Review

Novel Applications of Microbial Fuel Cells in Sensors and Biosensors

Francisco Ivars-Barceló 1, Alessio Zuliani 2, Marjan Fallah 3, Mehrdad Mashkour 3, Mostafa Rahimnejad 3, * and Rafael Luque 2,4, *

1 Departamento de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, Paseo Senda del Rey, 9, 28040 Madrid, Spain; accfib@hotmail.com
2 Departamento de Química Orgánica, Universidad de Córdoba, Edificio Marie-Curie (C-3), Ctra Nnal IV-A, Km 396, E14014 Córdoba, Spain; zuliani.alessio@gmail.com
3 Biofuel and Renewable Energy Research Center, Department of Chemical Engineering, Babol Noshirvani University of Technology (BNUT), Shariati Ave., Babol 47148-71167, Mazandaran, Iran; mrjnfallah@gmail.com (M.F.); m.mashkour1990@gmail.com (M.M.)
4 Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya str., Moscow 117198, Russia
* Correspondence: rahimnejad@nit.ac.ir (M.R.); rafael.luque@uco.es (R.L.)

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Abstract: A microbial fuel cell (MFC) is a type of bio-electrochemical system with novel features, such as electricity generation, wastewater treatment, and biosensor applications. In recent years, progressive trends in MFC research on its chemical, electrochemical, and microbiological aspects has resulted in its noticeable applications in the field of sensing. This review was consequently aimed to provide an overview of the most interesting new applications of MFCs in sensors, such as providing the required electrical current and power for remote sensors (energy supply device for sensors) and detection of pollutants, biochemical oxygen demand (BOD), and specific DNA strands by MFCs without an external analytical device (self-powered biosensors). Moreover, in this review, procedures of MFC operation as a power supply for pH, temperature, and organic loading rate (OLR) sensors, and also self-powered biosensors of toxicity, pollutants, and BOD have been discussed.

Keywords: microbial fuel cells; biosensors; power supply; self-power; pollutants; wastewater

1. Introduction

Bio-electrochemical systems (BESs) are promoting the development of innovative technologies that combine biological redox catalytic activity with abiotic electrochemical reactions and physics [1–3]. BESs are normally classified by their applications, such as the generation of chemicals (e.g., formate or methane [4,5]) and energy [6], as well as water desalinization [7]. Regarding the matter in question, BESs that generate energy are defined as bio-electrochemical fuel cells, which are subdivided into enzymatic fuel cells (EFCs) [8,9] and microbial fuel cells (MFCs) [10]. Specifically, MFCs use microbes to catalyze electrochemical reactions for electricity production. As shown in Figure 1, MFCs generally consist of anodic and cathodic chambers separated by a proton exchange membrane (PEM) [11], although single chamber MFCs, with or without an air-cathode, also exist [12–14]. Microorganisms oxidize the organic or inorganic material in the anodic chamber to produce protons and electrons. The electrons generated are captured at the anode and transferred to the cathode through an external circuit. Hence, MFCs, using microorganisms as electrocatalysts, are capable of generating electricity directly from a large variety of organic and inorganic compounds [15–17]. Unlike the practically limitless number of potential anodic reactions in MFCs, the number of cathodic reactions is quite limited, and mostly consists of oxygen reduction to form water or hydroxyl ions [18–20].
Nevertheless, it must be mentioned that there is still much room for improvement in the reactor configurations and electrolyte design of MFCs, in terms of effective applicability and the reduction of production costs [21].

Derived from the versatility in the nature of feedstock used as an anodic fuel, an innovative dual-purpose has been lately introduced for MFCs as an energy production technology for wastewater treatment. In fact, MFCs could provide a self-sustainable or even a net positive energy output while removing pollutants, with a competitive life-cycle assessment [22–27]. For example, an MFC system has been implemented in a constructed wetland very recently. A constructed wetland (CW) is defined as a treatment system that involve natural processes to improve water quality [28]. From this study, it has been demonstrated that an MFC/CW system has a low environmental impact, but its operating cost is 1.5 times more expensive than that for standard CW systems [29].

Other recent research projects aim towards the application of MFCs in the provision of power for remote electronic devices such as sensors and biosensors [30], the matter at issue in this review. In general, a sensor can be defined as an electronic device capable of detecting properties and events occurring in its surrounding environment, and quantify their changes [31]. The measured input information is converted into an output electrical voltage or current that is eventually sent to other electronic devices, most usually a computer processor. Based on tremendous efforts done by researchers over the last few decades, measuring water quality such as pH, temperature, and concentrations of heavy metals are some essential applications of wireless sensors nowadays [32]. As shown in Figure 2, in the specific case of biosensors, a biological or biomimetic component acts as a sensitive detector for an analyte of interest. The signal resulting from the interaction with the analyte is transformed, by a physico-chemical component or transducer, into a physical quantifiable signal compatible with an electronic signal processor.

The function of a biosensor depends on the biochemical specificity of its biologically active material or bioreceptor [33]. Depending on the type of receptor, biosensors can be classified as enzymatic biosensors [34], immunosensors [35], genosensors or DNA biosensors [36], or tissue-based...
biosensors [35]. Biosensors can be also divided into several categories based on the transduction process, such as electrochemical, optical, piezoelectric, or thermal/calorimetric biosensors [37–39]. Biosensors have important applications in several fields, such as the food industry [40,41], medicine [42], the marine sector [43], and others.

Novel devices have recently been introduced as systems for DNA detection, which are capable of specific-sequencing with no external power, known as MFC-based DNA biosensors [44]. Asghary et al., with the help of Danesh Gostar Hamgam Ba Sanat Company (Babol, Iran), utilized a dual-chambered MFC system as a power supply to construct an analytical device for the monitoring and characterization of the DNA immobilization and hybridization events [45]. Specifically, the electrical power output of the MFC determined the hybridization of the DNA probe, and any discrimination of complementary DNA sequences, such as non-complementary sequences or one-base mismatched, was revealed. The experimental results using human serum as a sample, showed high sensitivity, significant stability, and acceptable reproducibility.

Even more captivating, MFCs themselves can be employed as self-powered biosensors, thanks to their intrinsic sensitivity to biological and physico-chemical parameters. Monitoring microbial activity [46], biocorrosion by microbial biofilms [47], biochemical oxygen demand (BOD) [48], toxicants [27], and pH and temperature variations [26], are among the most interesting applications [10,49]. Furthermore, MFC based (bio)sensors provide higher stability and sensitivity compared with conventional (bio)sensors [12].

Based on the above context, this review is divided in two differentiated sections. The first section is dedicated to identify the benefits and drawbacks of MFC integration as a power supply for sensors and biosensors, as well as to address the main factors influencing their power output performance, such as pH, temperature, and organic loading rate (OLR).

In the second section, the use of MFCs as self-powered biosensors for toxicants and BOD is discussed.

2. MFC Power Supply for Sensors and Biosensors

Most of the commercial sensor and biosensor devices are conventionally powered by electrochemical batteries (e.g., lithium batteries) with a limited and relatively short lifetime that have to be periodically recharged or replaced [50]. Finding efficient and self-renewable energy sources to produce enough power for remote devices, where batteries replacement is not feasible or convenient, is nowadays a strongly pursued challenge [51]. Within that context, self-renewable MFCs appear as a long-term alternative power supply for remote monitoring sensors and biosensors, as schematically illustrated in Figure 3. Replacing conventional batteries with MFC power supplies in remote sensors, considerably lowers operational costs and environmental risks [51,52].

![Figure 3. Schematic diagram of a remote sensor powered by MFC.](image-url)
A key factor for the MFC energetic efficiency is a suitable feedstock, either organic or inorganic, for which extensive research has been implemented [16,32,90]. Nevertheless, and despite all the advantages, the most challenging hindrance for further expanding the applicability of MFCs in sensors are the low power outputs intrinsically associated with them, along with unstable electric potentials generated below the working potential of conventional electronic components in sensors [53]. Accordingly, regardless of the feedstock employed, working principles of MFCs as energy sources, as well as power requirements and detailed performance of power management systems for remote sensors, have been investigated in order to provide rational solutions to overcome the aforementioned drawbacks of MFCs [32,51,52,54]. As a result, one of the approaches to increase the power output of MFCs relates to the connection of several MFCs in series or in parallel [55]. As a case in point, Jiang et al. recently developed a remote biosensor based on MFCs placed in parallel, for an alert system to prevent the use of a harmful water stream [56]. The sensor was designed with a cathode-shared integrating four MFCs, based on the principle that only the bioanode would be used as the sensing and transducing element. The sensor showed an immediate voltage decrease when exposed to a pH variation from 6 to 4. The compact design of the cathode-shared MFC sensor array assured the detection credibility, and even more interestingly, the number of integrated MFC sensors was alterable, based on the monitoring requirement. In addition, it has been demonstrated that, with the appropriate energy management system, an MFC is able to operate sensors and integrated telemetry systems for the wireless transmission of remote signals. However, one of the usage problems for these devices is the need of a high-power supply. In the same vein, neither the parallel or series design from Xinmin et al. could increase the open circuit voltage (OCV) of several anaerobic fluidized bed microbial fuel cells compared to the sum of OCV of the individual cells [20].

Beyond the approach based on parallel or series design, a more feasible strategy behind the enhanced operability of MFCs seems to be the use of ultra-capacitors (among other electronic devices and configurations) to store the low energy generated by the MFC in order to be delivered only when the level of output energy is adequate to provide enough power to operate the essential functions of the remote device in question [32,51,52]. Moreover, DC/DC converters have been successfully employed to increase and stabilize the electric potentials of MFCs, as schematically illustrated in Figure 4.

![Figure 4. Schematic diagram of a remote sensor powered by an MFC with a DC/DC converter.](image)

This technology has recently been applied for the design of a new type of floating microbial fuel cell (f-MFC) for the power supply of a remote environmental sensor and data transmission [57]. In detail, ten operating MFCs generated a cell potential in the range of 100–800 mV. Power production peaked around 3–3.5 mW, recorded after about 20–30 days of start-up period. The devices were
endowed with a power management system, based on a DC/DC converter. The tested f-MFC, equipped with a DC/DC converter, successfully allowed the supply of simple electronic devices (a LED-light and a buzzer), and the transmission of remote data. Interestingly, using dense rice plants (Oryza Sativa) to ensure the long-term performance, several artistically-defined “floating garden” MFCs were set in the context of demonstrative events at the 2015 Milan World Exposition EXPO2015. As a proof of the possible applicability of those cells, some of the “floating garden” MFCs were operative for more than one year [57].

Ultimately, several environmental factors, such as temperature, pH, organic loading rate (OLR), as well as the presence of toxicants and inhibitors, should be strictly considered in the design of MFCs as they could affect the power and electric potential outputs [30,58]. The influence of those key parameters, among others, must be understood in order to project the components and the configuration of an MFC-driven sensor to scale-up for practical applications [16,59].

2.1. Effect of Temperature

Different parameters of MFCs, such as activation energy, mass transfer coefficient, and solution conductivity, are related to kinetic and mass transfer processes of the system. Those processes are significantly influenced by changes in temperature, and so they affect the performance of the MFC for energy generation [60–63]. On the other hand, the influence of the temperature will change depending on the specific nature of the microorganism and the feedstock employed [58,62–75]. Therefore, different optimum temperatures will be required depending on the specific characteristics of the MFC. Various investigations have proved a significant enhancement of the power output by increasing the reaction temperature in the anode chamber [58,62,64–73]. That improvement in the power density has been related to an enhancement of the microbial metabolism and membrane permeability, as well as to the reduction of ohmic resistance due to a higher conductivity of the liquid solution by increasing the temperature [62,63].

It is worth mentioning that biofilm formation can be also be affected by temperature changes [58,62,64–75], since biofilm development at the anode has an important impact on the anodic biocatalytic activity, and therefore on the energy generation. In that way, some studies show that the initial temperature is crucial in the formation of the biofilm in a MFC, and consequently, in the time needed for the startup. Thus, higher temperatures lead to a stable biofilm and MFC operation in a short period of time, and therefore to a higher performance.

Regardless of the aforementioned, some microorganisms naturally prefer low-temperature environments to reach optimum performance, which is potentially useful for MFC-driven sensors to be placed in cold areas [62,63]. However, at extremely low temperatures, microbial reactions slow down and eventually MFCs cannot operate.

2.2. Effect of pH

As in every biological system, the pH is an essential factor in MFCs, affecting both anodic microbial activities and cathodic reactions [76,77]. Protons, produced by the oxidation of organic matter in the anode compartment of an MFC, pass into the cathode compartment through the PEM and usually react with oxygen generating water molecules [58]. Accumulation of protons, due to continuous operation and/or limited proton diffusion and migration through the membrane, will lead to acidification of the reaction medium in the microbial anode chamber. On the other hand, production and migration of protons from the anode also influences the pH in the cathode compartment. In fact, the continuous intake of protons by oxygen reduction reaction (ORR), under unbalanced replenishment of protons, favors the alkalinization [60,78–80]. Eventually, energy generation decreases due to the pH increment in the cathode chamber, according to the Nernst equation for ORR [81]. Indeed, low operational pH benefits oxygen reduction, increasing the current output from an MFC. However, too low pH in the anode may negatively affect the biofilm performance and stability, decreasing bacterial activity, and consequently, the electron and proton generation. Despite the influence on the
biofilm formation, the specific response to the pH variations, which strongly depends on the type of microbe and conditions needed for its growth, will affect other primary parameters, such as ion concentration, membrane potential, and proton motive force [68,76,82–85]. Thus, the performance for energy generation in conventional double-chamber MFCs depends on the pH gradient between anode and cathode compartments, each of them usually presenting a different optimum pH. On the other hand, the performance of single-chamber MFCs, with only one electrolyte, is determined by mixed effects of the electrolyte pH on both anodic and cathodic reactions [58].

In general, the operational pH range for most MFCs is reported to be between 6 and 9, with an optimum usually at neutral pH [58,68]. Nevertheless, optimal performance can be found at higher pH ranges, between 8 and 10, for air-cathode MFCs [58,86]. Changes in current densities above a factor of 4 have been reported for pH variations of 1 unit in MFCs [68]. Therefore, active pH control by means of chemical buffers, such as phosphate [64], bicarbonate [87], borax [88], or synthetic zwitterionic compounds [89], have been proposed in order to keep steady-state current production. However, in spite of keeping a constant pH, the use of chemical buffers interferes with the MFC performance due to interactions with the electroactive microorganisms, electrodes, and/or proton exchange membrane [58,64]. Therefore, the unavoidable strong impact on the power output, along with an inherent increase of operational cost derived from their use, make chemical buffers not feasible for real applications. A step forward is the harnessing of local sources of carbon dioxide for the in situ generation of a carbonate/bicarbonate buffer, by reaction with hydroxide ions in the MFC cathode, proposed as a promising cost-efficient alternative for overcoming the pH-buffering challenge in MFCs [76,77,90–92].

Alternatively, self-sustaining pH control MFCs have been built as hybrid systems between single and dual chamber MFCs [93]. In detail, an aerobic microbial oxidation of acetate by the biofilm attached to the air cathode of a single chamber MFC (SC-MFC), was responsible for the self-sustaining removal of accumulated protons in the effluent of the dual chamber MFC (DC-MFC). It has been demonstrated that the hybrid exhibited the highest electricity output performance and the most effective conversion of acetate into electricity at high power levels, compared with the MFC consisting of an isolated single or dual chamber. In addition, due to the beneficial role of self-sustaining pH control by SC-MFCs, the hybrid stack demonstrated a stable operation time of around 15 hours, which was almost two times higher than that reached using isolated MFCs.

2.3. Effect of Organic Loading Rate

Organic loading rate (OLR) can be defined as the rate of biological oxygen demand (BOD) per volume unit of solution. BOD is an indicative measure of the oxygen required by aerobic biological organisms to oxidize the organic matter (usually considered as pollutants) contained in a solution at isothermal conditions. Hence, OLR is conventionally used to quantify the incoming mass rate of organic matter in a reactor for wastewater or sludge treatment. At this point it must be noted that the potential use proposed for MFCs is as a self-powered reactor technology in a waste water/sludge treatment [22], regardless of the fact that inorganic substrates can be also used. In that sense, OLR applied to a reactor is also known as volumetric loading rate, expressed in kg of BOD per unit volume of the reactor per day. The organic loading rate can also be defined per unit weight of microbial mass, and be used to measure the potential for substrate conversion in an MFC.

Regardless of the waste removal, operating at optimum OLR or sludge loading rate (SLR) is critical for an effective performance of MFCs, since both power density and current efficiency depend on the substrate conversion rate directly related to OLR [63,71,94–103]. Thus, the energy generation is generally boosted by increasing the OLR up to a maximum, from which higher loading rates decrease the power output of the MFC. The higher OLR translates into a higher availability of feedstock to be oxidized in the anode, which favors the metabolic activity of the electroactive biofilm and explains the enhanced power generation. On the contrary, an increased OLR has been related to lower efficiency for electron transfer processes from anode to cathode, hindering the adequate performance in an MFC [97].
As a case in point, Joo-Youn Nam et al. studied an MFC for the treatment of wastewater. As shown in Figure 5 [100], the decreasing of coulombic efficiency while OLR increases is unambiguously clear.

![Figure 5. Electron conversion efficiency and energy generation from fermented wastewater under 1 kΩ of the external resistance [100].](image)

Eventually, the optimization of MFC BOD biosensors pass through the prevention of oxygen diffusion [104], suppression of methanogens [105], and overcoming cathode limitations [106].

3. MFC as a Self-Powered Biosensor versus a Traditional Whole-Cell Biosensor

The high sensitivity of the MFC’s performance to a number of environmental and biological factors make them suitable to act, in turn, as biosensors [21,107,108]. Therefore, properly combining energy generation and sensing functionalities from MFCs, self-powered devices, i.e., operated without any external electricity supply, can be designed to operate autonomously for remote detection and quantification of desired parameters [109,110]. Indeed, several reviews have already been reported regarding those unique and novel applications posed for MFCs as electrical biosensors [54,111].

At this point, it should be mentioned that the IUPAC definition for “electrical biosensor” is a self-contained integrated device providing specific analytical information using a biological recognition element contacting with an electrochemical transduction element (anode/cathode electrodes in MFCs) [112,113]. Biological components for the analyte recognition in conventional biosensors are mostly enzymes, fluorescence proteins, and other fluorescence/pigment molecules [114–116]. In a conventional biosensor, an external power source is required to operate all electronic components, including the transducer and others, responsible for the signal conversion, amplification, and transmission, which noticeably limits applications in remote environmental monitoring. In contrast, the biological sensing element in the case of an MFC are the microbes, which give a measurable response as an output electrical current through the anode/cathode electrodes from the MFC itself [48,117,118]. Since the analytical output signal is already measured as an electric current, MFC-based biosensors do not need an external transducer. Therefore, MFC-based biosensors are considered to be recyclable and sustainable devices with higher cost- and energy-efficiency than conventional biosensors [111].

According to what has been discussed so far, monitoring microbial activity and related parameters, such as biochemical oxygen demand (BOD) or detection of inhibitors and toxicants, appear as the most obvious applications for MFC-based biosensors. Especially promising are their applications for rapid monitoring of environmental factors such as pH, temperature, composition, and concentration...
of organic matter, and other parameters related to the quality of water effluents (Table 1), for which MFC-based biosensors have been considered as the next generation of biosensing technology [30].

Table 1. Summary of viable reported applications of MFC-based biosensors.

<table>
<thead>
<tr>
<th>Parameter Measured</th>
<th>Power, Voltage, or Current</th>
<th>Detection Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD5</td>
<td>0.26–0.90 mA</td>
<td>32–1280 mg L$^{-1}$</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>0.063–0.55 mA</td>
<td>-</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>72 mW m$^{-2}$</td>
<td>17–183 mg L$^{-1}$</td>
<td>[121]</td>
</tr>
<tr>
<td></td>
<td>3.7–5.2 mA</td>
<td>20–200 mg L$^{-1}$</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>0.05–1.1 mA</td>
<td>2.6–206 mg L$^{-1}$</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>0.7–1.9 mA</td>
<td>50–100 mg L$^{-1}$</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>0.2–1.7 mA</td>
<td>-</td>
<td>[124]</td>
</tr>
<tr>
<td></td>
<td>0.05–8 μA</td>
<td>2–10 mg L$^{-1}$</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>0.0015–0.2 mA</td>
<td>-</td>
<td>[126]</td>
</tr>
<tr>
<td>Organophosphorus</td>
<td>0.005–0.042 mA</td>
<td>1–10 mg L$^{-1}$</td>
<td>[127]</td>
</tr>
<tr>
<td>Cd(II) and Pb(II)</td>
<td>0.005–0.035 mA</td>
<td>0.1–1 mg L$^{-1}$</td>
<td>[127]</td>
</tr>
<tr>
<td>Ni</td>
<td>0.15–2.25 mA</td>
<td>10–30 mg L$^{-1}$</td>
<td>[128]</td>
</tr>
<tr>
<td></td>
<td>0.022–0.132 A m$^{-2}$</td>
<td>0–88 mg L$^{-1}$</td>
<td>[128]</td>
</tr>
<tr>
<td>Na dodecyl sulfate</td>
<td>0.85–1.7 mA</td>
<td>10–50 mg L$^{-1}$</td>
<td>[128]</td>
</tr>
<tr>
<td>Bentazon</td>
<td>0.9–1.4 mA</td>
<td>1–3 mg L$^{-1}$</td>
<td>[128]</td>
</tr>
<tr>
<td>Cu</td>
<td>0.7–1.5 A m$^{-2}$</td>
<td>-</td>
<td>[129]</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.05 ± 0.04–0.1 ± 0.03 mA</td>
<td>-</td>
<td>[130]</td>
</tr>
<tr>
<td>E. Coli</td>
<td>0.1–0.38 mA</td>
<td>-</td>
<td>[122]</td>
</tr>
<tr>
<td>Microbial activity</td>
<td>0.6–12.4 A m$^{-2}$</td>
<td>0–13 nmol l$^{-1}$</td>
<td>[131]</td>
</tr>
<tr>
<td></td>
<td>0–0.30 mA</td>
<td>-</td>
<td>[132]</td>
</tr>
<tr>
<td>Oxygen Dissolved</td>
<td>5.6–462 mA m$^{-2}$</td>
<td>0–8.8 mg L$^{-1}$</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td>9.5–17 mW m$^{-3}$</td>
<td>-</td>
<td>[134]</td>
</tr>
<tr>
<td></td>
<td>0–0.092 mW</td>
<td>0–8 mg L$^{-1}$</td>
<td>[135]</td>
</tr>
<tr>
<td>Volatile fatty acids</td>
<td>0.22–1.29 mA</td>
<td>0–40 mg L$^{-1}$</td>
<td>[136]</td>
</tr>
<tr>
<td>Anaerobic digestion</td>
<td>0.01–0.095 mA</td>
<td>-</td>
<td>[137]</td>
</tr>
</tbody>
</table>

4. MFC-Based Biosensors for BOD Detection

Biochemical oxygen demand (BOD) is a well-known essential parameter for assessing water quality. Concretely, a five-day BOD test method (BODs) has typically been used as a standard method to determine biodegradable organics concentration in wastewater [11,138]. The test consists in measuring the amount of dissolved oxygen (DO) before and after incubation of a water sample for five days at 20 °C [139]. This method is time and labor consuming, and requires strong experience to get reproducible results. In that sense, BOD assessment by MFC-based biosensing appears as a simpler alternative method, less time consuming, and with higher reproducibility and accuracy than a five-day BOD test. Hence, the use of MFCs for measuring BOD is being gradually introduced during the last few years. The BOD measurement in an MFC is based on the proportionality existing between the current efficiency of the cell (also known as Coulomb- or Faraday-efficiency) and the amount of oxidizable organic matter contained in the feedstock/fuel used to operate the MFC system [140].

Accuracy and reproducibility, fast response (rapid monitoring), long-term operational stability, and minimum maintenance service are the most important advantages of an MFC-based BOD biosensor compared with conventional ones [141]. For example, Kim et al. developed an MFC-based device for remote BOD detection displaying over 5 years of stable current generation [118]. Temperature, pH, conductivity, and inorganic solid content have been reported to significantly affect the sensitivity of the sensor. Nevertheless, there are many other critical factors affecting the stability and sensitivity of
MFC-based biosensors for BOD monitoring, such as the dissolved oxygen concentration in the cathode chamber, external resistance, effluent flow rate, and any other factor, as long as it will influence the electricity generation of the MFC [30,48].

Restricted diversity of bacteria and organic substances present, as well as low metabolic rates, are the main disadvantages of MFC-based BOD biosensors [15,142]. Investigations addressed to identify versatile and highly active electrogenic microorganisms, capable of effectively oxidizing various types of organic substances, is currently considered as the most viable approach to enhance the performance and scope of MFC-based sensors for BOD detection [143].

BOD control is of particular interest for the monitoring of microbial activity and pollutants in groundwater [144]. As most of the monitoring approaches are often costly, time consuming, and not applicable to the subsurface environment [145], MFC BOD sensors offer rapid, simple, non-invasive, and cost-effective solutions. With this aim, Zhang et al. designed a novel submersible microbial fuel cell [131]. The cell was used as a self-powered sensor for in situ monitoring of BOD and microbial activity of groundwater. Using real contaminated groundwater, the cell detected microbial activity and BOD in less than 3 hours, with deviations ranging from 15% to 22% and 6% to 16%, respectively.

More recently, Kharkwal et al. developed an MFC-based BOD sensor with long-term stability using MnO$_2$ catalysts [146]. Specifically, manganese dioxide was used as a novel, innovative, and low costing cathode to reduce MFC production costs, aiming towards possible scale-up applications. The cell was tested using both sodium acetate solution and real domestic wastewater. BOD values predicted by the biosensor were in agreement with the BOD$_5$ values, with slight variations in the range from 3% to 12%. The MFC BOD biosensor at issue was demonstrated to be stable for over 1.5 years.

5. MFC-Based Biosensors for Water Toxicity Detection

Detection of toxicity in water is a crucial parameter to determine necessary actions for providing safe water within the appropriate degree of quality for consumption by humans, animals, and crops. To this effect, MFCs appear as appropriate sensitive systems, since any toxicant present in the aqueous feedstock will affect the metabolic activity of microbes, and therefore the rate of substrate intake, which is, as already mentioned above, directly related to the current output of an MFC. Therefore, any change in the presence and content of toxicants in fluent water can be easily detected by monitoring the perturbations in the electric current generated by MFCs [128,147], reducing the time and costs (personal, reactants, and analysis equipment) compared to conventional methods [148].

Among the most significant advances in the last 10 years is the simple and planar silicon-based miniaturized MFC, developed as a prompt response toxicity biosensor by Dávila and co-workers in 2011 [149]. Regardless of the biosensing application, maximum power density of about 6.5 $\mu$W/cm$^2$ was reported to be provided by the silicon-based MFC.

Eventually, performance and sensitivity to different toxicants in an MFC-based toxicity sensor strongly depends on the type of electroactive microbes used in the cell. Therefore, the selection of microorganisms with specially enhanced sensitivity to specific toxicants is critical to design appropriate devices according to the required monitoring needs.

6. Conclusions

This contribution clearly illustrates the potential of MFCs in the field of sensors and biosensors, also attracting researchers’ interest all over the world. MFC’s power output is known to be low in comparison with other electricity energy sources. However, MFCs can be utilized as an effective, sustainable, and long-term source of power in low-power electronic equipment, such as remote sensors. MFCs can also be considered as self-powered biosensors for monitoring BOD, DO, and toxicity in water nowadays, due to the high sensitivity demonstrated to those parameters. Rapid response time, low-cost operation, and possibilities to be self-powered are some of the remarkable advantages of the mentioned devices with high promise for extending applications.
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