# Chapter 14
# Current Applications and Future Perspectives of Microbial Fuel Cell Technology


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**Abstract** This chapter aims to discuss the current and potential applications of microbial fuel cells (MFCs), a suitable technique for energy harvesting. In the last few years, MFC technology has been extensively investigated due to its capacity for wastewater treatment with simultaneous generation of bioelectricity, with many efforts devoted to increasing the efficiency of these devices. Although their practical implementation remains a challenge, the scope of application has been expanded to several fields in which they have achieved encouraging results. Among the drawbacks, the scaling-up of MFC systems poses issues for large installations. The strengths and limitations of these bioelectrochemical devices are analyzed for their potential application in terms of electricity generation at large scale and power supply to small electronic devices, municipal and industrial wastewater treatment, metal removal, water decolorization, added-value chemical production, and biosensing. Several strategies proposed in the literature for the scaling-up of the technology are also analyzed.

**Keywords** Microbial fuel cells · Bioenergy · Wastewater treatment · Scaling-up · Persistent pollutant removal · Chemical production · Sensing

## 14.1 Introduction

Bioelectrochemical systems (BESs) have gained great attention for multiple applications in the last few years, including power generation, water treatment, production of chemicals, sensing, and desalination. BESs can be classified according to the biocatalysts employed into microbial and enzymatic systems. The first type can be

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further categorized into microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial solar cells (MSC), and microbial desalination cells (MDCs) (Shemfe et al. 2018; Bajracharya et al. 2016). Among them, MFCs have been widely studied over the last decade, which has translated into an exponential rise in the number of scientific publications on these devices. Although the concept was presented for the first time in 1911 by Potter (1911), it was only until the early 2000s when the interest for these green devices really began to spread among the scientific community (Santoro et al. 2017; Zhou et al. 2013).

MFC devices exploit microbial metabolism to transform the chemical energy of a given substrate into electricity. In this respect, the nature of substrates that can be employed for power generation varies from pure organic compounds to waste materials, which enables obtaining a twofold benefit, waste treatment or valorization with simultaneous electricity generation. Bacteria oxidize the organic matter in the anode chamber, generally under anaerobic conditions, which implies a low potential reaction, releasing protons and electrons in the process. The separator allows protons to be selectively transferred to the cathode, while electrons are led through an external circuit in order to obtain an electrical current. In addition, the cathodic reaction consists of the reduction of oxygen, a high redox potential reaction in which oxygen combines with the protons and electrons resealed in the anode (Bajracharya et al. 2016). Nevertheless, the configurations of MFCs reported in the literature are very diverse, with multiple set-up options. These include separator-less devices, double-chamber systems, with anodic and cathodic compartments and single-chambered fuel cells with the cathode exposed to the air. Moreover, they can be set up in a wide variety of designs, including cylindrical and rectangular shapes and self-stack and multitubular assemblies (Zhou et al. 2013). Other specific configurations are intended for certain functionality requirements such as submersibility (Hernandez-Fernandez et al. 2015). Figure 14.1 displays the two general configurations of MFC systems.

Despite the progress made in the last few years and the potential of MFCs, the real implementation of the technology is still very limited. In this regard, there are still remaining challenges needing to be addressed to overcome important limitations and encourage its deployment. Among them, it is necessary to develop high-efficiency anodes to enhance microorganism kinetics, optimize biofilm development, and improve electron transference processes between biocatalysts and the electrodes, especially when waste substrates are employed (Santoro et al. 2017). In such cases, Coulombic efficiencies and power densities are generally low. Another bottleneck of the technology is the cathodic oxygen reduction reaction (ORR) due to the low kinetics and high overpotential. While noble materials such as platinum offer high catalytic activity, its high cost has promoted the search for other efficient and affordable catalysts that can be used as an alternative at the cathode. In this sense, many options including carbon nanomaterials and transition metal oxides have been investigated (Ben Liew et al. 2014).

Apart from electrode components, the separator is another key component with a central role in determining MFC performance. Its optimization is very important and poses a challenge when the system has to be scaled up. As already mentioned,

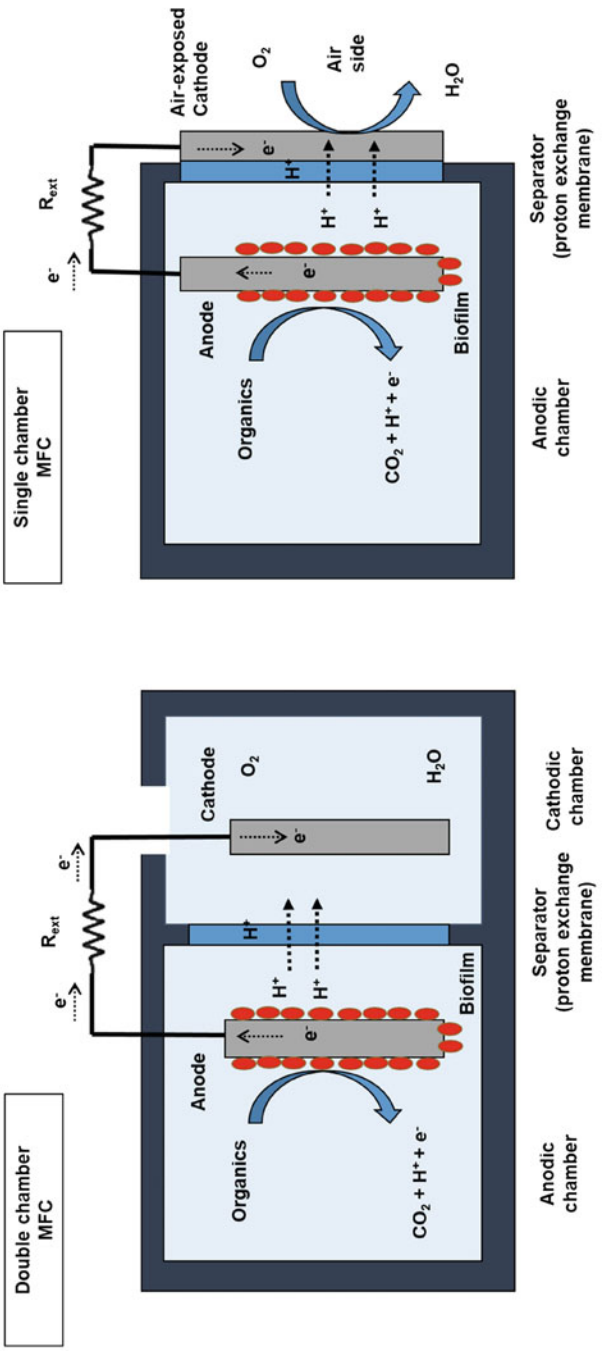


**Fig. 14.1** Schematic representation of single- and double-chamber MFC systems

separator-less configurations have also been developed but, in such cases, and due to undesirable diffusion phenomena between anode and cathode compartments, the efficiencies are even lower than in standard configurations containing a separator. Nafion® is the most often used separator in MFCs, however, as in the case of platinum as a standard catalyst, Nafion® membranes offer several disadvantages such as high cost and oxygen crossover issues. Thus, a large number of potential alternative options have been studied to replace Nafion® membranes, including cation, anion, and bipolar membranes, glass fibers, ultrafiltration membranes, porous fabrics materials, ionic liquid-based membranes, and ceramic separators, among others (Santoro et al. 2019; Logan 2010).

As seen, most of the components and the processes in MFCs are being subjected to intensive research in order to improve their performance with the ultimate objective of bringing this technology into the market for real implementation and commercialization. Nevertheless, the potential of the technology is very high and this has resulted in a diversification of the fields in which it can be applied. This chapter reviews the applications of MFC technology, which in turn depends on the scale of the devices. These applications range from urban and industrial wastewater treatment with simultaneous bioelectricity generation, to sensors development and chemical production.

## 14.2 Microbial Fuel Cell Applications

MFCs constitute a versatile technology with multiple applications. The most obvious is the generation of bioelectricity by exploiting organisms' metabolism from a suitable substrate. However, these devices offer an ideal framework for other uses including sensing, chemical recovery, feedstock treatment or, more specifically, removal of persistent pollutants (Greenman et al. 2019; Sawasdee and Pisutpaisal 2014). Also, in terms of versatility, there are different strategies when scaling up these devices according to the required applications. MFCs can be employed for large-scale purposes or, alternatively, can be miniaturized for small-scale uses. In both cases, multiple units can be stacked, for instance, to increase the level of power density, water treatment capacity, or voltage response. In addition, they offer modularity in terms of component design and connections between units (Logan et al. 2015). As it is to be expected, the design and configuration of MFC devices will have to be selected according to the end-use requirements. Following, the main applications reported so far for MFC technology are described.

### *14.2.1 Power Generation and Supply*

As mentioned above, protons and electrons are generated at the anode as a result of the metabolism of substrates performed by electroactive microorganisms. While a

final high-potential electron acceptor is needed at the cathode in order to complete the circuit, a suitable electron carrier is required at the anode chamber to transfer the electrons released in the oxidation process to the anodic electrode. Certain bacteria such as *Shewanella, Geobacter*, and *Rhodoferax* species are capable of generating electricity from several organic compounds. Electrons can be released in these bacteria through nanowire-shape pili, cell membranes, or by molecular carriers (Yamasaki et al. 2018). At the anode, bacteria attach to the electrode material and colonize the available surface developing a biofilm. Thus, in principle, electrons can be directly transferred from the substrate to the anodic electrode through the conductive biofilm, in the absence of a redox chemical mediator, which can pose toxic issues to bacteria populations and can increase the operational costs (Hernandez-Fernandez et al. 2015).

One of the advantages of MFCs is the great variety of organic substrates that can be effectively exploited to generate electricity. Especially, the use of urban and industrial wastewater effluents underlines the benefits of the technology due to the possibility of waste valorization for internal energy recovery and organic matter removal. Many works have already shown the possibility of using a considerable range of industrial wastewaters from different sources as feedstock. They include food processing, brewery, distillery, dairy, and agro wastewaters, among other options (Chen et al. 2014; Tharali et al. 2016; Ogugbue et al. 2015; Pandey et al. 2016). Apart from wastewater coming from urban or industrial facilities, other types of waste feedstocks such as leachate landfill (Li and Chen 2018) and human urine (Ieropoulos et al. 2012) have shown their potentiality for energy generation in MFCs.

The power densities achieved in MFCs can greatly depend on the type of materials that form the devices, on the substrate and on the scale employed. Conversely, it is necessary to differentiate from single units and stack MFC devices, which are formed by several units. The miniaturization of MFC devices can lead to higher power densities; however, the net power in a single unit would be very low due to the limited substrate capacity and the assembly of multiple units would be required for higher power supply. Generally, the highest power densities have been obtained with volume capacities below 30 mL. For example, optimized configurations with advanced strategies have reached maximum power densities of almost 7 W $m^{-2}$ (normalized to anode surface) with an anode volume of 2.5 mL (Fan et al. 2007) and of over 1.5 kW $m^{-3}$ (normalized to volume) working with 12 mL of anode capacity (Fan et al. 2008). When it comes to the order of liters, power densities are usually lower than 35 W $m^{-3}$. For instance, a system with a capacity of 250 L formed by two MFC modules outputted 0.5 W $m^3$, which can be considered relatively low (Feng et al. 2014). This would suggest that the scaling-up of MFCs is problematic and challenging, and thus the shift of the capacity from the order of millimeters to the order of liters does not necessarily translate into an increase in power density.

The main limitations regarding the scaling-up of MFCs are associated with the rise in internal resistance because of (1) potential losses given by the increasing distance between electrodes, (2) increasing separator resistance, and (3) the

resistances of the solutions in the anodic and cathodic compartments. With the objective of enhancing power performance, it is required to maximize the ratio between available electrode surface area and MFC volume capacity and to minimize the spacing between the anode and the cathode while developing high efficiency and innovative materials for the components (Santoro et al. 2017; Logan 2010; Wei et al. 2011).

The recent trends for the design of large-scale reactors are based on the stacking and modularization of single MFC units. Considering voltage output, a single reactor is limited by a pair of electrodes, and the voltage is generally lower than 0.8 V. MFC units can be assembled in parallel or in series mode in order to increase current density or voltage output, respectively. Nevertheless, several issues have been also reported for the operation of MFC stacks, including voltage reversal, additional contact voltage losses, or fuel starvation. Under continuous operation, other problems can arise due to electrical and hydraulic connections. The connection of multiple MFCs in continuous mode requires to share in-flow and out-flow streams. Some works have addressed this aspect by measuring the voltage loss for different connection modes in an MFC stack, finding that when the MFCs are connected both electrically and hydraulically at the same time, the voltage output is up to 36% lower than when they are electrically connected but hydraulically isolated (Zhuang and Zhou 2009). This implies that it would be preferable to separately feed the MFC of a stack, with single recirculating loops for individual units, which is not considered a feasible option towards the large-scale implementation of MFCs in terms of wastewater treatment. In fact, it has been reported that cascade operation with the outlet of a unit being connected to the inlet of the following unit can provide higher COD removal rates. To sum up, even the modularization of MFC can pose several challenges for large-scale plants.

There are several attempts of large-scale MFC operation. One of the recent examples consisted of a plant with a total capacity of 1 $m^3$, which was set up with 50 modules (Liang et al. 2018). When artificial wastewater was employed, the power output was as high as 125 W $m^{-3}$ or equivalently 7.6 W $m^{-2}$. In the case of municipal wastewater, the maximum power decreased down to 60 W $m^{-3}$, equivalent to 3.6 W $m^{-2}$. As it can be inferred, the use of real and complex substrates can cause a decrease in power performance. Other examples include a 96-module MFC configuration of 200 L of capacity that was capable of supplying enough power for a 12 V water pump (Ge and He 2016). Other pioneering attempts to set up modularized MFCs of 1 $m^3$ fed with brewery wastewater were unsatisfactory due to the limited current generated and problematic operation (Logan 2010).

Apart from large-scale applications, MFC has proven to be capable of supplying power to small electronic devices. The energy generated in MFCs can be employed for powering electrochemical sensors and small-scale telemonitoring systems such as wireless sensor networks (WSNs) to transmit data gathered by sensors to a remote location. If the sensing systems are intended for environmental monitoring, MFCs can represent a green opportunity to power these systems with no impact (Yang et al. 2014). Usually, WSN devices require a minimum of 3 V and given the low outputs of MFCs in terms of voltage and currents, it is necessary to store the energy

generated in components such as capacitors that can then provide power at the required amount. This approach has been proved successful for wireless data transmission (Shantaram et al. 2005).

Floating MFCs are an attractive option to harvest energy in natural water bodies. This configuration usually includes a floating cell structure with the electrodes physically separated by an electrically isolating material (Huang et al. 2012). These floating devices can be placed, for example, in lakes or rivers to power remote environmental sensors. Recently, Schievano et al. (2017) operated floating MFCs in Italian ponds for over a year. Each of the devices installed generated a cell potential of up to 0.8 V and power outputs of up to 3.5 mW. The floating systems, displaying a simple design, were capable of powering LED lights and remote data transmission devices, showing the viability of using low power density from MFCs (40 mWh/day) to power environment sensors.

In addition to using external devices coupled to MFCs for energy storage, it has been proved that the anode and the cathode in MFCs can be utilized as negative and positive electrodes for the design of an inner supercapacitor to increase power. This type of design is known as supercapacitive MFCs and is capable of generating higher current pulse discharges and power than conventional devices (Santoro et al. 2019, 2016). The highest performances provided by single MFCs have been achieved in these supercapacitive designs. For example, high-voltage cathodes made of bilirubin oxidase outputted a power performance of 19 mW with pulse currents of up to 45 mA (or 84 W $m^2$ per cathodic surface area) (Santoro et al. 2016). Supercapacitive operation has also been used to increase the power of ceramic MFCs. These MFC types represent a promising option for scaling-up, due to the properties of ceramic separators, which include very low cost, structural strength, significant stability, and modularity, in comparison to other separator options (Yousefi et al. 2017). Very recently, a supercapacitive MFC stack constructed with low cost ceramic separators and using a Fe-N-C catalyst based cathode was capable of generating around 37 mW (stack based on 28 MFCs and 1 L of total capacity, power density equivalent to 36.9 W $m^{-3}$) (Santoro et al. 2019).

Several proof-of-concept works have employed MFCs to power robots. Artificial agents (called EcoBots I and II (Ieropoulos et al. 2005)) have been directly powered by MFCs. Advanced designs presented by Leropoulos et al. (Ieropoulos et al. 2010) comprise self-sustainable robots that can complete a thermodynamic cycle of ingestion–digestion–egestion (called EcoBot III). The design of this artificial agent demonstrated the autonomy of MFCs as a power source and showed that miniaturization of MFCs could represent a real option for scaling-up. This research group has also intensively investigated the use of urine as a substrate in MFCs. As mentioned, the versatility of MFCs allows them to be operated under a wide range of waste types, including human urine, which has shown to be capable of generating electricity enough to power mobile phones and for LED internal lighting (Sawasdee and Pisutpaisal 2014; Walter et al. 2017).

### *14.2.2 Wastewater Treatment*

MFCs can be fed with biodegradable substrates ranging from municipal and industrial wastewater to landfill leachates and other effluents of waste nature. In the first studies on the technology, synthetic wastewaters have been usually employed to investigate MFC performances with the objective of understanding the working principles in these devices and optimizing the operational variables. Real waste effluents can present complex matrixes and greatly disfavor efficiency in comparison to model effluents. However, in order to reach the practical implementation of MFCs, many works have already addressed the operation with waste substrates (Gude 2016; Ortiz-Martínez et al. 2015).

The removal percentage of organic matter from the feeding substrate is one of the main parameters that are usually monitored in MFCs. Removal rates of over 90% can be achieved depending on the hydraulic retention time (HTR), substrate concentration, temperature, and fuel cell design. The nature of the substrate has a strong influence on bacterial populations and biofilm development, and thus on power and current density and Coulombic efficiency. This last parameter is of special relevance when electrical generation is the main purpose since it is calculated as the rate between the real charge transferred to anode surface and the theoretical maximum charge considering the complete substrate oxidation into electricity. In this sense, the total COD removal in MFCs can be due to electrogenic pathways that generate electricity from the organic matter or due to alternative fermentative mechanisms not contributing to the generation of energy, since exoelectrogenic bacteria compete with other microorganisms for the substrate. As a representative case, the work of Jahdav et al. (2009) achieved a 90% of COD removal in MFCs after 200 h of operation with synthetic wastewater, but with very low Coulombic efficiencies ($\leq$1.5%).

Conventional organics such as acetate or glucose have been usually employed to feed MFCs inoculated with electrogenic microorganisms. There are many examples in the literature employing these compounds, and they can also provide different efficiencies. Chae et al. (2009) compared the performance of acetate, glucose, butyrate, and propionate in two-chambered MFCs inoculated with anaerobic sludge for over a year of operation. Among them, acetate yielded the highest Coulombic efficiency CE (over 72%), while butyrate, propionate, and glucose offered efficiencies below 40%. In the case of glucose, the yield was as high as 15%, due to its fermentation by non-electricity generating bacteria that were present in the inoculation sludge. In general, it has been proved that the performance of MFCs when using complex waste substrates can be reduced fivefold when compared to the use of simple substrates (Gude 2016).

In addition to wastewater treatment in terms of COD reduction, MFCs are investigated as a means of removing different types of pollutants in wastewater streams, such as metals and persistent pollutants like xenobiotics.

#### 14.2.2.1 Municipal and Industrial Wastewater Treatment

The average energy consumption in activated sludge processes for domestic wastewater treatment amounts to 0.3–0.6 kWh $m^3$. In wastewater treatment municipal plants, energy is mostly consumed in aeration (40%), sludge treatment (30%), and other processes such as additional pumping (30%) (Ali et al. 2018). Municipal wastewaters can contain over 9 times more energy needed for their treatment (Heidrich et al. 2011). The possibility of electricity recovery with simultaneous wastewater treatment in MFCs has raised high expectations on this technology to replace conventional wastewater treatments to reduce energy costs (Li et al. 2014). Another benefit of MFCs is that these systems produce much lower sludge in comparison to activated-sludge reactors (ASR). In a recent work, Asai et al. (2017) specifically addressed the comparison between the total amount of waste sludge generated in MFC systems and that produced in an ASR (respective volume capacities of 1.5 L). The daily production of waste sludge in MFCs was found to be much lower in comparison to the ASR when both systems were fed with artificial domestic wastewater and also with artificial industrial wastewater, with respective COD values of 500 and 1500 mg $L^{-1}$. Between 80 and 100 operation days, the daily production of waste sludge domestic wastewater yielded around 10 mg $L^{-1}$ $D^{-1}$ in the MFC and 50 mg $L^{-1}$ $D^{-1}$ in the ASR. In the case of industrial wastewater, the yields were about 35 mg $L^{-1}$ $D^{-1}$ for the MFC and 90 mg $L^{-1}$ $D^{-1}$ for the ASR. Despite these promising advantages, MFCs are yet to be further studied to address the limitations that hinder its practical implementation, mainly low power densities, material costs, and scaling-up for high treatment capacity. As already noted in the previous section, the maximum power outputs achieved in MFCs (with volume capacity in the order of liters) are several watts per cubic meter.

Many works have addressed the treatment of municipal wastewater in MFC devices, including some pilot-scale plants in real urban treatment plants. Zhang et al. (2013) constructed an MFC of 4 L of treatment capacity to be installed in a real plant in Milwaukee (USA) without temperature control (temperatures varying from −10 °C to 36 °C) and fed with primary effluent without further pretreatment. The total maximum COD removal was 70%, but at high HRTs (11 h) and in favorable conditions of warm temperatures. MFC operation and COD removal were severely affected by cold temperatures. In terms of normalized energy recovery (NER), the maximum output achieved was 0.003 kWh $kg^{-1}$-COD. Jiang et al. (2011) constructed a reactor of 20 L of capacity using primary effluent in continuous mode characterized by COD values in the interval of 100–500 mg/L. In this case, COD removal efficiency was 66% for an HRT of 5 h with a concomitant power density of up to 0.17 W $m^{-3}$, equivalent to 0.003 kWh $kg^{-1}$-COD. As mentioned before, a modularized pilot plant with a total capacity of 1 $m^3$ was set up and run for 1 year (Liang et al. 2018). In terms of wastewater treatment, COD removal rates of 70–90% were achieved for municipal wastewater with COD concentrations below 50 mg $L^{-1}$ and with maximum energy recovery of 0.005 kWh $m^{-3}$. The total construction costs of the plant amounted to 36 kUSD.

Also recently, an MFC formed by four individual cells with 45 L of total volume capacity was installed in a full-scale plant in Bottrop (Germany) (Hiegemann et al. 2016). The most favorable results were attained for 22 h of HRT, with respective removals rates for TSS, nitrogen, and COD of 40, 28, and 24% and a Coulombic efficiency of almost 25% (the initial value of COD was 118 mg/L). While the removal rate of COD achieved can be considered lower in comparison to other studies, the removal of nitrogen was unexpectedly high. Conversely, TSS removal was due to hydrolysis processes that convert the particulate matter into a soluble substrate. The NER was 0.36 kWh $kg^{-1}$-COD. With these results, simulated scenarios for full-scale MFCs implemented in the plant provided over 4% of total energy savings.

While the scaling-up of MFC systems still remains a challenge for their integration in wastewater treatment plants, many attempts have been made to study the possibility of treating wastewater originated in industrial facilities, which would require smaller scale installations. A wide range of industrial wastewater types has been assessed in MFCs, including effluents coming from brewery, distillery, food, dairy, cheese whey, starch processing, swine, paper, pharmaceutical, and refinery industrial facilities (Gude 2016). In comparison to municipal wastewater, the use of this type of effluent can offer significantly higher amounts of organic matter.

Food processing wastewaters are rich in organic constituents such as carbohydrates or organic acids, which can be easily biodegraded by bacteria. With this type of wastewater, significant COD removal rates and Coulombic efficiencies (up to 70%) have been reported (Mohamed et al. 2017). Mansoorian et al. (2016) evaluated the treatment of industrial wastewater from a protein food industry in dual-chamber MFCs of 1.5 L of capacity (Mansoorian et al. 2013). This type of effluent was characterized by an initial COD loading of around 1900 mg $L^{-1}$ and a $BOD_5$ loading of around 1300 mg $L^{-1}$. The system was operated with feeding rates from 0.2 to 1.6 mL $min^{-1}$. In this case, it was possible to achieve removals rates of COD and $BOD_5$ of up to 86 and 79%, respectively. They also monitored other common parameters in water treatment, observing removal efficiencies for TSS, VSS, and $SO_4$ of 68, 62, and 30%, respectively, and removal rates for $NH_3$ and P of 73 and 18%. Some of these elimination mechanisms in MFCs have not been fully understood yet. According to the authors, the decrease in the content of TSS and VSS could be explained by the action of biologically catalyzed mechanisms that degrade complex organic matter in colloidal form. Conversely, some microorganisms are capable of employing sulfate as the final electron acceptor, converting it into sulfide. Interestingly, the removal of ammonium was very high in a system operated in anaerobic conditions, implying that anaerobic oxidation, denitrification mechanism, and other removal pathways can occur in MFCs with bioelectricity generation. The reduction of the content of phosphorus was not as impressive. In this case, the conversion of organic phosphorus into orthophosphate can also take place (Mansoorian et al. 2013; Luo et al. 2002).

Brewery wastewaters have shown to be a very suitable feeding effluent for MFCs. They usually display high levels of COD (1000–5000 mg $L^{-1}$) (Gude 2016; Wen et al. 2010a). High removal efficiencies from 79% to 85% have been achieved with

Coulombic efficiencies of up to 38% and power densities of 11 W $m^3$ in small capacity MFCs (Wang et al. 2008). The removal efficiencies reported for this type of wastewater (95%) can be even higher when using high HTRs (>14 h) (Wen et al. 2010b). In distillery industries, spent wash is produced in the alcohol production process, generating recalcitrant wastes with high COD and BOD contents that can be used in MFCs. In this case, COD removal efficiencies of 60–80% have been reached (Pallavi and Udayashankara 2016).

Other types of substrates can present more complex compositions. For example, livestock industry wastewater can offer extremely high contents of organic material (up to COD loadings of $10^5$ mg $L^{-1}$), but they can also contain high amounts of nitrogen-rich compounds and other organic materials that are difficult to be biodegraded (e.g. cellulose). On its part, dairy wastewaters are composed of carbohydrates, proteins, and fats, and they have also been effectively used in MFC devices. Mohan et al. (2010) achieved high substrate degradation (COD removal of over 95%) together with high removal of proteins (78%) and turbidity (99%) in batch mode.

MFCs are also capable of treating wastewater from the petroleum refinery industry, which can contain a wide variety of chemicals (e.g. sulfides, cyanides, benzenes, ammonium compounds, among others). Along with significant COD removal, Guo et al. (2016) reported oil removal rates of 66–84% from refinery wastewater in MFC using granule graphite and activated carbon in the anodic chamber. Aromatic organics, saturated hydrocarbons, and volatile phenols were the main pollutants present in the wastewater employed. The overall pollutant removal mechanism was described as a combination of adsorption on the carbon materials and by the action of microbial metabolism.

Table 14.1 summarizes the main results obtained with different types of industrial wastewater (COD removal rates and power density).

#### 14.2.2.2 Specific Compound Treatment

Under the perspective of water treatment, the applications of MFCs have been extended to the recovery or removal of heavy metals. These species can be frequently present in effluents coming from industries devoted to petroleum refinery, metal plating, or the production of pesticides and paint. Moreover, ligands such as ammonia can form stable complexes with many metal ions, which make them more difficult to be recovered. The conventional techniques based on chemical, physical, and biological methods for the treatment of heavy metals require high energy consumption and can be ineffective when metal concentrations are low (from 1 to 100 mg $L^{-1}$). MFCs have shown to be an alternative for metal energy removal. In the anode, bacteria can reduce ion metals, which are then deposited. Moreover, it is possible to use compounds with high redox potential as electron acceptors instead of oxygen at the cathode; several ion metals can be used for this purpose (Ezziat et al. 2019; Mathuriya and Yakhmi 2014). This last approach is the most frequent, generally implying the use of double-chamber MFCs. The possibility of removing

**Table 14.1** Wastewater types used in MFCs for treatment and energy generation (power output included as reported, i.e. normalized to anode area or volume)

| Wastewater type | Maximum COD removal (%) | Maximum power performance | Ref. |
|---|---|---|---|
| Food processing | 60 | 338 mW $m^{-2}$ | Mohamed et al. (2017) |
| Brewery | 85 | 12 W $m^{-3}$ | Wang et al. (2008) |
| Distillery spent wash | 80 | 26 mW $m^{-2}$ | Liu et al. (2004) |
| Dairy | 95 | 1.10 W $m^{-3}$ | Venkata Mohan et al. (2010) |
| Refinery | 84 | 330 mW $m^{-3}$ | Guo et al. (2016) |
| Paper production | 80 | 60 mW $m^{-2}$ | Velasquez-Orta et al. (2011) |
| Cheese production | 80 | 3.2 W $m^{-3}$ | Kelly and He (2014) |
| Slaughter house | 93 | 578 mW $m^{-2}$ | Katuri et al. (2012) |
| Swine wastewater | 83 | 45 mW $m^{-2}$ | Min et al. (2005) |
| Pharmaceutical | 78 | 2.2 W $m^{-3}$ | Velvizhi and Venkata Mohan (2011) |

heavy metals including chromium, copper, iron, cobalt, vanadium, or manganese, among others, has been already proved in MFCs (Ezziat et al. 2019).

When using the anode for metal removal, heavy metals pose toxic issues to the bacterial populations inoculated. Thus, maximum tolerable concentrations need to be determined to ensure bacterial activity. For instance, high removal rates have been achieved for heavy metals such as Cd and Zn (90% and 97%, respectively) in the anode of single-chamber MFCs with simultaneous energy production (3.6 W $m^{-2}$) (Abourached et al. 2014). In this case, the maximum tolerable concentrations were in the order of 200–400 μM. The strategy involved the use of a low amount of sulfate and lactate in the electrolyte to remove metals via sulfide precipitation and biosorption. It is worth noting that heavy metals removal can be accomplished with simultaneous COD removal and power generation. Recently, yields of ion removal of 72% from synthetic hydraulic fracturing flowback water have been reported along with a COD decrease of over 90% and power generation of around 2600 mW $m^{-3}$.

As mentioned above, the principle of metal removal when treated in the cathode is based on their use as electron acceptors. Several examples include the reduction of Cu(II) into Cu(0) with very high efficiencies (Ter Heijne et al. 2010), the removal of Cr(IV) at concentration of 200 mg $L^{-1}$ with simultaneous energy production (Sahinkaya et al. 2017), or the removal of mercury ($Hg^{2+}$) through precipitation in the presence of $Cl^-$ followed by electroreduction at the cathode (Wu et al. 2017). The number of works addressing the removal of heavy metals in MFCs at the cathode is relatively high and reveals the prospects of the technology to accomplish this objective (Ezziat et al. 2019).

Other works have addressed the in situ remediation of rivers to remove organic matter or heavy metal species. The operation of lab-scale sediment MFCs with anoxic cathodes showed the possibility of reducing Ag(I), Cu(II), and Hg(II) with efficiencies higher than 90% after 60 days operation (Wu et al. 2017). Metal complexes can be even more stable and difficult to be removed, but Zhang et al. (2012) demonstrated the possibility of eliminating copper-ammonia with an efficiency of 96% after 12 h from solutions in the cathode chamber containing concentrations of this compound of 13.55 mg $L^{-1}$. In the process, $Cu_2O$ and Cu crystals were deposited over the surface of the cathode.

While many studies have proven the feasibility of MFC metal removal from aqueous effluents, very few have actually dealt with the further separation of the reduced metallic products that can be deposited over the MFC components, such as the electrodes. This can be a challenge when using electrodic materials like carbon cloth, graphite, or activated carbon, from which metal separation is difficult to be performed. Conversely, the use of alternative electron acceptor species to oxygen can lead to increasing power generation and ultimately to expanding the scope of application of MFC technology

Not only metal ions can be treated in MFCs, but other pollutants such as nitrates have also been used as terminal electron acceptors. For example, nitrate can be reduced to $N_2$ via denitrification (Jia et al. 2008). This strategy can be extended for the removal of other compounds like permanganate (You et al. 2006) and persulfate (Li et al. 2009).

Finally, MFCs can serve as a means for azo dye decolorization with simultaneous energy recovery. This process can be performed in the anodic or the cathodic chamber. Dyes are xenobiotic compounds whose colors are due to the presence of the azote bond (–N=N–). Wastewater effluents from textile industries present this type of persistent disposal causing serious toxicity issues. The degradation of dye in MFC anodes has been linked to oxidative mechanisms performed by bacteria instead of sorption by dead and live cells. Alternatively, if dyes are used in the cathode, they can play the role of final electron acceptors while water is decolorized (Ilamathi and Jayapriya 2018). The interest in this application of MFC technology has greatly increased in the last years. Azo dyes such as acid orange 7, Congo red, Alizarin yellow R, thionine based textile dyes, or reactive blue 160 have been successfully removed from water in MFC devices, with removal efficiencies between 73 and 96% (Ilamathi and Jayapriya 2018; Ding et al. 2010; Cui et al. 2014), depending on the dye type, initial concentration, and operation time, with simultaneous power generation.

### *14.2.3 Biohydrogen and Other Chemicals Production*

The bioelectrochemical reactions taking place in MFCs offer a framework to perform different reaction pathways for the production of value-added chemicals. This approach usually requires the use of hybrid systems in which MFCs are integrated.

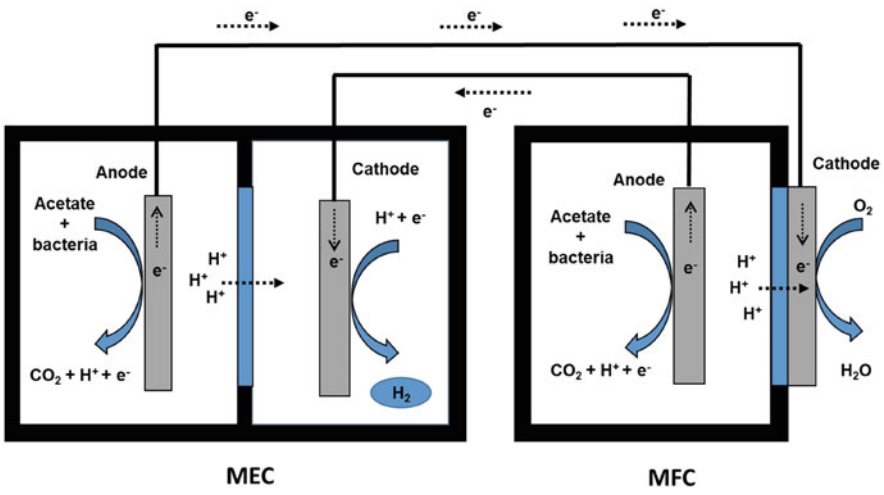


**Fig. 14.2** MFC-MEC coupled system for hydrogen production

Microbial electrolysis cells (MECs) consist of a modification of MFC systems in which the objective is to produce hydrogen, requiring an external voltage source to perform the process. Liu et al. (2005) showed that it is feasible to produce hydrogen at the cathode by supplying additional potential (>0.2 V) to that naturally generated by bacteria. The external voltage requirement in an MEC device is notably lower in comparison to that required in electrolysis processes (1.8 V in principle). These authors achieved production rates of up to 9 mol-$H_2$ per mol-glucose by applying external voltage.

However, the coupling of pure MFCs with MECs devices allows avoiding the necessity of using external power supply for $H_2$ production as described in Fig. 14.2. In this hybrid system, an MFC unit is utilized as an energy source for the second one. Sun et al. (2008) reported a coupled MEC-MFC configuration to produce $H_2$ with no other external electric power source, achieving 1.60 mol-$H_2$ per mol-acetate.

Another route for hydrogen production consists of the promotion of acidogenic bacteria in the anaerobic digestion taking place in MFC anodes (Chandrasekhar et al. 2015). In the anaerobic digestion, the first stage comprises hydrolysis of large organic substrate to be transformed into small molecules. Subsequent acidogenesis converts them into short-chain compounds (e.g. ketones, fatty acids, alcohols), which can be transformed into $H_2$, $CO_2$, and $CH_3COOH$ (acetic acid) by the action of acidogenic bacteria. If not avoided, methanogenic bacteria can transform hydrogen into methane, which would be undesirable for this purpose. Thus, for hydrogen production, the boost of acidogenesis while inhibiting methanogenesis stage can help to produce hydrogen. This can be accomplished by heating and acid treatment to reduce the growth of methanogens while enriching acidogenic bacterial populations (Lao-Atiman et al. 2017).

Further efforts have been addressed to develop hybrid systems combining dark fermentation with MFCs and MECs. With this strategy, Wang et al. (2011) achieved to generate 0.48 $m^3$-$H_2$ $m^{-3}$ $day^{-1}$ (normalized to MEC volume). Further research efforts are required to enhance the efficiency of coupled MFC-MEC units by optimizing operational conditions (e.g. initial organic concentration, buffer conditioning for increasing conductivity, etc.) and through the development of highly efficient and low-cost component materials (Zhang et al. 2019).

In addition to hydrogen production, other chemicals production processes have been implemented in hybrid MFC-MEC systems. Zhao et al. (2012) electrochemically reduced $CO_2$ into formic acid in the cathode of an MEC assisted by an MEC for external voltage supply, in a similar way as was described in Fig. 14.2 for hydrogen production. In this case, it is necessary to supply $CO_2$ to saturate the cathodic solution. Formic acid was produced at a rate of 21 mg $L^{-1}$ $h^{-1}$. The MEC system included a cathode electrode covered with multi-wall carbon nanotubes (CNTs) and tetraamino functionalized cobalt phthalocyanine with the purpose of reducing the overpotential of the $CO_2$ conversion into formic acid.

Other chemicals can be produced in MEC systems such as hydrogen peroxide and ethanol, in which extra voltage could be provided by MFCs. For instance, to produce hydrogen peroxide via the bioelectrochemical oxidation of organic matter in the anodic chamber coupled to the reduction of oxygen to hydrogen peroxide at the cathode, it is necessary an additional voltage supply of 0.5 V (Steinbusch et al. 2010). Also, Steinbusch et al. (2015) showed the possibility to reduce acetate into ethanol with biocathodes based on mixed cultures and by applying 0.55 V as external voltage. New chemical production routes may be developed in the future for hybrid MFC-MEC systems.

### *14.2.4 Biosensing*

Previously in this chapter, the use of MFCs to power wireless sensor networks (WSNs) has been mentioned. Nevertheless, these bioelectrochemical devices can also be employed as biosensors themselves. They have been employed for sensing water quality and toxicity, as well as for pH and temperature monitoring. MFCs could be implemented in natural environments and be operated online with minimum impact, offering a simple and fast response in testing assays for target water analytes. The principles of biosensing in MFCs lie on the fact that any disturbances of the metabolic pathways of the microorganisms can cause a change in the electricity generated in a single device, and therefore anodic biofilm can act as a bioreceptor, while the anode electrode would play the role of a transducer. Thus, changes in operational parameters such as the presence of specific compounds, pH, temperature, or conductivity can be correlated with changes in the MFC response. If needed, an amplifier can be added to obtain an easily measurable signal as displayed in Fig. 14.3 (Chouler and Di Lorenzo 2015; Pietrelli et al. 2016).

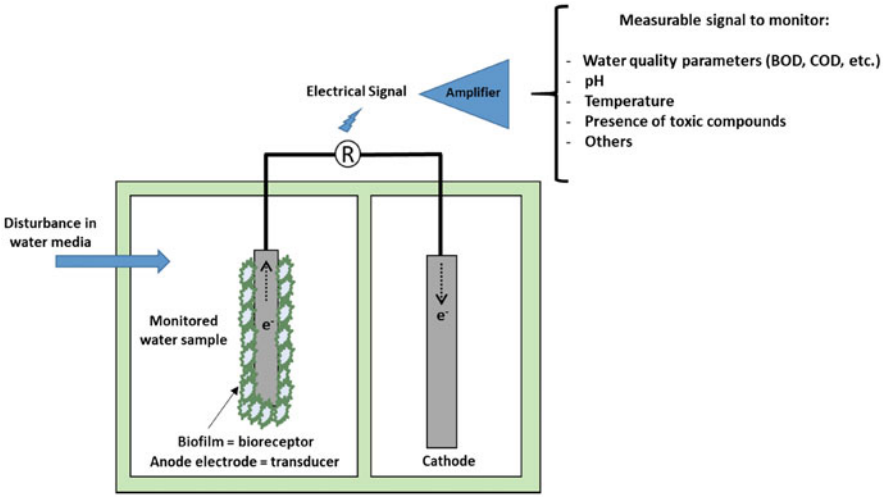


**Fig. 14.3** MFC systems as biosensor for water sample monitoring

The determination of biochemical oxygen demand (BOD) is usually performed through incubation tests, which can last up to 5 days. Within a certain range of concentration, the electrical signal obtained in an MFC can be used to determine the BOD in a feeding solution. In fact, the first application of MFCs as biosensor for BOD was already reported in 1977 before the interest for this technology would outburst in the earliest 2000s (Karube et al. 1977). In this early work, it was possible to measure the current generated as a proportional response to glucose-glutamic concentration up to 400 mg $L^{-1}$, which as the saturation value (corresponding to a current of 100 μA). In this regard, it is important to obtain a stable response from the system that can be correlated to the substrate concentration. Further efforts have been devoted to MFCs as biosensors for BOD determination within the 3–500 mg $L^{-1}$ range (Chouler and Di Lorenzo 2015; Di Lorenzo et al. 2009, 2014).

MFCs can also be applied for the detection of compounds of toxic nature in water media. The first attempt was reported for pollutants like pesticides, heavy metals (e.g. Pb and Hg), and polychlorinated biphenyl (PCB), with lower detection limits set at 1 mg $L^{-1}$ (Kim et al. 2007). The application of MFCs as biosensors was extended for the detection of other heavy metals (Liu et al. 2014) as well as for sulfonamides (sulfamethoxazole), antibiotics (sulfadiazine), and ammonia derivatives (chloramine B) (Patil et al. 2010). Depending on the specific compounds, the lowest concentration limits can vary from 0.01 μg $L^{-1}$ (for antibiotics such as sulfadiazine) to 0.16 mg $L^{-1}$ (for chloramine B).

Finally, MFCs can be utilized for the analysis of common parameters such as pH and temperature. The influence of pH in MFC performance is significant, since it can greatly affect ion concentrations, biofilm development, and membrane potential (Yang et al. 2014). Changes in current output of several orders have been correlated for pH shifts of up to 1 unit. By means of buffer solutions (e.g. phosphate, borax,

bicarbonate) it is possible to maintain pH and obtain stable current production. Thus, variations in pH can be correlated to MFC performance (Pietrelli et al. 2016; Ivars-Barceló et al. 2018). In the same way, another important factor influencing MFC responses is temperature, to which MFCs are very sensitive, especially in terms of compartment conductivities and microbial activity. This influence could be exploited for temperature sensing with MFC devices (Pietrelli et al. 2016).

## 14.3 Outlook

MFCs can convert chemical energy directly into electricity through oxidative and reductive reaction pathways with concomitant wastewater remediation. Intensive research on the technology in the last few years has opened the way to different applications in several fields. However, in order to advance towards large-scale applications and practical implementation, multiple limitations need to be overcome in the near future.

The main applications of MFC devices discussed in this chapter comprise power production at different scales, wastewater treatment, including municipal and industrial effluents, removal of specific and persistent pollutants and heavy metals, hydrogen production, and biosensing. Thus, one of the strengths of this technology is its versatility. Moreover, MFCs can be fed with many waste types ranging from urine to landfill leachate. Although the Coulombic efficiencies with this type of complex substrates are low, the removal rates of oxygen chemical demand that can be achieved are significant.

Among the biggest challenges for the deployment of MFC technology is the scaling-up for practical applications, with the objective of increasing the capacity of water treatment. Recent works have shown that modularization is one of the most plausible options. Moreover, in comparison to conventional wastewater treatment, the amount of sludge produced is significantly lower. Yet, the power densities obtained in large-scale installations are relatively low. New strategies should be developed to enhance the reaction kinetics and electron-transfer rates in MFCs. The scaling-up cannot be limited to the optimal enlargement of the anode but to the improvement for electrodes, membranes, and catalysts.

Conversely, the use of MFCs to power small devices offers promising prospects and has already been proved. One of the most interesting applications in this regard consists of the use of MFC to harness energy in natural environments to power sensing platforms and remote transmission data. The integration of MFCs in small devices may be approached in the future.

Another advantage of the technology is the capacity to remove heavy metals and azo dyes from water effluents. Traditional methods to remove heavy metals can be energy intensive and ineffective for low metal concentrations. MFCs have shown to be successful to reduce several metal ions when acting as electron acceptors in the cathode at a wide range of concentrations. One limitation may be given by the further

separation of metal deposited onto the materials that form the MFC components, such as carbon materials.

The sensitivity of the technology to many factors such as substrate concentration, ion species, pH, or temperature can be also exploited for sensing purposes with online mode operation. Finally, it can be expected that the next research efforts will further focus on the development of hybrid systems for biohydrogen and chemical production. These pathways have been less explored in comparison to wastewater treatment and can bring new opportunities in the future, also as a result of the combination of MFC with other technologies.

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