objective of augmenting COD removal efficacy and electrical power retrieval. Outcomes underscore the critical role of electrode types, particularly the anode, influencing bacterial growth, removal kinetics, and electron generation. The enhancement of electrode surface area proves instrumental in advancing volumetric power density. Configurations that obviate the need for a membrane between anode and cathode compartments, coupled with unrestrictive electrode spacing, exhibit substantial potential in surmounting challenges like pH imbalance and elevated internal resistance. In summation, MDCs represent a promising avenue for sustainable water treatment and energy harvesting in the field of biotechnology.

Keywords
Microbial Desalination Cells, Green energy, Sustainable Development, Electrode, Cell Configuration

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Introduction

The global population growth and climate change have placed the availability and safety of drinking water at the forefront of current global concerns [1]. Despite the Earth's vast natural water reserves, only 3% is considered freshwater [2], and within this 3%, only 1% is surface water accessible to humans, while the rest remains underground or in inaccessible natural reservoirs such as ice [3]. Given the limited availability of freshwater resources and the exorbitant cost of obtaining and supplying freshwater from distant sources to water-scarce regions, there is a growing concern about water scarcity worldwide. Despite these challenges, efforts to utilize seawater and brackish water as potential drinking water sources have once again become a focal point [4].

In the 1950s, there were approximately 225 desalination units worldwide [5]. Currently, about 16,000 desalination plants operate globally, producing nearly 95 million cubic meters of freshwater per day in 177 countries [1]. In Bahrain, Kuwait, Qatar, and the UAE, almost half of the total water consumption is derived from desalination plants [1]. Overall, the MENA region comprises about 47.5% of the world's desalination capacity, with 62.3% for urban applications and 35% for industrial purposes [6].

Global water demand was approximately 4,500 billion cubic meters in 2010, and it is estimated to reach 6,900 billion cubic meters by 2030, considering population growth and economic development (Figure1). The household sector, including the demand for drinking water, is expected to increase by 2% annually [7].

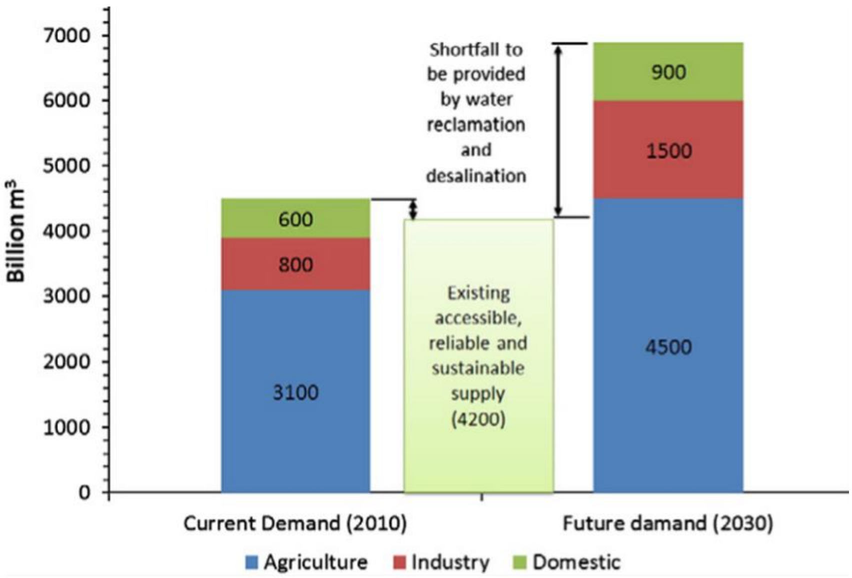

Figure 1: Global water demand projection between 2010 and 2030 [7]

According to the United Nations' report on water consumption, half of the world's population will live in water-stressed areas by 2030. Cost-effective wastewater treatment and seawater desalination can alleviate pressure on freshwater resources [8].

Iran's geographical location in a warm and arid region has led to inadequate precipitation, resulting in the drying of rivers and many groundwater sources, intensifying water scarcity in certain areas. Currently, 39% of the world's population resides within 100 kilometers of the seas, and 60% of the world's cities, with populations exceeding 6 million, are situated along coastlines [9]. Seawater desalination is becoming a cost-effective and efficient solution for water scarcity, especially in coastal regions [1]. The daily desalination of approximately 22 million cubic meters of seawater worldwide includes around 22 million cubic meters in the Persian Gulf, with Iran contributing only 200,000 cubic meters. Iran possesses vast brackish water reserves, particularly in the northern and southern regions, making desalination a more prominent focus. The salinity levels in the Persian Gulf reach around 40 psu (practical salinity units), decreasing to 5.40 psu in the summer. The salinity in the Strait of Hormuz ranges from 36 psu (inflow) to 37 psu (outflow), and the Oman Sea has an approximate salinity of 36 psu [10]. The salinity or salt concentration varies across different sections of the Caspian Sea, with the northern Caspian having a salinity of 5–10 ppt, the middle Caspian with 7–12 ppt, and the southern Caspian with 13 ppt. Various factors contribute to these differences, such as increased freshwater inflow from rivers in the north and western coastal areas, causing lower salinity, and the water flow characteristics in the sea surface and high evaporation rates on the eastern and southern coasts contributing to increased salt levels in those areas [11].

Currently, various desalination processes are gradually being used to address water scarcity in water-deficient regions. Different methods for desalting water have their advantages and disadvantages concerning raw water treatment, process operations, and water quality management [12].

Two main identified methods for water desalination are thermal desalination and membrane desalination [13].

The MED (Multi-Effect Distillation) method is a prominent commercial thermal desalination technology, utilizing the natural cycle of water evaporation and condensation to produce low-salinity water. In contrast, the RO (Reverse Osmosis) process involves pumping seawater through a membrane under pressure, allowing pure water to pass through while discharging remaining saltwater. The RO system comprises a pre-treatment process, high-pressure pump, membrane assembly, and post-treatment process. Most modern reverse osmosis plants have energy recovery systems, contributing to the overall reduction in desalination costs based on RO technology. However, for high salinity, high turbidity, high feed water temperature, and the presence of marine life (such as some Gulf sites), the costs will be higher (close to MED) since the RO unit requires an expensive pre-treatment system [14].

Among the membrane techniques, Electrodialysis (ED) is a process based on the transport of ions through selective membranes under the influence of an electric field. ED gained attention after World War II and developed for industrial wastewater treatment from the early 1970s. ED is an electrically-driven process in which mineral salts and other species are transferred from one solution to another through selective ion-exchange membranes under the influence of a direct electric current [15].

Energy requirements, water production costs, technological advancements, and environmental impacts are crucial parameters for comparing major desalination technologies [14][12]. In this context, the savings in costs and energy consumption per unit of produced water are highlighted as a relative advantage among different desalination methods. The cost of producing desalinated water depends on factors affecting both capital (CAPEX) and operational (OPEX) expenses. Some technologies have high CAPEX (land, engineering, unit purchase, transport, installation, etc., up to commissioning), while others have higher OPEX (labor, maintenance and replacement of spare parts, energy, and chemicals). The cost per unit used is $/m3 of produced water [14].

Desalination technology costs have significantly decreased over the past 30 years due to research and development, leading to reduced energy consumption and improved designs. Table 1 lists some desalination methods based on predicted costs. Most desalination costs are related to capital and energy prices, while operating and maintenance costs are relatively constant [14].

Table 1: A comparison of energy requirements, greenhouse gases produced, production capacity, and costs in various desalination technologies (based on 1 cubic meter of desalinated water) [4,6].

Methods of desalination	MED	RO	RO	RO
capacity (m3/d)	> 5000	> 100	> 50	> 1000
Cost (USD/m3)	2.5-3	12.5-16.8	7-9.8	2.1-5.6
Energy,KWH	2KWH	3.7-4.5		
CO2,Kg	18.05	3.01		
NOX,g	21.41	7.20		
SOX,g	26.49	6.83		
PM10,g	1.02	0.20		

Thermal and membrane technologies have a high capability to produce significant amounts of water with suitable quality. In a comparative analysis of the total costs associated with the construction, operation, and maintenance of these industries, and, more importantly, the energy consumption for freshwater production, the MED (Multi-Effect Distillation) method demonstrates a relative superiority [16]. Although the initial construction and procurement costs of thermal MED are higher than the membrane RO method, the proximity of thermal technologies to power plants, utilizing the waste heat from power plants for freshwater production, makes them much more cost-effective. In fact, by colocating power plant facilities and desalination using the thermal MED method, a single investment can yield two essential products: electricity and freshwater. In countries rich in energy resources such as oil and gas (e.g., countries in North Africa and the Middle East), the adoption of thermal desalination systems like MED is significantly more attractive. Currently, over 90% of the thermal desalination industry worldwide is concentrated in North Africa and the Middle East. On the other hand, the energy consumption in the RO method is primarily related to pumping salty water through membrane layers, making it a single-function process with lower economic efficiency. Due to the high cost of membrane components, their vulnerability, and the need for more maintenance and replacement, the costs associated with services and maintenance of membrane desalination facilities are much higher than thermal facilities [17].

Table 1 summarizes the energy requirements and emissions associated with various desalination processes. Thermal desalination processes such as Multi-Effect Distillation (MED), with high electricity and heat energy demands, exhibit severe environmental impacts compared to the Reverse Osmosis (RO) seawater desalination process. The table also indicates that using waste heat for supplying thermal energy demand leads to a significant reduction in greenhouse gas emissions. Another crucial reason for the gradual increase in costs and sustained decrease in fossil fuel amounts, making them less economically viable. Given these undeniable drawbacks, Renewable Energies (REs) are introduced as a promising alternative to conventional energy sources [6] [18]. To ensure sustainable use of desalination technology, the effects of each major desalination project must be assessed and reduced through a specific Environmental Impact Assessment (EIA) for the project and location [19].

Research has shown that seawater desalination through existing technologies such as Reverse Osmosis (RO), Electrodialysis, etc., requires considerable energy and costs and is not a sustainable long-term option. Moreover, the rapid industrialization and population growth have led to the production of large volumes of wastewater, which, due to its energy-intensive treatment process, heavily relies on fossil fuels. The United Nations estimates that about 80% of wastewater is discharged without prior treatment due to the high energy consumption of the treatment process. Consequently, these challenges have prompted research and development towards compact energy processes, focusing on sustainable and renewable energy methods that can utilize the energy stored in wastewater and contribute to global wealth creation [20].

Microbial Desalination Cells (MDC) are a type of bioelectrochemical reactor that combines the principles of Microbial Fuel Cell (MFC) for wastewater treatment and electrodialysis for seawater desalination [21] [22]. Microbial Fuel Cells (MFC) are a type of bioelectrochemical system and emerging technology where biological organisms act as biocatalysts to produce bioelectricity through the oxidation of organic matter. MFCs have great potential not only in municipal wastewater treatment for electricity production but also in the treatment of groundwater containing various pollutants such as benzene and resistant pollutants like dyes [23, 24]. MDC, a new technology, can be used as a pretreatment system in desalination due to the high cost of membranes in the Reverse Osmosis (RO) process [25].

In fact, MDC can generate about 1.8 kilowatt-hours of bioelectricity from the energy available in 1 cubic meter of wastewater. In comparison to traditional RO, more than 3 kilowatt-hours per cubic meter of electrical energy can be saved. Using this new technology, two low-quality water streams (brine and treated wastewater) are converted into two high-quality water streams (desalinated water and treated wastewater), suitable for subsequent uses [26].

Typically, MDCs consist of a three-compartment reactor comprising an anode compartment (anolyte), a middle compartment (artificial brackish water containing NaCl), and a cathode compartment (catholyte). Ion-exchange membranes, anionic exchange membrane (AEM) between the anode and desalination, and cationic exchange membrane (CEM) between the cathode and desalination, facilitate ion exchange. Electrodes are connected to an external circuit through a conductive wire [27,28].

In a microbial desalination cell, the flow of electricity is generated by treating various types of wastewaters. This electricity can address or eliminate issues related to wastewater treatment and disposal. Microorganisms in anaerobic micrograms oxidize organic matter, perform oxidation in the anode, produce hydrogen, and release electrons. The freed electrons are conducted through an external circuit towards the cathode in the cathode compartment, creating an electric current. In this system, there is no need for an external source to produce direct electrical current. Exoelectrogenic microorganisms generate electrical energy by oxidizing organic matter and transferring electrons to an electron acceptor outside their cells, creating energy outside the cell [29].

Recent advancements in this process and future challenges, with a practical and industrial perspective, play a role in addressing some factors. Although MDCs have been used for various applications, there are still reported operational challenges that have limited their development, including ion interference during desalination, membrane fouling, pH imbalance, and the limited potential of exoelectrogen potentials [27, 30, 31]. Therefore, in this study, in addition to introducing recent advances, we address the problems and challenges of using MDC stacks and provide solutions to these issues.

Challenges and Solutions:

A Review of Scientific Studies and University Research

The Microbial Desalination Cell (MDC) as an environmentally compatible technology for desalinating brackish water was first introduced by Cao and colleagues in 2009 [32].

In recent years, microbial fuel cells (MFCs) have been extensively examined as a novel energy source. In the period from 1970 to 2020, a total of 11,397 articles have been retrieved from the Web of Science (WoS). Countries such as China, the United States, and India are the main hubs of MFC research, contributing 26.47%, 16.95%, and 7.69% to the publications, respectively. Figure 2 illustrates the number of published articles until the end of 2020 [33].

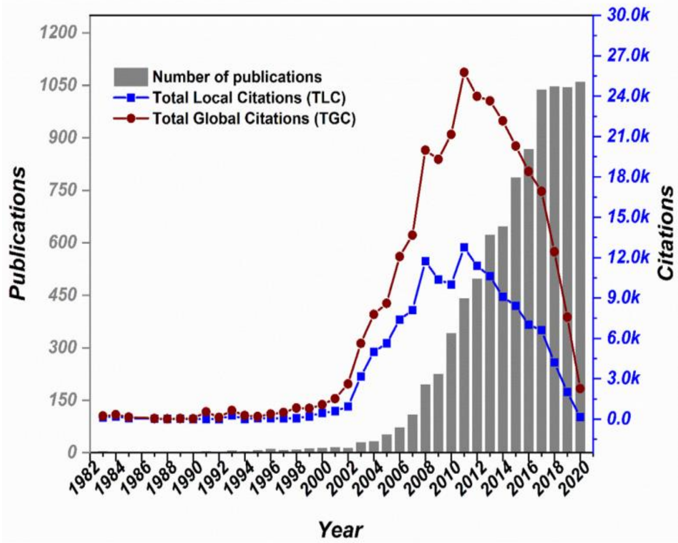

Figure 2: Number of Published Articles in the Field of Microbial Fuel Cells (MFC) Until 2020 [33]

Effect of pH

Adjusting pH is one of the most crucial parameters for improving the efficiency of microbial desalination cells (MDCs). In this cell, the middle desalination compartment prevents the ion transfer between the anode and cathode compartments [34]. Consequently, +H ions in the anode compartment accumulate due to the oxidation of organic matter, and -OH ions in the cathode compartment accumulate due to oxygen reduction. This leads to significant acidification and alkalization in the anolyte and catholyte [8, 35]. Acidification of the anolyte (with a potential pH reduction to 4) can reduce the activity of the anodic biofilm, while alkalization of the catholyte (with a potential pH increase to 12) can increase the voltage loss (95 millivolts per unit increase in pH), ultimately reducing the overall system performance [36].

So far, identified strategies to mitigate pH imbalance in the anolyte and catholyte include i) using a large volume of electrolytes to dilute the ions causing pH imbalance, ii) utilizing buffered anolyte and catholyte to resist pH changes, iii) employing bipolar membranes and adding additional compartments to collect acid and alkaline solutions, (IV) recirculating catholyte into the anolyte compartment in series or adding catholyte to the anolyte, and (v) using acids and bases to regulate pH. However, these strategies come with their specific limitations, including (a) the need for pumping a large volume of electrolytes, (b) re-release of buffered ions in the desalination solution and associated risks, (c) low overall Coulombic efficiency (CE) due to high internal resistance of bipolar membranes, (d) energy requirements for recirculation, and shear forces generated by the recirculation flow that can separate the biofilm from the anode, and (e) the cost of chemical buffer materials [20].

Impact of Microorganisms

Typically, anaerobic sludge from industrial or domestic wastewater treatment plants, anaerobic sediments, primary industrial or municipal wastewater, and even farm soil contain exoelectrogens that can be separated from their respective sources and used for pure or mixed cultures. These microorganisms, due to their organic matter oxidation and electron transfer properties, are among the most crucial determinants of the efficiency of microbial desalination cell (MDC) systems, and their desirable growth and survival are of utmost importance. These bacteria are influenced by various factors, including salt concentration, temperature, pH, and the environment [29]. In the future, genetic engineering may be employed to enhance the electrogenic activity of the microbial community, next-generation materials may be used as anodes and cathodes, various wastewater sources may be examined as anolyte, and life cycle analysis and exergy analysis (determining the energy losses in the process) may be conducted [27].

Microorganisms generate electrons after metabolizing food, and these electrons need to be transferred to the electrodes. The biofilm can be divided into three regions: a dense inner core that plays a vital role in the extracellular electron transfer (EET) process, an intermediate region that acts as the electron acceptor-limited zone, and an outermost layer of the non-active or least-contributing region to the EET process [37, 38]. The three-dimensional network formed by bacteria near the electrode surface makes the microbes assessable for the transfer of more extracellular electrons to the electrodes [39].

Considering the anaerobic conditions in the anode compartment, the average kinetic values of the important groups of acid-forming and methane-forming bacteria are shown in Table 2.

Table 2: Average kinetic values of acid-forming and methane-forming bacteria [40]

Process	Conversion rate gCOD/gVSS.d	Y gVSS/gCOD	K_s mgCOD/l	μ_m 1/d
Acidogenesis	13	0.15	200	2.00
Methanogenesis	3	0.03	30	0.12
Overall	2	0.03-0.18	-	0.12

Catholyte and Anolyte Solutions

The high redox potential of electron acceptors on cathodic electrodes will enhance desalination performance. Therefore, cathodic electron acceptors significantly impact Total Dissolved Solids (TDS) removal, electricity recovery in the system, and the rate of brackish water desalination [41]. Chemical cathode, air cathode, and MDC biocathode [42], ferricyanide [43, 44], potassium phosphate buffer (MDCP100) [45], oxygen, dichromate, permanganate, and hypochlorite [41], phosphate buffer solution (PBS), non-buffered saline solution, and biocatholyte [46] are used as catholyte in microbial desalination cells.

Microbial-based technologies, using organic waste present in wastewater as a substrate through microbially catalyzed electrochemical reactions, generate electricity [22]. The treatability of a wide range of wastewater types, including municipal wastewater, industrial wastewater, sludge, and combined raw and municipal wastewater, has been investigated in microbial desalination cells [47]. Acetate and glucose are the most commonly used substrates in microbial desalination cells, being easily soluble in water and used as a nutrient supplier in the anolyte [48].

The use of biocathodes in MDC, due to reduced operational costs, environmental compatibility, long-term stability on chemical electrodes, and effective removal of pollutants from wastewater, is economically, environmentally, and socially sustainable. In biocathode MDC, bacteria, yeast, fungi, or algae act as a catalyst in the reduction reaction, preventing the use of expensive metallic catalysts and eliminating the toxicity produced by chemical cathodes. Microalgae, as a biocathode, have the ability to produce four times the dissolved oxygen concentration through photosynthesis compared to external air aeration. Therefore, the use of microalgae increases the power output while consuming zero energy [49].

In 2022, Dong et al. demonstrated in a simulation of a three-compartment microbial desalination cell during brackish water desalination that the biocathode method showed a 5% increase in salt removal and a 4.9% increase in current and power density compared to the ferricyanide-oxidase method. When the biocathode MDC was used for desalination of household reverse osmosis brackish water, a maximum current and power density of 23.81 μA/cm2 and 20.337 μW/cm2, respectively, were achieved. Furthermore, 83.9% COD removal in the desalination compartment and reduction in ions were recorded, with up to 79%, 76.5%, and 72% for sodium, potassium, and calcium, respectively, in a batch operation for 31 days with stable pH (≈7) [50].

In 2023, Nadzari et al. presented the performance of a microbial desalination cell that utilizes microalgae species Chlamydomonas sp. (UKM6) and Scenedesmus sp. (UKM9) as the terminal electron acceptors in the cathode compartment of photosynthetic microbial desalination cells (PhMDC). The results showed that PhMDC-UKM9 and UKM6 produced power densities of 1942 mW/m3 and 1714 mW/m3, with desalination rates of 44% and 32%, respectively. The desalination closely approached practical seawater application with a salt concentration of 35 grams per liter [51].

Stack Architecture:

Over time, the structure of microbial desalination cells (MDCs) has undergone changes aimed at process improvement. Generally, in terms of structure, the following classifications can be considered: three-compartment MDC, two-compartment MDC, and membrane-less MDC.

The three-compartment reactor consists of an anode compartment (anolyte), a middle compartment (brackish water), and a cathode compartment (catholyte), which is the common configuration shown in Figure 3.

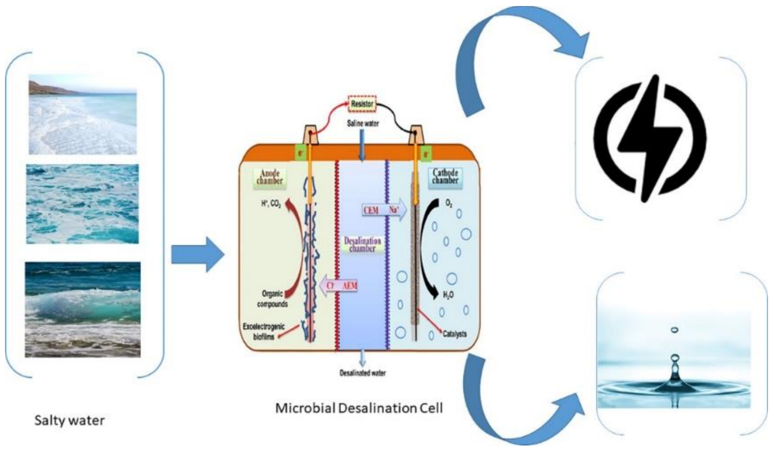

Figure 3: Three-Compartment MDC [52]

Another type is the two-compartment MDC, which was created by modifying the single-compartment membrane-less microbial fuel cell (MFC) by adding an ion-exchange membrane (IEM) layer. In 2020, Tahereh Jafari and her colleagues designed a new type of two-compartment tubular MDC (TTMDC) in an article titled "A Novel Two-Compartment Microbial Desalination Cell for Bioelectricity Generation, Wastewater Treatment, and Desalination with a Focus on pH Control." The TTMDC was designed with a new arrangement of anions and cation-exchange membranes. It comprises an internal desalination compartment and a single-compartment air-cathode MFC. The real and schematic view of TTMDC is shown in Figure 4. Results demonstrated that pH, using unbuffered domestic wastewater as an electrolyte, with high energy production (8 mW), current generation (43 mA), Coulombic efficiency (84%), COD removal (85%), and desalination rate (24.3 mg/h) were continuously balanced in batch operations [20].

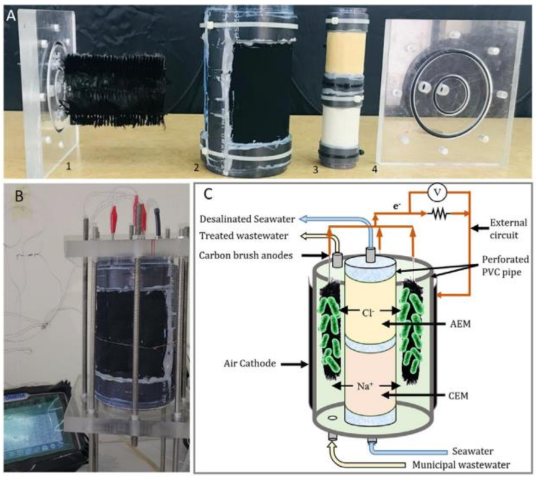

Figure 4: A) Components of TTMDC Reactor: 1. Anode fiber brushes 2. Air cathode module 3. Membrane module 4. Acrylic sheet with washers B) TTMDC preparation C) Schematic view of TTMDC system [20]

In 2018, Kookhavyan and his colleagues evaluated microbial desalination cells with photosynthesis (PMDCs) using a microalgal biocathode (Chlorella vulgaris). They assessed three different process configurations: Static (batch feed, SPMDC), continuous flow (CFPMDC), and a photobioreactor MDC (PBMDC) to study the impact of operations and process design on wastewater treatment, water desalination, electricity generation, nutrient removal, and biomass development. The schematic and real views of PMDC are shown in Figure 5. The removal rates of Total Dissolved Solids (TDS) and Chemical Oxygen Demand (COD), as well as power density, increased with the concentration of TDS in the desalination compartment. COD removal and nutrient removal potentials were similar in all three experimental configurations. Experimental studies indicate that SPMDCs are more suitable for producing bioelectricity due to the formation of biofilm, while CFPMDCs or photobioreactors are more suitable for producing microalgal biomass [53].

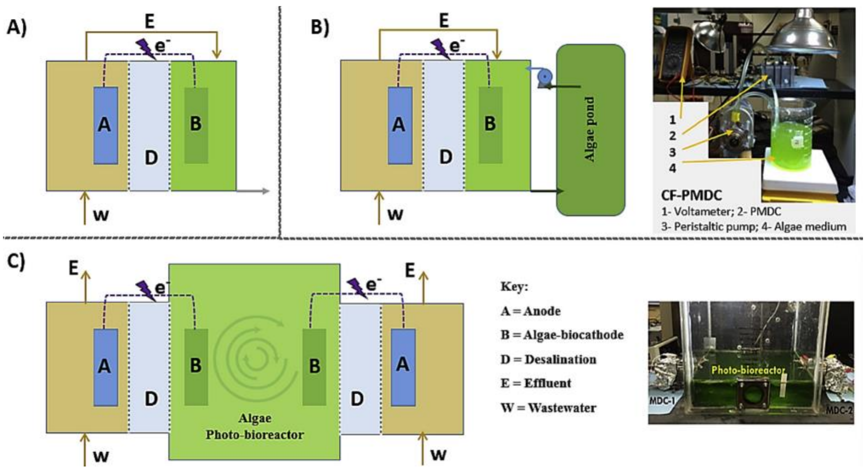

Figure 5: Configurations of Photosynthetic Microbial Desalination Cells (PMDCs): A) Batch feed (SPMDC), B) Continuous flow (CFPMDC), C) Photobioreactor (PBMDC) [53]

Another type is the five-chambered MDC consisting of an anode chamber, a cathode chamber, a desalination chamber, and two concentrate chambers, all constructed with acrylic sheets. In 2019, Paradaens and his colleagues worked on four MDCs, each having an anode chamber, a cathode chamber, a desalination chamber, and two concentrate chambers, operating in batch mode. The schematic view of this stack is shown in Figure 6. The performance of these MDCs for Total Dissolved Solids (TDS) removal and power generation using various cathodic electron acceptors, namely oxygen, dichromate, permanganate, and hypochlorite, was investigated. The use of chemical cathodic electron acceptors enhances the desalination efficiency and power recovery in MDC. Among all electron acceptors, hypochlorite demonstrates the highest efficiency in TDS removal and power recovery. Dichromate and permanganate require pH adjustment as they exhibit high oxidation states under acidic conditions. Electrochemical analysis confirms the suitability of hypochlorite as an electron acceptor with low internal resistance in the system. The partial regeneration of HOCl during the use of hypochlorite as a catholyte makes it more stable, suggesting it as a feasible chemical catholyte option for practical applications in the system. Therefore, cathodic electron acceptors significantly impact TDS removal and electricity recovery in the system [41].

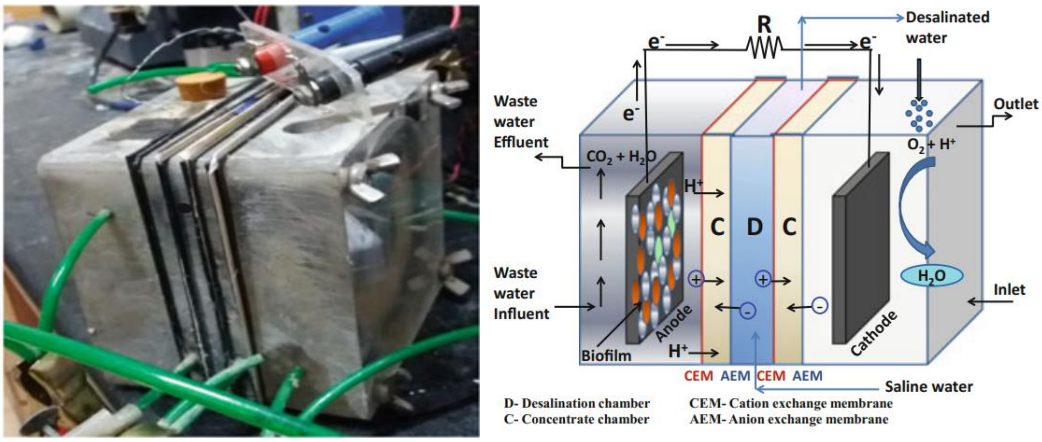

Figure 6: Schematic and real view of multi-chambered MDC [41]

Electrode Roles

Although anode and cathode electrodes play important roles in the performance of fuel cells, the anode electrode is one of the most crucial components in microbial fuel cells (MFCs). It provides the necessary surface for the growth of bacteria, which transfer the electrons produced from the breakdown of organic materials to the cathode through the anode. Therefore, the design of materials constituting the anode is one of the significant challenges in the functionality of fuel cells. Recently, studies on the configuration, materials, and design of anodes for high-performance MFCs have gradually increased. Anode materials must possess several essential characteristics to meet the requirements of high performance, such as good biocompatibility, high conductivity, high chemical stability, thermal and mechanical stability, and a large surface area. Previous studies in this field indicate that modifying the anode to achieve a high specific surface area, proper electron transfer capability, and strong bacterial adhesion (robust biofilm) has attracted researchers to conduct new investigations in the field of fuel cells [54].

Reviewing the various types of electrodes and their structure plays a crucial role in enhancing electron transfer, biocompatibility, and conductivity in microbial fuel cells (MFCs) [55] [56]. Increasing the effective surface area of electrodes relative to the reactor volume through various methods will lead to improved volumetric power density [57]. In fuel cells, both electrodes (anode and cathode) play a vital role, but bacterial growth, removal rate, electron production, and transfer are the responsibility of the anode electrode [58].

In 2010, Bruce and colleagues conducted a review of recent advances in the field of electrodes. Research has shown that increasing the total effective surface area of electrodes relative to the reactor volume will lead to improved volumetric power density. By using oxygen and a separator between the electrodes, with a cathode surface area of m^2/m^3, the power production reached kw/m^3 1.55 [57].
In 2015, Liu and his colleagues introduced polyurethane sponge coated with activated carbon (ACS), a three-dimensional material with a mesh structure acting as a stable substrate for biofilm attachment and growth. It was synthesized through the chemical oxidation of black carbon deposition (CB) using (APS/H2SO4). The capital cost of ACS was only $2.5 per square meter for a thickness of 3 millimeters, which is lower than the price of most commercial carbon electrodes. In comparison to the carbon cloth (CC) anode, the composite anode exhibited 2.2 times higher output voltage (926 milliwatts per square meter) and a shorter start-up time (23 hours) [59].
In 2015, Chen and colleagues recommended polyvinyl alcohol (PVA) glue, which is biocompatible and hydrophilic due to oxygen-containing groups, as an anode connector for MFCs. PVA has been proposed as an alternative to polytetrafluoroethylene (PTFE) as a connector for anodic electrocatalysts used in MFCs. An MFC based on E. Coli, using PVA in the anode electrocatalyst with its CNT, produced the highest maximum power output of W/m^2 1.631, which is 97.9% higher than an MFC using PTFE as a binder (W/m^2 0.824). However, PVA may have a negative impact on electron transfer between the anode and the bacteria, as it possesses properties of an electronic insulator [60].
In 2021, Zafar and colleagues also suggested polyvinyl alcohol (PVA) as a substitute for PTFE glue for anodic electrocatalysts in MFCs, citing its water-friendliness and biocompatibility [61].
Similarly to Chen and colleagues in 2015, Narayanasamy also stated in 2020 that, compared to PTFE binders, PVA binders provide about 98% higher power density in E. coli-based MFC [60, 62]. Yang and colleagues, in 2014 [18], developed the air cathode of MFC using a simple one-step phase inversion process with an SS base, PVDF binder, and activated carbon. They reported that the air cathode made with PVDF binder shows similar power density to cathodes made with more expensive binders like PTFE [63].
Simone and colleagues in 2022 mentioned that the use of metal-based electrodes has recently gained attention due to their better conductivity and mechanical properties compared to carbon fiber materials. Stainless steel (SS) has emerged as the preferred metal electrode due to its high resistance to corrosion in aqueous environments, excellent conductivity, and mechanical properties. However, surface modification is usually necessary to improve the surface for biofilm adhesion and, consequently, increase the required power density. The use of nano-carbons or carbon granules as a catalyst for SS surface modification is more prevalent. As shown in Figure 2-12, in SS surface modification, polymer adhesives are used for the mechanical connection of the surface modifier to the SS base to form a composite electrode [64].

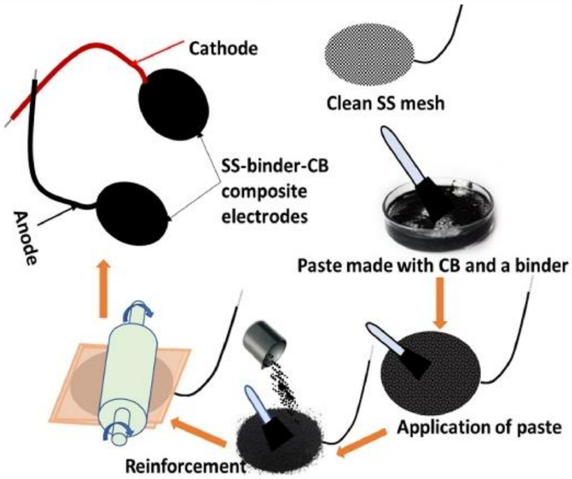

Figure 7: Electrode bonding and strengthening process [64]

Saimon and colleagues in 2021 reported in a study that electrodes made using epoxy for attaching carbon black to an SS base perform better than a simple carbon electrode, which is commonly used in SMFCs [65].

Yang and colleagues in 2023 introduced a microbial desalination cell with a flow electrode (FE-MDC) in a study, utilizing activated carbon (AC) particles and carbon nanotubes (CNTs) as electrodes to enhance electron transfer. The energy recovery of electricity (0.371 KWh/m³) and overall Coulombic efficiency (66.7%) of FE-MDC were more than twice that of a conventional MDC without a flow electrode. As a result, salt and COD removal efficiency increased to 77.8% and 91.2%, respectively. Finally, as shown in Figure 8, a continuous operation state (continuous) was created for FE-MDC, and the effluent flow electrode was returned to the anode compartment for reuse. The output voltage, COD removal, and salt removal during operation reached 610 millivolts, 78.8%, and 76.1%, respectively [66].

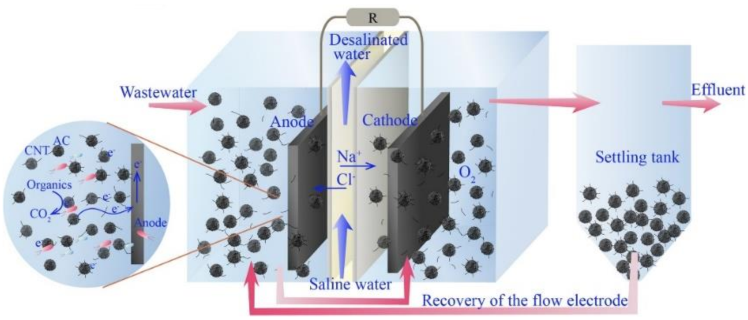

Figure 8: Schematic View of Microbial Desalination Cell (FE-MDC) with Flow Electrode [66]

In 2016, Perisa Nouri and her colleagues investigated energy extraction from an optimized single-chambered microbial fuel cell (MFC) with a novel configuration designed to treat chocolate industry wastewater. They utilized a spiral stainless steel mesh in the anode compartment as an electrode to increase the specific surface area. Ultimately, under the conditions of 35°C and pH=7, the MFC achieved the highest power density (16.75 W/m3) with significant reductions in COD and wastewater turbidity by 91% and 78%, respectively. The Columbic efficiency reached 45.1%. The schematic of the constructed MFC is illustrated in Figure 9 [67].

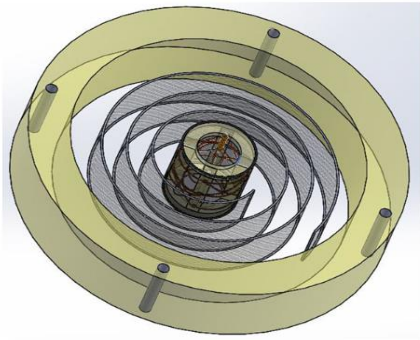

Figure 9: Schematic View of the Anodic Surface-Modified Microbial Fuel Cell (AS-CMFC) [67]

In 2020, Narayanasamy and colleagues highlighted the potential of developing composites with surface and mass-modified electrode materials to overcome the main challenge of low power density in microbial fuel cells (MFCs). Polymers containing nitrogen and fluorine, such as polyacrylonitrile (PAN), polyaniline (PANI), polytetrafluoroethylene (PTFE), polydopamine (PDA), and polyacrylamide (PAM), are considered potential candidates for mass or surface modification in the presence of redox-active species to enhance biocompatibility and cathode reduction efficiency [62].

In 2011, Gasmi and collaborators used activated carbon nanofibers derived from polyacrylonitrile (PAN) as an alternative catalyst to platinum for the oxygen reduction reaction (ORR) in the cathode. They employed chemically electrospun carbon nanofibers (ACNFs) with MKoH8, resulting in up to 200%, 34.7%, and 16% higher power production compared to plain carbon paper, physical ACNFs, and chemical ACNFs with MKoH4. However, the main drawback was that the cost of ACNFs with MKoH8 was 2.65 times higher per unit power compared to traditional platinum cathodes [68].

It has been established that simple carbonization (graphitization)/pyrolysis of polymeric precursor enhances carbon content and preserves an effective porous structure, facilitating the doping process with heteroatoms such as N and F. On the other hand, polymer materials like polyvinyl alcohol (PVA), polyvinylidene fluoride (PVDF), epoxy resin, and polyester, when used as binders for connecting metal oxide/metal ion with carbonaceous materials like activated carbon, activated carbon, and graphite, effectively improve the anode's performance. Pang and colleagues, in 2018, worked on a batch process of 35 individual MFCs on a fabric layer, as schematically depicted in Figure 10. Polyester was utilized as a supporting material in constructing the electrodes for MFCs [69].

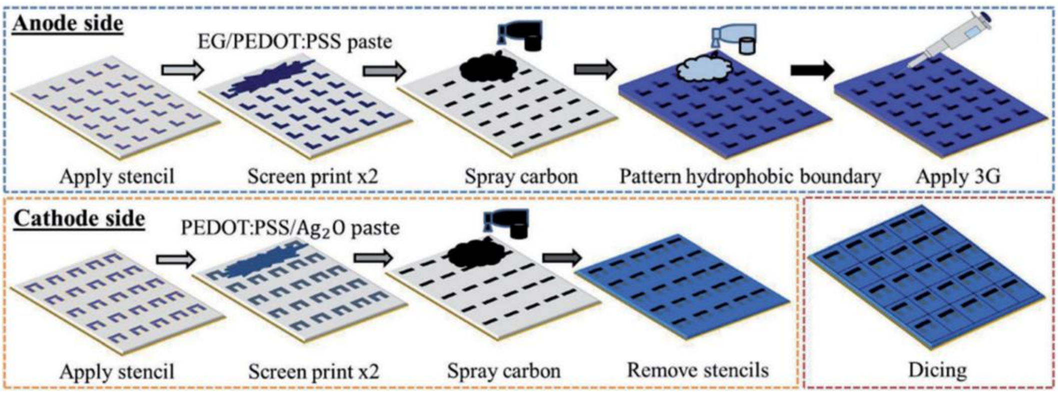

Figure 10: Schematic View of the Batch Process for 35 Individual MFCs on a Fabric Layer [69]

Additionally, Zhi and colleagues in 2011 investigated electron transfer in biofilm and enhanced oxygen reduction reaction kinetics on fiber-based carbon nanotube (CNT) anodes. They observed a maximum current density of 27.2 A/m², which was 2.6 times higher than carbon cloth anodes (2.8 A/m²). This indicates that the microscopically porous layer with a coordinated coating exhibits strong interaction with microbial biofilm, facilitating electron transfer from exoelectrogens to the CNT cloth anode. Consequently, the CNT coverage serves as a crucial electron mediator between the biofilm and the fabric substrate. A schematic comparison of the electrode configuration and electron transfer mechanisms is illustrated in Figure 11.

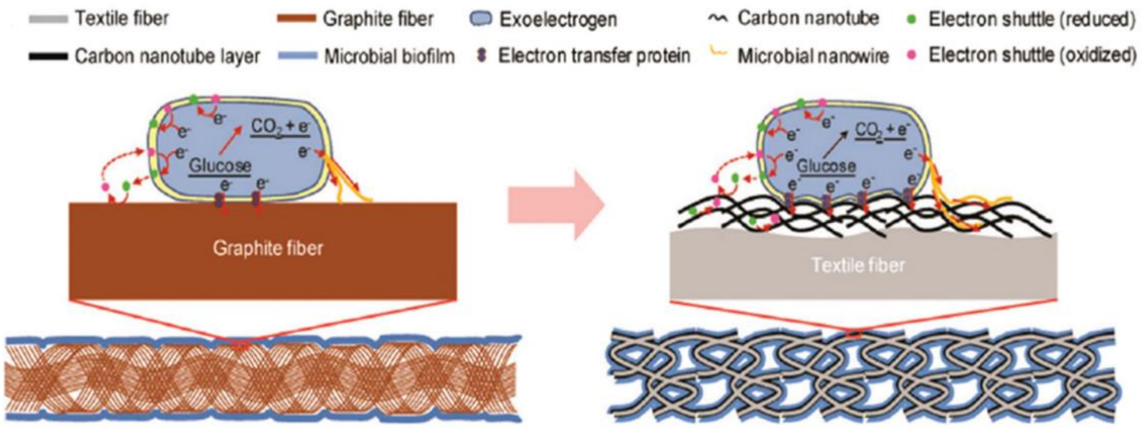

Figure 11: Figure 2-16: Schematic diagram of the electrode configuration and electron transfer mechanisms for CNT-Textile anode (right side) compared to a commonly used carbon cloth anode (left side) [70].

In 2023, Fatemeh Mohammadsadegh and her colleagues conducted an investigation to enhance power production capacity in microbial fuel cells (MFCs). They examined carbon felt electrodes doped with bio-Nickel (bio-Ni@CF) and graphite plate electrodes doped with bio-Nickel (bio-Ni@GP) under constant temperature conditions. The polarization curve obtained during four loading stages using different anode electrodes showed that the maximum voltage of 468 millivolts was achieved using the bio-Ni@CF electrode. This indicates an increase of 35%, 18.37%, and 9.82% compared to GP, CF, and bio-Ni@GP electrodes, respectively. These results demonstrate that nickel-doped carbon-based electrodes can serve as suitable and stable catalysts and supported conductors to enhance the efficiency and increase power generation in MFCs [71].
Figure 2-17 provides an overview of various carbon materials used as electrode materials in MFCs. Due to their excellent electrical conductivity and chemical stability, carbon materials hold promise for scaling up. Three-dimensional materials such as carbon brushes and meshes generally produce higher current densities than two-dimensional materials like carbon paper and graphite rods or plates, thanks to their larger surface area.

Figure 12: Digital View of Common Carbon Electrodes Used in MFCs [62]

Polymer-coated conductive carbons, such as polyaniline, polypyrrole, and polythiophene, have been synthesized in various forms using different synthesis strategies, and their morphology plays a crucial role in the power output of microbial fuel cells (MFCs). Electrochemical experiments have shown that both electron transfer resistance and charge transfer resistance are low due to the high specific surface area, which provides a large surface for microbial growth and the diffusion of charged species. Generally, two types of techniques, namely chemical polymerization and electropolymerization, are used in the synthesis of conductive polymers. Table 2-4 compares various Single-Microbial Electrode (SME) based on Polymer/Carbon Composites (PCSMEs) as anodic materials in microbial fuel cell applications.

Table 3: Comparison of Various Polymer/Carbon Composite-based Anodic Small and Medium Enterprises (PCSMEs) for Microbial Fuel Cell Applications [62]

Anode	Cathode	Percentage of polymer used as binder	Significance of polymer	Power density/ increased by
PCBMEs as anode material				
Thin film made of graphite (5 μm in diameter) and PTFE emulsion (0.15 mm)	Pt/C (0.2 mg cm^{-2})	30% PTFE	Chemical stability and hydrophobic nature and form porous microstructure network	760 mW/m^2 (533% w.r.t. low PTFE content)
PVA coated carbon felt (3.0 cm × 3.0 cm)	Pt/C on Cp (0.2 mg cm^{-2})	10% PVA	Better hydrophilicity and stronger interaction of PVA with bacteria	1.631 W/m^2 (97.9% w.r.t. PTFE)
PPy-PAN/CNT	CC/Pt (0.5 mg cm^{-2})	10 wt% PAN	Three-dimensional network structure of interwoven nano- tubes, which enabled more specific surface area	455 mW/m^2 (40% w.r.t. CC)
Graphite polymer composite electrode (GPF) (4 × 4 × 0.5 cm)	Gr plate	75% PF resin with natural graphite powder (25% w/v)	Lack of efficient electron transfer from the anode (GPF) to cathode	114 mW/m^2 (−57% w.r.t. graphite plate)
PCBMEs as cathode material				
Graphite fiber brushes	AC and PTFE on SSM	10 wt% PTFE	Minimize the amount of binder in order to reduce charge transfer resistance	1100 mW/m^2 (12% w.r.t. Pt/C)
Graphite block	Fe^{3+} doped Graphite epoxy composite electrode (Fe^{3+} - GECE)	24% of epoxy with graphite powder	Inexpensive, easy to use and regenerate new surface	1679.9 ± 98.04 $\mu W/m^2$ (328% w.r.t. Gr block)
Graphite block	Ni doped Graphite polyester composite electrode (Ni-GPECE)	50% (unsaturated polyester) with graphite	Curing at room temperature, high chemical resistance and low cost	1575 ± 223.26 $\mu W/m^2$ (1557% w.r.t. Gr block)
Carbon mesh	PVDF-based activated carbon on SSM	10% (w/v) PVDF solution containing 26.5 mg/cm^2 of AC and 8.8 mg/cm^2 of carbon black (CB)	Less expensive, more durable, and easy to manufacture	3.96 ± 3.01 W/m^3 (118% w.r.t. Pt/Cp)

AC activated carbon, *CB* carbon black, *CC* carbon cloth, *CF* carbon felt, *CNF* carbon nanofiber, *CNT* carbon nanotube, *Cp* carbon paper, *PANI* polyaniline, N_2 nitrogen atmosphere, *SS* stainless steel, *SSM* stainless steel mesh, *PAN* polyacrylonitrile, *Ppy* polypyrrole, *Pt* platinum, *GPECE* graphite polyester composite electrode, *GECE* graphite epoxy composite electrode, *PVDF* polyvinylidene fluoride, *PTFE* polytetrafluoroethylene, *Gr* graphite, *PVA* polyvinyl alcohol, *PAN* polyacrylonitrile

The electron transfer rate at the electrode surface plays a crucial role in increasing power output in fuel cells [72, 73]. The choice of electrode materials is essential for both the anode and cathode, each serving a vital role [74]. Carbon-based electrodes, including carbon and graphite, are key materials for both the anode and cathode due to their higher surface area, good biocompatibility, low cost, and excellent mechanical strength. Graphene or graphene oxide-based nanocomposites can serve as ideal alternatives for electrode modifications, replacing expensive catalysts for both anodes and cathodes in fuel cells. The advantages include cost reduction in electrode fabrication and the synthesis of graphene oxide from waste materials such as biomass, agricultural waste, plastics, etc. [75].

In theory, graphene boasts a remarkable surface area of approximately 2630 square meters per gram, significantly surpassing other carbonaceous materials [76]. Deng and colleagues asserted in 2017 that graphene exhibits higher electron mobility compared to other carbon materials [77]. Furthermore, in 2020, Jacob and his team worked on reduced graphene oxide (rGO) and concluded that rGO demonstrates very close similarities to pristine graphene, providing an effective platform for bacterial growth on electrode surfaces [78].

Most biological reactions occur on the anode surface, and the higher specific surface area of graphene nanocomposites contributes to the porous structure of the electrode, aiding in bacterial growth. This macro-porous surface provides microbial access to the internal electrode surface without blocking the pores [75].

In a 2014 study, Ho and colleagues fabricated three-dimensional (3D) macro-porous structures with carbon nanomaterial coatings (graphene, carbon nanotubes, or active carbon) on stainless steel fiber felts (SSFFs). These modified electrodes provided a broad surface for reactions, surface transfer, and a biocompatible interface, ultimately demonstrating a maximum power density of 2142 mW m-2 for the graphene-modified anode [79].

Conclusion

Addressing current challenges in the MDC process is a pathway to enhance this system and transition it from the laboratory stage to a viable and economical alternative for desalination and simultaneous wastewater treatment with energy recovery. This review article focuses on significant challenges in MDC usage, provides suitable solutions to overcome them, and enhances the system. To increase desalination rates, improve wastewater COD removal efficiency, and recover electrical power, some key operational challenges in limiting MDC development need attention. These challenges include ion interference during desalination, cost-effective and fouling-resistant membranes, pH imbalance, electrode type and their conductivity, the potential limitation of exoelectrogenic bacteria, and high internal resistance.

Among various configurations used in MDCs, studies indicate that configurations leading to membrane removal between the anode and cathode compartments and no restriction in electrode spacing may have great potential to achieve desirable results and address the mentioned challenges, especially pH imbalance and increased internal resistance.

The results of this research indicate that future studies should focus on improving biofilm production, biological pH regulation, and electron transfer by modifying the constituent materials of the anode and its configuration. This could involve creating a three-dimensional electrode structure, improving porosity, specific surface area, roughness, conductivity, and corrosion resistance, making the electrode cost-effective and biocompatible, and enhancing wastewater treatment and desalination efficiency. Additionally, the use of light-based biological cathodes as an energy source can significantly reduce operational costs. It is suggested that research areas in future studies should prioritize the enhancement of MDCs by changing the rectangular configuration to a cylindrical one with high efficiency.

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