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Review

Microbial Fuel Cells (MFC): A Potential Game-Changer in Renewable Energy Development

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Abstract: Currently, access to electricity in the cities of the Global South is so limited that electrification remains low in rural areas. Unless properly tackled, one-third of the world's cities will suffer from energy scarcity. The emergence of microbial fuel cell (MFC) technology accelerates the deployment of decentralized and sustainable energy solutions that can address the looming energy shortage. This review consolidates scattered knowledge into one article about the performance of MFC in optimizing electricity generation from phosphorus (P)-laden wastewater, while removing the target nutrient from wastewater simultaneously. It is obvious from a literature survey of 108 published articles (1999–2022) that the applications of MFC for building a self-powered municipal water treatment system represents an important breakthrough, as this enables water treatment operators to generate electricity without affecting the atmospheric balance of CO_2. Using a pyrite-based wetland MFC, about 91% of P was removed after operating 180 days, while generating power output of 48 A/m^2. Unlike other techniques, MFCs utilize bacteria that act as micro-reactors and allow substrates to be oxidized completely. The Earth's tiniest inhabitants can efficiently transform the chemical energy of organic matter in unused wastewater either into hydrogen gas or electricity. This facilitates wastewater treatment plants powering themselves in daily operation or selling electricity on the market. This MFC technology radically changes how to treat wastewater universally. By exploring this direction along the water–energy–food nexus, MFC technology could transform wastewater treatment plants into a key sustainability tool in the energy sector. This suggests that MFCs provide a practical solution that addresses the need of global society for clean water and electricity simultaneously.

Keywords: carbon neutrality; circular economy; decarbonization; net-zero; resource recovery

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1. Introduction

As a hub of global urban systems, cities have recently encountered opportunities and risks in contributing to carbon neutrality. The United Nations (UN) estimated that by 2050 about six billion people would inhabit cities due to rapid urbanization [1]. As the urban population increases by 2% annually, squeezing two-thirds of the world's inhabitants into just one-third of land mass of cities brings global challenges such as energy shortage [2]. Currently, access to electricity in the cities of the Global South is so limited that electrification remains disproportionately low in rural areas. Unless immediately tackled, one-third of the world's cities will suffer from the energy scarcity [3]. It is projected that the global demand for electricity will grow by 25% by 2030, as the demand for energy will outgrow its supply to cities by the next decade.

As the engines of economic development, cities have become the seismographs of global energy demand due to their mandatory service to provide public with reliable energy supply. Since cities contribute to 85% of global energy demand [4], they have become a central locus of climate change mitigation and the incubators of new solutions for energy shortage (Figure 1). While cities seek solutions to live up to the 2030 UN Agenda, urban development needs to prioritize their need for renewable energy. To cope with the looming energy shortage, electricity, which can be generated from multiple sources, is a key enabler of the energy transition in contributing to the decarbonization of global economy with benefits including CO_2 reduction, energy security, and enhanced efficiency.

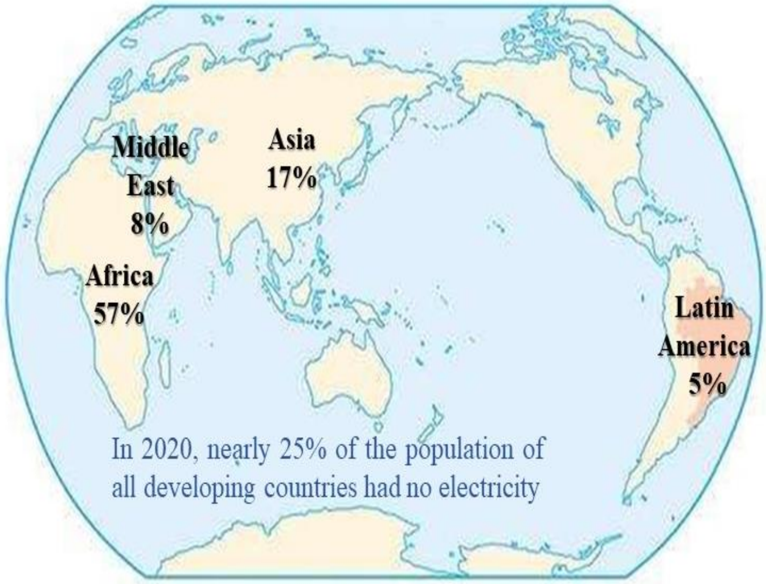

Figure 1. Global energy scarcity.

Global electricity demand has increased by 5000 Terawatt-hours (Twh) in the past decade, accounting for one-fifth of total energy consumption [5]. As electrification is central to climate conservation, uncovering other alternatives of renewable energy is critical for cities to contribute to UN Sustainable Development Goal (SDG) #7 'Affordable and clean energy', which serves as a marker for the world to achieve decarbonization goals. UN SDG #7 represents the need of universal access to affordable and clean energy for all through global cooperation. The urgency and roadmap to the carbon neutrality of global economy through renewable energy is a top universal agenda. In 2019, energy sector was responsible for 40% of global CO_2 emissions (about 13 gigatons) [6]. With coal, gas, and oil combined, the energy still accounts for two-thirds of the final energy consumption mix. Therefore, decarbonizing the energy sector is critical to meeting climate goals, while shifting away from fossil fuel consumption to electricity-driven solutions. However, the speed of decarbonization varies, depending on the country's access to electricity and its electrification rate.

To tackle the challenge of global climate change, the world needs to achieve carbon neutrality between 2050 and 2070. It needs to accelerate the energy transition to achieve a low-carbon and sustainable energy system. Carbon neutrality refers to net-zero anthropogenic emissions of greenhouse gas (GHG) when CO_2 emission is equivalent to its absorption. Hence, energy transformation plays roles in tackling climate change and achieving net-zero emissions.

In addressing energy issues sustainably, generating alternative sources of energy without impacting the surrounding environment represents one of the bottlenecks in mitigating climate change [1]. Generating electricity without emissions is considered an ideal measure to reduce GHG emissions, leading to a sustainable environment. As practical challenges still exist, innovative technologies are vital to reducing the rising impacts of GHGs and attaining sustainability with a non-hazardous environment. The world encounters a two-fold energy challenge: meeting growing demand, while lowering carbon emissions. This decade is decisive for the transition from fossil fuels to renewable energy [5]. As the gap in GHG emissions reduction is widening, all countries need to accelerate a low-carbon transition of energy systems, which puts forward a higher standard of requirements for technology innovation; their comprehensive integration and speedy application is more urgently required than before.

Since electricity is the core energy vector to reaching decarbonization goals in energy systems with benefits that go well beyond CO_2 reductions, turning municipal wastewater into electricity is a strategic effort to convert unused resources into another option for energy. The emergence of MFCs offers a window to accelerate the deployment of decentralized and sustainable energy solutions that can address energy scarcity for urban populations, while contributing to decarbonization goals. In addition to energy generation using electrochemically active bacteria, the MFC has evolved into other applications such as sensors for environmental quality monitoring [6].

A preliminary work undertaken by Nguyen and Babel [7] on MFC mainly focused on its ability to remove biological nitrogen (N) from wastewater. In spite of its novelty, their review did not directly elaborate the removal of other macronutrients such as phosphorus (P). This particular nutrient is critical to the world's food security, as half of the world's fertilizer demand depends on P's availability as a raw mineral for fertilizer production [8]. In addition, their review did not address the roles of online sensors in MFC applications, neither for toxicity detection nor for online monitoring of water quality [9].

To bridge the knowledge gaps, this article synthesizes scattered knowledge on the performance of MFC in removing P from P-laden wastewater, while consolidating the information into one article about how to optimize bioelectricity generation from the same source. This work also critically evaluates development trends on the design and operation of MFCs with efficient electrodes that can be used to generate electricity from wastewater using bacteria, while simultaneously treating it.

By developing a clean, low-carbon, safe, and efficient energy system through MFCs, it is expected that this work will advance our scientific understanding towards MFCs as one of the practical solutions for addressing climate change impacts caused by fossil fuel dependence, while reducing dependence on fossil fuel consumption and meeting energy demands in the developing world. It is also anticipated that the scientific community would have a better understanding of the potential of hydrogen gas as a fuel for decarbonization in the energy sector, while promoting a sustainable transition to net-zero emissions in the long-term.

2. MFC: An Option in Renewable Energy Development

The intensive energy requirement of conventional wastewater treatment for aeration demands an alternative technological option that requires less energy for its operation [10]. Due to its cost-effectiveness, biological processes such as activated sludge have been widely used for wastewater treatment. However, this technique depends on the ability of bacterial population to maintain acceptable effluent quality. If the treatment is interfered with, the bacterial population respond to the varying influents. When this occurs, exceeding effluent limits lead to environmental damage and costly fines [11]. Consequently, treatment facilities have to be overhauled, resulting in a loss of time and financial resources [12].

To address this bottleneck, MFC, which has the capability of addressing wastewater treatment and sustainable energy generation, matches with the UN's SDG in developing clean and affordable energy. Its application enables water treatment operators to generate electricity, which is readily available for use, while treating and recycling wastewater at the same time without affecting the atmospheric balance of CO_2. As an off gas of MFC operation, the CO_2 can be discharged without further treatment [13]. The emission is associated with the proportion of emission due to electricity or heat consumption. Therefore, its contribution in the energy sector is minimum when the secondary energy source has low CO_2 intensity. Finding niche applications of the CO_2 from MFC operation can promote the world's progress toward carbon neutrality in the long-term [14–16].

For MFC technology, municipal wastewater is a trove for producing electricity using bacteria. The novelty of MFC is reflected by its ability to use bacteria for this purpose [17,18]. The MFC facilitates electricity generation from organic matter in wastewater by converting chemical energy in biodegradable substrates through bacterial metabolism. The wastewater has chemical energy in the form of organic matter [19]. Organic carbon in the wastewater can be recovered as biogas in sludge digestion.

The total chemical energy of organic compounds in wastewater is about 10 kWh/m^3 of wastewater effluents, including 30% of extractable energy [20]. Hence, the chemical energy can fuel the MFC when its reactor generates power through electron flows in an external circuit (Figure 2) [21]. This condition enables MFC to generate energy from a wide range of wastewater and inexpensive materials of electrodes [22]. The ability of the bacteria to act as biocatalysts for electrochemical energy transformation offers practical solutions to dealing with energy shortage, resource depletion, and environmental pollution, thus contributing to climate neutrality and zero-waste paradigm [23,24].

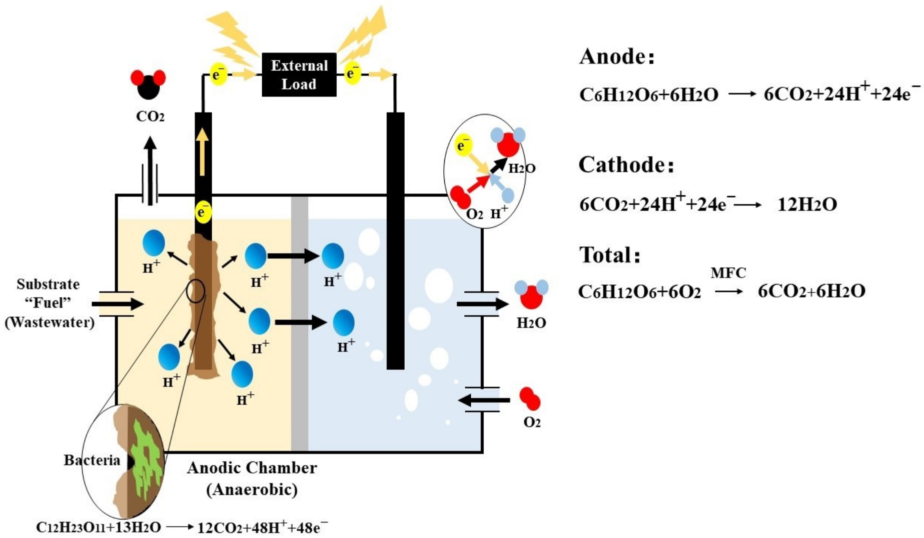

Figure 2. Proof of concept of MFC.

An MFC is a unique type of battery—part electrochemical cell, part biological reactor. Typically, it contains two electrodes, separated by an ion exchange membrane. Electrodes are used as acceptor (anode) and donor electrons (cathode) separated by a separator such as membrane and/or salt bridges [25,26]. Each chamber has an electrode as an electron conductor and bacterial life support. Organic substrates are filled into anode chamber as an electron donor. On the anode side, bacteria grow and proliferate, forming a dense cell aggregate, known as a biofilm, that adheres to the MFC's anode. In the course of their microbial metabolism, the bacteria convert the organic substrate into CO_2, protons, and electrons [27]. The MFC's operation is eco-friendly. Instead of toxic gas in oil or a diesel engine, the emissions from the MFC's operation include CO_2, water, and waste heat that can be reused [28].

Without requiring a complete overhaul of wastewater treatment processes, electricity generation using MFCs would recover bioenergy from organic residue in the wastewater using bacteria as a biocatalyst [29]. By extracting energy from the wastewater, an MFC exhibits its potential to power sensors in remote areas, where it is not feasible to substitute batteries. To enable wastewater treatment to be cost-effective, an effective approach of resource recovery to the existing treatment techniques needs to be developed [30].

When wastewater is used as an anode fuel, an MFC performs water treatment while recovering energy [31]. MFC utilizes bacteria that act as microreactors and allow substrates to be oxidized completely. The bacteria can efficiently transform the chemical energy of organic compounds in the wastewater into power [32]. Electrons flow from anode to cathode through external wire, resulting in electrical current. The anode-respiring bacteria oxidize organic pollutants present in waste streams and transfer the electrons to the anode. With bacterial population attached on the bioreactor's infrastructure, the scavenged electrons flow through electrical circuits, terminating at the MFC's cathode and generating electricity as a by-product [33]. The ions are transported through the fuel cell's ion membrane to maintain electroneutrality, although the membrane is excluded.

Under natural conditions, bacteria use oxygen as an electron acceptor to produce water. In the oxygen-free environment of the MFC, specialized bacteria that send the electrons to an insoluble electron acceptor, called the MFC's anode, play key roles [34–36]. Electron exchange occurs between the two electrode chambers [37,38]. In the anode chamber, oxygen-starved organic compounds of the liquid waste are oxidized and generate H^+ and e^-, from which the MFC extracts electricity.

During the operation, bacteria consume food from the liquid waste for survival, and people reciprocally obtain electricity for energy. This represents a win–win collaboration between humans and nature for environmental conservation [39,40]. While the main function of an MFC is bioenergy production, with respect to environmental sustainability, other benefits of MFCs include their contribution to waste reduction and/or the production of recycled water. For this reason, MFCs may be linked to municipal waste streams in cities to provide a sustainable energy production system for wastewater treatment [41].

With respect to its significance to the economy, this work contributes to the circularity of materials and hydrogen economy through wastewater treatment applications. It is expected that MFC progress could contribute to waste minimization and pollution prevention due to wastewater, while recovering and reusing macro-nutrients such as P from it for mineral fertilizer production [42]. This makes MFCs a potential game-changer in renewable energy development in the future.

3. Mechanism of Electricity Generation by MFC

Scientific exploration in MFC results from its ability to operate at varying weather and pressure using *Geobacter sulphurreducens* that form biofilms onto electrodes. The biofilms promote electron flows to electrodes and release a *c*-type cytochrome that accumulates at the biofilm–electrode interface to promote electron transfer to electrodes [43]. The bacteria attached with the MFCs remove the need to isolate costly enzymes, as they provide inexpensive substrates for its operations. The process occurs in a small bioreactor, where the microbes are retained in stable conditions for a period of time as biofilms, thus saving operational and maintenance (O&M) costs [44].

An MFC acts a battery-like energy generator that produces electricity through an electrochemical process. As MFCs convert chemical energy directly into electricity, they have the potential to operate at high efficiency. By exploiting their electron transfer abilities, MFCs produce energy directly, without combusting the organic compounds in wastewater, while treating them without requiring traditional energy. This facilitates users to comply with their obligations at a lower cost. However, it has the same ability to eliminate organic matter as efficiently as conventional wastewater treatment plants do [45].

An MFC is dependent on biofilms for electron transfer. When it is used, a large surface area is required to accumulate on the anode's chamber. It is important to develop bioelectrodes with capability of resisting fouling. A key to the disparity lies in the fact that MFCs must operate at neutral pH in the anode chamber to maximize growth and activity of the micro-organisms that catalyze the reactions. At the cathode, OH^- causes an increasing pH due to the limiting rate of their transport. Furthermore, every unit of pH increase at the cathode leads to an energy loss of 59 mV [45]. The cathode's pH could reach pH > 12, implying a major loss [46]. To ensure that they do not re-mix, the membrane is placed to separate the electrode from the other, while ensuring that there is no leakage from the cell's assembly [47].

By harnessing bacterial metabolism for energy generation that can be sold to produce income for wastewater treatment operators, the income not only defrays the cost of MFC operations, but also keeps on enhancing its prototype design for operations. The power produced by the MFC's operation supplies the need for energy, while the value of energy produced by the MFC creates a jobs. Decentralized electricity production also makes cities livable, with low-voltage applications that could be powered using MFCs, supplying a sustainable energy system for water treatment [48]. This provides an affordable and practical way to operate the system for a decentralized process using a wide range of wastewater for water reuse and energy supply [49].

MFCs are eco-friendly because they produce far fewer CO_2 emissions. Furthermore, MFCs can continuously generate electricity as long as the fuel and the oxidant are provided to the cell. As the fuel in the cells is stored externally, it is not internally depleted. Hence, the MFC is ideal, as the device does not have moving parts, making it a reliable source of power [50].

With this paradigm in mind, researchers aim at developing an anaerobic MFC with efficient electrodes that can be used to generate electricity from wastewater, while at the same time treating it with a minimum amount of waste generated during its operation. In the short-term, the MFC represents a temporary solution to the unresolved issue of providing energy to undeveloped areas without requiring changes to existing network facilities. By using bioenergy from MFCs, GHG emissions can be reduced substantially. It would be an important breakthrough in the field of energy recovery if energy produced from MFCs could be integrated into electricity networks. Successful operation of MFCs can open the door to their commercialization and deployment. Although the systems are promising in generating clean energy, there are improvements needed to enable their widespread application to attain carbon neutrality [51].

MFC utilization contributes to sustainability such as by GHG emission reduction, energy generation, and reduction of carbon footprints. When applying a certain voltage to bacteria for biodegradation of organic pollutants, this leads to water electrolysis, generating H_2 from the wastewater (Figure 3). To contribute to decarbonization, MFC can reverse the process by producing hydrogen (H_2). One metric ton of H_2 contains 33.3 MW·h of clean energy [52]. Hydrogen may be the safest gas known with high diffusion rate for CO_2, and it burns in air to form water. For a sustainable zero-emission energy and carbon-neutral future, hydrogen is considered a next-generation source of energy, which has potential to replace fossil fuels such as oil, gas, and coal. The annual production of clean hydrogen, a low-carbon energy carrier, would need to increase more than sevenfold for the world to hit net-zero emissions in 2050.

Energy production in the recovered H_2 would help industries offset the treatment costs of wastewater. This decarbonization strategy is more beneficial than landfill gas (LFG) that not only generates a bad odor, but also contains CH_4 that contributes to climate change. As society is benefited from technological revolutions, using H_2 gas as a fuel benefits it in the long-term. Unlike fossil fuels, during its production, H_2 does not emit CO_2 into the atmosphere, reducing environmental impacts and protecting the environment [53].

As compared to natural gas that takes millions of years to develop, hydrogen or electricity can be produced on-site by MFCs for a relatively short time with much less CO_2 emission. This provides net GHG savings with respect to carbon neutrality. As compared to MFCs, hydrogen production from the extraction of natural gas contributes 2% to all anthropogenic CO_2 emissions into the atmosphere, accelerating climate change. With the hydrogen being produced originating from fossil fuels, there is a growing need for a cleaner and more environmentally friendly option for its production.

For this reason, the world needs to achieve carbon neutrality between 2050 and 2070 by accelerating the energy transition to achieving a low-carbon and sustainable energy system. Measures to address climate change have shifted course toward achieving carbon neutrality by 2050. In 2020, the EU unveiled a long-term strategy with a firm commitment to climate neutrality by 2050. The roadmap toward decarbonization society has begun not only in Japan, China and Korea, but also in Indonesia and Malaysia. This movement will inevitably lead to carbon neutrality in other countries [54].

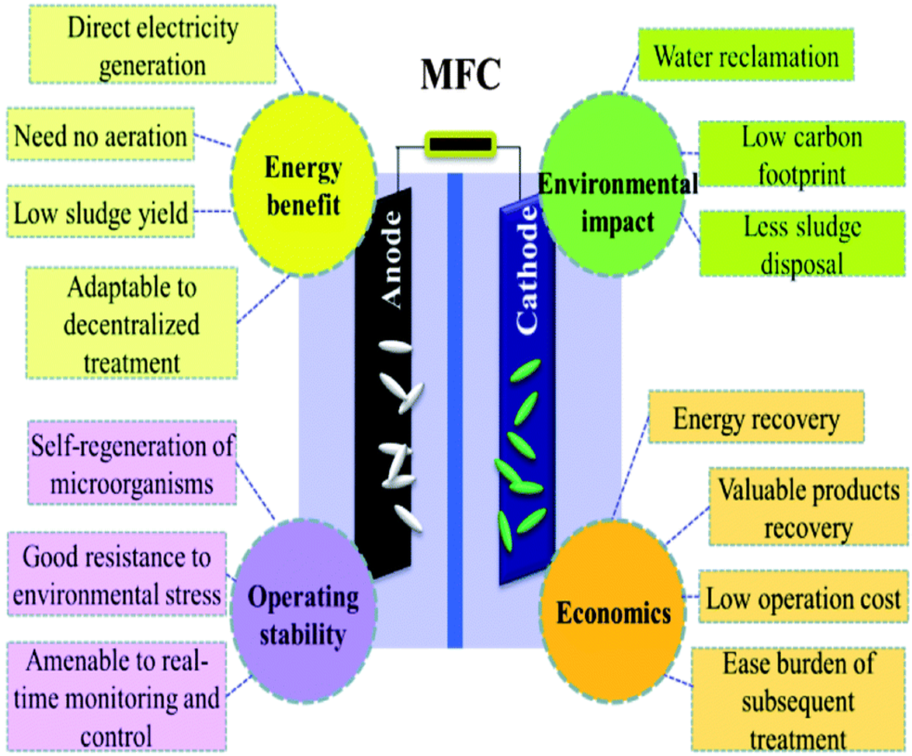

Figure 3. Unique selling points of MFC.

4. Technological Strengths of MFC

Traditionally, wastewater treatment is costly due to energy consumption. In an aerobic process, existing conventional technology using activated sludge consumes 60% of energy for aeration (Figure 4). The air cathode of an MFC uses oxygen directly from air, lowering energy consumption cost. MFCs also reduce treatment cost by producing electricity on-site to power plant's operation. MFCs can efficiently operate at ambient temperature with low strength of wastewater, and yields less solids to be disposed of in landfills, making it economically attractive compared to existing water technologies [55].

Unlike activated sludge, MFC-based treatment has the potential to treat wastewater without aeration, but through the growth of bacteria while generating bioenergy. Although the idea of generating energy using bacteria may not be new, as a practical technology of energy production, MFC utilization is promising. As a by-product of MFC operations, electricity justifies the cost of operating this system by itself [56]. By assuming that continuous operations of MFCs reach 15 Watts/m^3 of wastewater flowing through it, if an MFC system is installed at a wastewater treatment plant for 5000 inhabitants, it produces 0.75 MW, enough to power about 500 homes [57].

When calculating the price/Watt installed, power output/m^2 and MFC's lifespan are important. As MFC's power outputs range from 0.25 to 3.75 W/m^2, the price/Watt installed at its lower limit is over USD 4000 [58]. If the higher limit is applied, the price would decrease to USD 30/m^2, less than USD 6/Watt, including operations and maintenance costs [59]. If electrochemical techniques progress and the price of electrodes decrease, this treatment method can convert organic materials of wastewater into electricity.

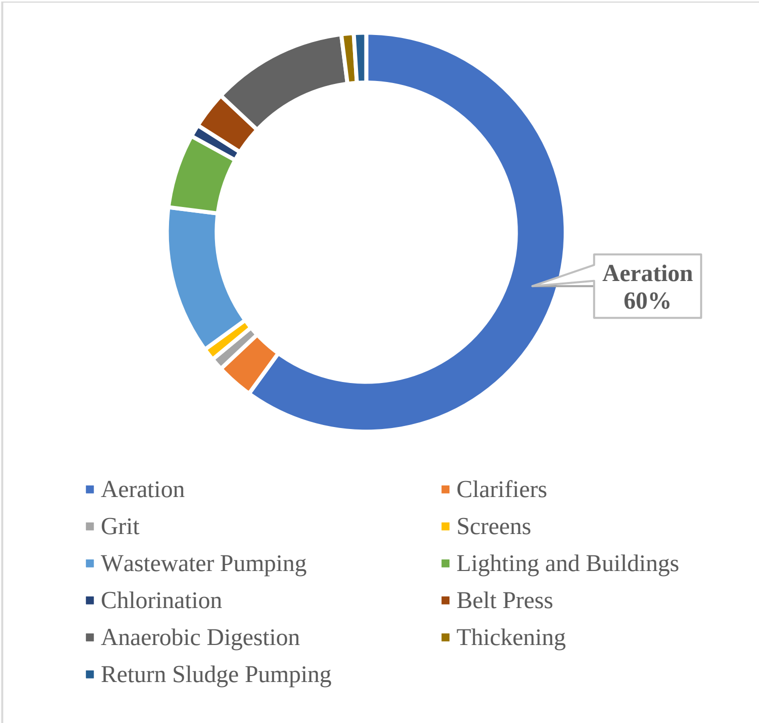

Figure 4. Energy consumption in activated sludge.

However, the removal of contaminants in wastewater at zero energy cost would warrant the use of MFCs for this goal. MFC technology reflects a frontier science. So far, only a few works have been translated into a practical configuration using an affordable and suitable material. An MFC reactor, designed with low-cost and compatible biomaterials for bioelectricity production, paves the way forward for industrial application in the next stage (Figure 5). This technology is expected to lead to another necessary step toward achieving carbon neutrality.

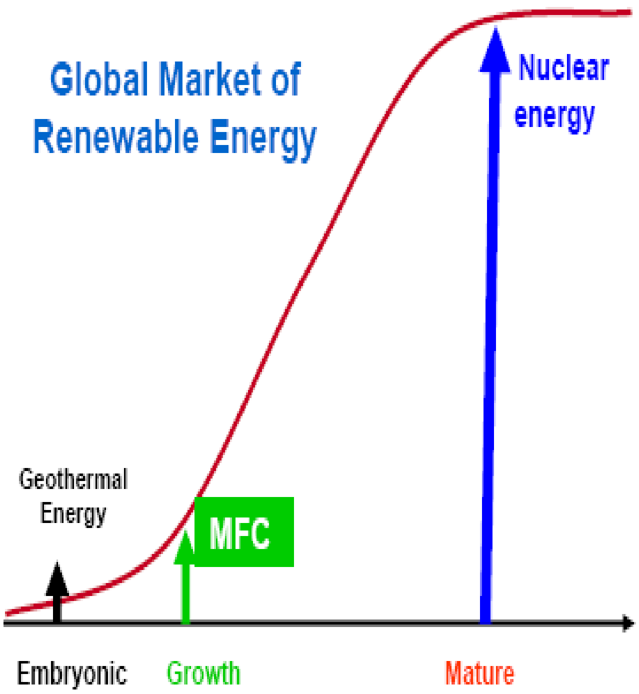

Figure 5. MFC among renewable energy.

For this purpose, well-designed and cost-effective MFC technology is essential to accelerating electrification in the developing world. If enacted swiftly, favorable climate technology and energy policy could level the playing field between electricity and other power sources. This will encourage the adoption of sustainable technologies, leading to less consumption of polluting fossil fuels.

Principally, anaerobic MFCs are capable of generating electricity from municipal wastewater and treating wastewater with low oxygen requirements using cost-effective and ecofriendly processes. Wastewater treatment plant operators can be self-sustaining with power generated by MFCs on-site, where they can use the energy generated for operating water treatment plants or for market commercialization. Eventually, the application of anaerobic MFC would enable treatment of wastewater with minimal energy investment and less carbon footprint during water treatment, and recovery of chemical energy laden in the wastewater in the form of bioenergy produced through anaerobic processes.

5. Bottlenecks of MFCs

In spite of their potential, a variety of bottlenecks need to be addressed before MFCs are commercialized on the market. Low electricity production, high internal resistance and high material cost are the major obstacles of MFC technology implementation. This could be explained due to the fact that MFCs depend on biofilms for promoting mediator-less electron transfer. When MFC is utilized for wastewater treatment, a large surface area is vital to biofilm accumulation on the anode chamber [59]. Consequently, this needs electrodes with the capability to resist fouling, thus enhancing the operational cost of water treatment plants.

In addition, as the material cost of an MFC is expensive; scientists need to develop suitable materials that can overcome low energy production [60]. To scale up the reactor, the cost of MFC components such as anodes, cathodes, and membranes will increase to maintain its high performance. Stability, long-term performance, efficiency, and scaling up the process from a lab scale to full scale are future challenges. MFC's bottlenecks also include low electricity production, current instability, and high internal resistance. This makes them difficult to apply due to the high cost of MFC fabrication (electrode, proton exchange membrane, and mediator), and low power generation. If the bottlenecks can be solved, potential energy outputs and the MFC's versatility could transform the method of wastewater treatment universally. This could generate electricity on-site to treat water off the grid in remote areas.

6. Development Trends of MFC for Dual Functions

Any technical challenges in the MFC's development can be tackled with innovative research. To respond to a number of engineering challenges found in earlier studies, various technological interventions set a boundary between status quo and development trends, while pushing the frontiers of MFC technology toward sustainable development.

6.1. Electrode Development for Enhancing Power Output

While other MFC studies applied synthetic wastewater like that as derived from sodium acetate, a study [60] used fresh wastewater collected from a wastewater treatment plant with varying concentrations of organic compounds. MFC designs have been made of transition metals-based catalysts such as Pt and equipped with configurations that make retrofitting of the existing water treatment plants become impractical. Alternative electrodes from biomaterials and MFC configurations can be used for retrofitting wastewater treatment plants at pilot scale in the next stage of MFC development.

To increase power output, bacterial strains such as *G. sulphurreduces* were screened. In addition, anode performance in an earlier study [61] was improved by modifying substrate or the materials of an anode. This could be due to the fact that the micro-organisms populating the electrodes depend on carbon source and inoculums. Electrodes with compatible biomaterials that have capability of resisting fouling and overcoming low energy production were also investigated [62].

To enhance its power output during operations, the MFC system was developed for continuous operations of wastewater flowing through it [63]. Hence, MFC electrodes were produced from corrugated cardboard via a novel carbonization. The corrugated cardboard electrodes were used as anode and cathode materials. It was essential to develop suitable materials for the anode and cathode that could be used to overcome low energy production during operation while maintaining stable performance [53].

To improve anode performance, different chemically modified surfaces were studied [64] to determine if modifications would facilitate not only a rapid development of bacteria and their enrichment, but also fast reaction start-up and high electrochemical activity [65]. Hence, both hydrophilic (-$N(CH_3)_3^+$, -OH and -COOH) and hydrophobic (-CH_3) self-assembly monolayers were tested for if their presence would promote a synergistic cooperation between electro-active and fermentative bacteria under anodic conditions [66]. In addition, cathode performance can be enhanced. Normally, a cathode's performance is limited by a slow reaction rate of the oxygen reduction reaction. High energy is required to maintain the reaction rate at neutral pH. To achieve this goal, different low-cost cathodes were designed to improve the power output in a single chamber of an MFC, in which the cathode was exposed directly to an anodic solution [67].

The power output in the MFC cathode was also increased using a conductive carbon-based coating to increase roughness. This generated strong adhesion between the cathode and ceramic support by utilizing Fe–aminoantipyrine as a catalyst. This catalyst in the MFC was tested alongside graphene oxide [68]. In this case, the MFC could be installed without a membrane and the catalyst was directly exposed to the wastewater.

Hou et al. [69] shortened reaction start-up during its operation by immobilizing bacteria on a carbonaceous surface. This technique for enriching and isolating electroactive bacteria from wastewater led to the discovery of new electroactive bacteria that could be efficiently used by the MFC to treat it. For this reason, a silica encapsulation on existing biofilm was studied for a rapid detection of the entrapped bacteria [70].

Integrating MFC for water treatment purposes can be used to develop online microbial sensors for monitoring the level of organic concentrations in wastewater during its operations. This sensor took the repeatable patterns of energy clients and made them into solutions that can be built quickly, providing a short time to the value and lowering operational costs. The system alerted engineers so that problems could be rectified immediately. If sensors were installed throughout water treatment systems, water treatment operators could also measure energy outputs, in addition to turbidity, salinity, conductivity, and pH of the wastewater. The sensor installed during MFC operations helped operators understand energy demand in real time and effectively managed its supply and demand, and placed the control of energy consumption in the hands of consumers [71].

6.2. Phosphorus (P) Removal Using MFC

Conventional techniques such as biological processes have been tested for P recovery from wastewater [72,73]. However, these approaches are cost-ineffective and less productive due to low-purity products [74,75]. Electrochemical technology is ideal for P recovery from wastewater, in spite of its massive energy consumption [76–78]. In an MFC reactor, bioelectrochemical processes took place to remove P from wastewater along with power generation [79]. Struvite is the predominant form of recovered P from wastewater, which can be used as an efficient slow-release fertilizer [80]. Struvite results from the reaction of NH^{4+}, Mg^{2+}, $PO4^{3-}$, and six molecules of H_2O [81].

$$Mg^{2+} + NH^{4+} + PO4^{3-} + 6H_2O \rightarrow NH_4MgPO_4.6H_2O \downarrow \quad (1)$$

In an MFC, P can be recovered using precipitation. P is not involved in electron transfer via redox reactions [82]. Since wastewater is a rich source of $PO4^{3-}$, NH^{4+}, and Mg^{2+}, struvite precipitation represents a strategic approach to recovering P and N from wastewater. P content in struvite ranges between 10% to 15% (*w*/*w*), depending on the nature of influent [81]. During its operation, struvite solubility decreases at alkaline pH. As a result, struvite precipitation takes place on the cathode's surface in an alkaline environment [73].

Since struvite crystallization occurs at the pH range of 8 to 9, it was found that pH influences P precipitation. Through the oxygen reduction, the flux of alkali cations combined with proton consumption. This oxygen reduction leads to the accumulation of OH^- and pH increase at the cathode [59,80]. As a result, the solubility of phosphate reaches oversaturation resulting in P precipitation.

Ichihashi and Hirooka [73] utilized a single-chamber MFC to treat swine wastewater. They found that about 30% of P was recovered in the form of struvite. This recovery rate is attributed to pH buffering that takes place in MFC, since H^+ and OH^- accumulate at the chamber of MFC. They used an air–cathode single chamber of MFC using wastewater and obtained a P removal of 70–82% along with a current density of 6–7 A/m^2. The precipitated P in struvite formed on the cathode had irregular crystals with hexagonal cross-sectional surfaces [73].

In previous studies, the cathode adopted metal catalysts (Pt) for P recovery in abiotic and biotic electrochemical reactors [77]. Ji et al. [74] investigated an Fe^{2+}-modified biochar cathode to recover P from wastewater using a microbial electrolysis cell (MEC). It significantly increased the electrochemical performance of the MEC, as its current density increased from 17 to 21 A/m^3 and the P removal increased from 29 to 62%. After operation in MEC reactors, the P- enriched biochar can be used for soil amendment to promote the growth of plants [74]. A study conducted by Fischer et al. [83] reported that the release of ortho-phosphate after pH adjustment resulted in P recovery.

Hirooka and Ichihashi [77] found that the performance of the cathode decreased after struvite formation and removing the precipitates from it. They found that struvite precipitation at the cathode prevented the transfer of O_2 from taking place. They studied the effects of NH_4 and Mg on its precipitation and found that P was precipitated as struvite. As the amount increased, more precipitates were formed [76].

A low-cost activated carbon (AC) material was used by Santoro et al. [55] as a cathode to replace Pt. In a membrane-less single chamber of MFC, they treated feeding solutions (raw wastewater and synthetic wastewater) for power generation and P removal. They found that solution conductivity and pH affected the cathode and MFC performance.

Xie et al. [84] embedded MFC in anaerobic–anoxic–oxic (AA/O) reactor for water treatment and enhanced the efficiency of N and P removal. An AA/O reactor is widely used for nutrient removal. After 50 days of operation in an AA/O reactor using sewage, MFCs were embedded, and the MFC-AA/O bioreactor was operated for 60 days. The total nitrogen (TN) and total phosphorus (TP) removal with and without MFCs showed that after embedding the MFCs, the average TN removal increased from 76% to 90% and that the TP removal was enhanced from 47% to 67% (Table 1). This shows that MFCs not only generated power from wastewater, but also enhanced nutrient removal from wastewater.

Table 1. Comparison of phosphorous removal and power generation by various MFCs.

Type of MFC	Influent Used	Operational Time (Days)	P Removal (%)	Current Density (A/m^2)	Reference
Air–cathode single chamber MFC	Swine wastewater	76	82	6.0–7.0	[73]
Air–cathode single chamber MFC	Artificial wastewater	108	27	4.3	[77]
Microbial electrolysis cell	domestic wastewater	3	74	6.6	[78]
Single-chamber MEC	Simulated wastewater	23	66	20.7	[74]
Pyrite-based wetland MFC	Simulated wastewater	180	91	4.8	[85]
Anaerobic–anoxic–oxic MFC	Sewage waste	110	67	-	[84]
Two-chamber MFC	Synthetic wastewater	20	80	-	[76]

In a separate study, Almatouq and Babatunde [81] optimized the conditions for energy generation and P recovery in a dual-chamber MFC. They used a mathematical modelling approach and response surface methodology for studying process variables. To optimize power output and P recovery in an MFC, their study used an integrated modelling with complete factorial design. The MFC generated a maximum output of 1.62 kWh/m^2 and a P removal of 95% (Table 1).

Li et al. [59] used an airlift-type photosynthetic MFC for power generation and nutrient removal from swine wastewater. They successfully removed 99% of TP along with COD removal (96%), total organic carbon (TOC) removal (95%), and NH_4^+ removal (99%). In a separate study, Tao et al. [85] studied the effect of dissolved oxygen on P and N recovery along with electricity generation in a dual chamber MFC. It was found that TP removal with chemical precipitation was 80% (Table 1).

Ge et al. [86] investigated the recovery of total TN and TP along with bioelectricity generation using a pyrite-based-constructed wetland-microbial fuel cell (PCW-MFC). The maximum TP removal in the PCW-MFC was 91% after operation of 180 days along with N removal. Their process was considered as an eco-friendly and cost-efficient method by involving microorganisms, wetland plants, and substrates. The precipitated crystalline P on cathode was treated by immersion in a dissolution solution to remove from the cathode.

For the dissolution of precipitates, pH of the buffer solution should be lower, which increases the amount of dissolved P from cathode [76]. It is estimated that 27% of the P added to MFC was recovered in the dissolution solution. Less than 0.01% remained on the cathode. On the other hand, the amount of P removed from the liquid waste was 40% of the added P. Table 1 presents that there is a wide variation in MFC performance based on its type and design, mechanism involved, operational time and the nature of influent used.

6.3. Key Factors for P Removal

For promoting an efficient recovery of nutrients from MFCs, it is important to consider key factors, which not only enhance struvite formation, but also increase power output [86]. Operational stability of the MFC can also be optimized under these factors to achieve an optimum performance. They include biological, physicochemical, electrochemical, and operational factors. The quantities and catalytic activity of the micro-organisms in the MFC are a few examples of biological factors. The protons moving through an exchange membrane, the types of electrodes, electrolytic resistance [87], and the rate of reduction at the cathode represent physicochemical and electrochemical factors [88,89]. Operating factors include organic loading rates, pH, and the type and concentration of the substrate with an adequate removal of P [90].

Micro-organisms are crucial in the degradation of substrate and electron transport from the anode. It has been proven that nature and concentration of denitrifying bacteria in the MFC play roles in nutrient removal from wastewater. *Rheinheimera* bacteria show major progress in P removal along with power generation as they are accumulated on the cathode's surface in the bioreactor [84]. P recovery depends on precipitation by substrates, and assimilation and accumulation by micro-organisms [85]. High amounts of Fe, Al, Mg, or Ca are typically present in substrates with high P-binding ability [91].

Ge et al. [85] used pyrite, a ubiquitous sulfide mineral containing Fe and S as a substrate in a constructed wetland MFC, which not only enhances N removal, but also provides Fe^{3+} and Fe^{2+} as a metabolic intermediates for removing phosphates from wastewater. Another study undertaken by Cusick and Logan [90] found that as precipitation is brought on by an increasing pH; P removal is also dependent on the substrate's conversion to electricity. It was found that the longer the electrolysis time, the more P is removed from the abiotic system. The bioelectrochemical P recovery from P-rich waste streams by MEC-induced calcium phosphate precipitation was highlighted by Lei et al. [78]. In their study, with less energy input, PO_4^{3-} was eliminated with coexisting Ca^{2+} as calcium phosphate at the cathode's surface.

Santoro et al. [55] monitored the electrocatalytic activity of synthetic wastewater containing sodium acetate and phosphate buffer saline solution and compared it with different wastewaters such as fresh urine and raw wastewater. The cathode's nutrient recovery performance was impacted by conductivity and pH. With P concentration of 236 mg/L and NH_4 (570 mg/L), the recovery of P was 40% after 7 days of operation.

In MFCs, P recovery requires a certain pH level. Since P is insoluble in alkaline solutions, P removal depends on pH, which is best suited at pH > 8 for struvite formation. Cathodic pH was examined to understand the impact of COD concentration and cathodic aeration flow rate on energy output and P recovery. The findings demonstrated that raising pH caused an increasing P precipitation from 10% to 85% when cathode pH was raised from 7.5 to 9. Struvite became crystallized into tubular-shaped crystals under these circumstances. From the EDS spectrum of recovered precipitate, Mg, P, and O were identified as key elements [80,91]. Organic loading rate (OLR) also affects the metabolism, bacterial growth, substrate consumption, nutrient recovery, and electricity generation [81]. Hamza et al. [92] found that high OLR affected the production of energy by improving nutrient recovery such as P.

In another work undertaken by Almatouq and Babatunde [81], it was revealed that the cathode's electricity density, P precipitation rate, and columbic efficiency were affected by influent COD concentration and aeration flow rate at cathode. Depending on the COD concentration, cathode aeration flow rates had a varying impact on power density and P recovery. The generated current had a negative impact on P precipitation at cathode. Power output and P recovery improved when MFC operated at high COD concentration and high aeration flow rates. The results also demonstrate the importance of influent COD concentration and cathode aeration flow rate on power generation and P recovery [90,93]. The formation of struvite was also affected by molar ratio and aeration rate [94,95].

6.4. Feasibility of P Removal Using MFCs

MFCs have gained popularity due to their versatility of applications in the removal of pollutants, power generation, wastewater treatment, and environmental monitoring [83,87]. Unlike traditional biological wastewater treatment methods such as activated sludge, the advantages of MFC for water treatment include high efficiency, ambient operating conditions, small equipment sizes, minimal sludge generation, and rapid start-up. Several physicochemical, electrochemical, operational, and economic factors affect how well and efficiently MFC produces electricity and removes P from wastewater [76].

To enhance the overall performance of MFC, it is essential to comprehend the impacts of the various operational settings and economic variables on electricity generation and P recovery. Because struvite is drawn to the cathode surface and reduces the cathode's performance, cathode maintenance is important. The dissolution of accumulated precipitates on cathode restores its performance to the original level [82,85].

Zhuang et al. [96] determined that the catalyst might become covered if alkali salt formed in the cathodes, making it difficult to contact with oxygen. They rinsed a cathode that had been used for 60 days with water to remove alkali salt and uncovered that the performance reverted to the level of day 20 [97]. The precipitate from the cathode must be removed from MFCs in a timely manner for effective P recovery while producing good amounts of electricity. For large-scale applications, it is critical to reduce energy consumption and electrode costs for electrochemically recovering P from wastewater [83].

New low-cost cathodes and catalysts with large surface area and high commercial availability should be advantageous for oxygen reduction and P removal. Santoro et al. [55] used an activated carbon cathode with increased electrocatalytic activity and low cost to raise the performance of power density and P removal. PVC and graphite are examples of carbon-based compounds with a strong attraction to microbes. For MFCs to operate for an extended period of time, further research into electrode materials is required. The electrode material and the configuration of MFCs directly impact the cost of the process [98]. They need to be able to process wastewater as quickly as traditionally biological waste treatment systems. MFC power densities are ten times lower than those of chemical fuel cells [82,99]. The benefit of an MFC is that it produces sufficient power, while removing P from wastewater at the same time [100].

MFCs have not yet achieved the ideal performance due to short lifespan, low production rate, membrane fouling, high cost, and low efficiencies [101,102]. Improvements to the electrogenicity of micro-organisms, appropriate electrode selection, optimization of operational factors, effective recovery of by-products, minimization of capital cost, and maximization of power output are required to pave the way for better performance of P removal. The performance of MFCs needs to be improved in the future by genetically engineering microbes or employing mixed microflora to raise their electrogenic activity, which effectively improves electron transport from wastewater. It is crucial to make design modifications and to find balance between the operational and capital costs of MFCs for sustainable wastewater treatment [103].

7. Economic Feasibility Analysis

The economic feasibility of the MFC depends on the electricity output and the costs of materials used [103]. If its output can be increased for large-scale applications, in the long-term MFC would economically attract the market due to its practicality. It is expected that the renewable energy market will grow to USD 15.50 billion by 2030, while the water market is about USD 20.75 billion. Water industries forecast increasing energy consumption as the implications if sustainable, reliable, and eco-friendly solutions are not ready for widespread use by 2050 [74].

As MFC technology is under development, a rapid way of transferring it into the global market is to apply its technology in an area that is likely to yield maximum profit. A widespread application of MFCs as a cost-effective way of energy recovery from wastewater would make water infrastructures in the developing world become self-sufficient and sustainable. Although the amount of energy that could be captured from wastewater is insufficient to power a city, it is enough to operate a treatment plant and to attain energy sustainability of water infrastructures [104].

8. Online pH Monitoring in MFC Operations

Devices for online pH monitoring are practical with respect to their model. Therefore, pH monitoring is commonly utilized in MFC operations. Online pH sensors are useful for environmental monitoring and dosing control to meet water quality standards. Due to their widespread use, pH monitoring devices can perform analysis, maintenance, and operation. Digital solutions assist wastewater treatment operators in enhancing productivity and connectivity via online monitoring [59].

The introduction of a digital pH sensor offers accuracy and enhanced signal strength. Their key benefit over analog pH sensors is a substantial improvement in productivity. When digital pH sensors are fitted within the sensor body, this assists operators in processing the pH signal by converting it to a robust digital signal. Digital pH sensors can store not only calibration, but also configuration data in the sensor itself. This enables sensor commissioning and plug-and-play connectivity. Hence, calibration is not necessary when commissioning a pH sensor. The sensor can be pre-calibrated to be ready for use anytime. This could minimize the commissioning time of a pH sensor from 20 min to around 2 min when using digital platforms [105].

Digitalization also benefits other processes to improve productivity by utilizing pH sensor monitoring. Online monitors simplify recording requirements by continuously updating the processes. This enables abnormalities to be detected, alarms raised immediately, and correction implemented rapidly. Online monitoring can extend MFC operations via automated calibration, which ensures the accuracy of continuous monitoring without intervention. One benefit of digitalization with respects to legislative demands is that users and stakeholders have access to data within the instrument [106].

Traditionally, analog sensors could report issues with a sensor such as a plugged junction. If operators received an update, it was too late for them, as the probe would not be in line with the commission. Digital probes enable operators to enhance sensor monitoring without requiring complicated wiring [107]. The diagnostics can predict endof-life by minimizing process downtime and altering maintenance requirements in a timely manner. While offering an added layer of security with respect to protected access, online monitoring can provide a graphical analysis. This facilitates users to visualize data trends in applications. Audit logs may record any abnormalities by tracking diagnostic faults. Finally, the capability of transferring data via USB drives enables rapid information access.

9. Concluding Remarks

As climate change is a huge threat faced by all human beings, net-zero emissions/carbon neutrality has become a global goal for the entire civilization. Achieving carbon neutrality requires a deep systemic change in global energy consumption. Developing renewable hydrogen as fuels is crucial to decoupling global industrialization from CO_2 emissions. This offers a huge opportunity for the world to resolve this global issue.

The utilizations of MFC itself as a self-powered water treatment system is a breakthrough. Using a pyrite-based wetland MFC, about 91% of P was removed after operating for 180 days, while generating a power output of 48 A/m^2. A wastewater treatment plant can power itself in its operation while selling electricity to the market. This radically changes conventional water technologies, the way wastewater is treated universally, and its associated energy consumption, substituting the most widely used activated sludge for wastewater treatment. By exploring this direction along the water–energy–waste nexus, MFC technology that combines environmental engineering, microbiology, and sustainability into an applicable solution would transform today's wastewater treatment plants. Eventually, MFCs provide a practical solution that directly addresses the need of society for clean water and energy at the same time, shining a light of hope on the road to carbon neutrality and decarbonization [108].

As the power sector decarbonizes and helps the world prevent the worst effects of climate change, the adoption of sustainable energy through MFC operations will continue to expand globally, especially when pressured by rising awareness and environmental concerns from all stakeholders. Nonetheless, the adoption modes still pose intense challenges, such as costly capital investments, low financial returns, inconsistent energy supplies due to uncontrollable natural factors and a lack of rudimentary and technical knowledge. It is of critical importance that all of these challenges be addressed to make sustainable energies more economically appealing for mass adoption in the future.

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