

Jai Sankar Seelam, Deepak Pant, Sunil A. Patil,  
and Balasaheb P. Kapadnis

## Abstract

Attributed to their multifaceted abilities, microorganisms have been constantly explored for several applications ranging from product synthesis, energy recovery to waste treatment. Biological production of electricity has been an important area of research in the past decade and half. Bioelectrochemical systems (BESs) offer a promising solution in aiding the energy development sector due to its supplementing ability to generate electricity from wastes and wastewaters. This chapter lays focus on the mechanisms and applicability of microorganisms to tap the potential in the wastes and wastewaters to function as active substrates for bioelectricity generation. Simultaneous bioenergy recovery is an added advantage in the BESs along with waste treatment. The main emphasis is on the electron-transfer mechanisms across microorganisms and electrodes, reactor architecture, and operating conditions. A brief overview on the potential of various solid wastes and wastewaters from domestic, agricultural, and industrial sectors is also included. The advancements in the field of microbial electrocatalysis have been highlighted under various sections which shed some light on the possibilities of active integration of

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J.S. Seelam (✉)

Department of Biotechnology, Indian Institute of  
Technology Kharagpur, Kharagpur 721302, India

Separation and Conversion Technologies, Flemish  
Institute for Technological Research (VITO),  
Boeretang 200, Mol 2400, Belgium  
e-mail: [shankar.jaishi@gmail.com](mailto:shankar.jaishi@gmail.com);  
[seelam@iitkgp.ac.in](mailto:seelam@iitkgp.ac.in)

D. Pant

Separation and Conversion Technologies, Flemish  
Institute for Technological Research (VITO),  
Boeretang 200, Mol 2400, Belgium  
e-mail: [pantonline@gmail.com](mailto:pantonline@gmail.com); [deepak.pant@vito.be](mailto:deepak.pant@vito.be)

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S.A. Patil

Laboratory of Microbial Ecology and Technology,  
Ghent University,  
Coupure Links 653, B-9000 Ghent, Belgium  
e-mail: [sunilmicro12@gmail.com](mailto:sunilmicro12@gmail.com); [sunil.patil@ugent.be](mailto:sunil.patil@ugent.be)

B.P. Kapadnis

Department of Microbiology, Savitribai Phule Pune  
University, Pune 411 007, India  
e-mail: [kapadnisbp@gmail.com](mailto:kapadnisbp@gmail.com);  
[bpkap@unipune.ac.in](mailto:bpkap@unipune.ac.in)

BESs with other existing bioprocesses. Further technical and technological advancements can supplement the capability of waste to bioenergy conversion concept of BESs to tackle the energy sustainability and waste management issues.

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## 10.1 Introduction

The quest to find sustainable ways for producing electricity has become a challenging task for the scientific and industrial world. Modernization and industrialization may have eased the living style but have massively increased our dependence on electricity for its regular maintenance and functioning. To meet this high energy demand from the over burgeoning population, many unsustainable resources are being extensively exploited which not only lead to their rapid depletion but also have a negative toll on the environment. Consequently, this has led to the development of clean and green alternate technologies for electricity generation during the past few decades. This advancement looked one step ahead by tapping the potential of wastes and wastewaters to serve as a potential feedstock for energy recovery thereby curtailing the dependence on conventional carbon-based fuels. This also serves the purpose of reducing the costs incurred in waste treatment systems. One such promising technology that has been developed over the last decade is the bioelectrochemical systems (BESs) such as microbial fuel cells (MFCs) which employ microbial communities for the conversion of chemical energy present in the wastes and wastewaters into the electrical energy (Oh and Logan 2005; Min and Logan 2004; Liu et al. 2004; Moon et al. 2006; ElMekawy et al. 2014a, b). An MFC is a bio-catalyzed system which harnesses bioenergy in the form of electrical energy through microbial oxidation of biodegradable organic matter present in the wastes or wastewaters under mild reaction conditions (ambient temperature and pressure) (Logan 2004a, b; Aelterman et al. 2006; Moon et al. 2006). The energy recovery is usually accompanied by or linked to simultaneous waste treatment (Patil et al. 2009; Pant et al. 2013; Sevda

et al. 2013a). In this chapter, emphasis is laid on the mechanism of biological generation of electricity by microorganisms by degrading the organic matter present in waste particulates and wastewaters. In subsequent sections, a brief description on various feedstocks, technical, and technological advancements in the BESs is included.

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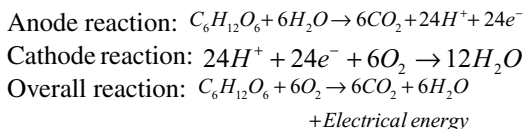
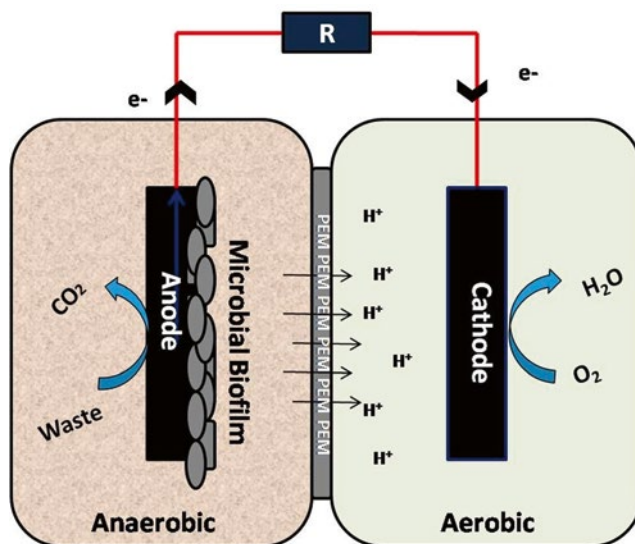
## 10.2 MFCs: Fundamentals and Technology

### 10.2.1 MFC: Principle

Electrocatalytic conversion of chemical form of energy stored in the chemical bonds of organic matter, wastes, or wastewaters to electricity using microorganisms is the principle mechanism of a MFC. A typical MFC comprises of anode and cathode chambers, which are separated by an ion exchange separator (Fig. 10.1). Anodic oxidation and cathodic reduction reactions govern the electrocatalytic activity in MFCs (Mohanakrishna et al. 2015). In the anode chamber, microorganisms oxidize the organic matter present in the wastes to produce carbon dioxide, electrons, and protons. The diffusion of protons from anodic to cathodic chamber through an ion exchange membrane generates a potential difference between the anode and the cathode which leads to the flow of electrons, i.e., current from the anode to the cathode through an external circuit. Conventionally, oxygen functions as a terminal electron acceptor which combines with the electrons and protons at cathode surface to form water as an end product.

General electrode reactions considering glucose as an electron donor and O<sub>2</sub> as a terminal electron acceptor are presented below:

**Fig. 10.1** Schematic diagram of a double-chambered microbial fuel cell.  $R$  resistance and  $PEM$  proton exchange membrane. The oxygen reduction reaction at the cathode can be abiotic or catalyzed by the microorganisms



The overall reaction is breakdown of the substrate into carbon dioxide and water with electrical energy as a main product.

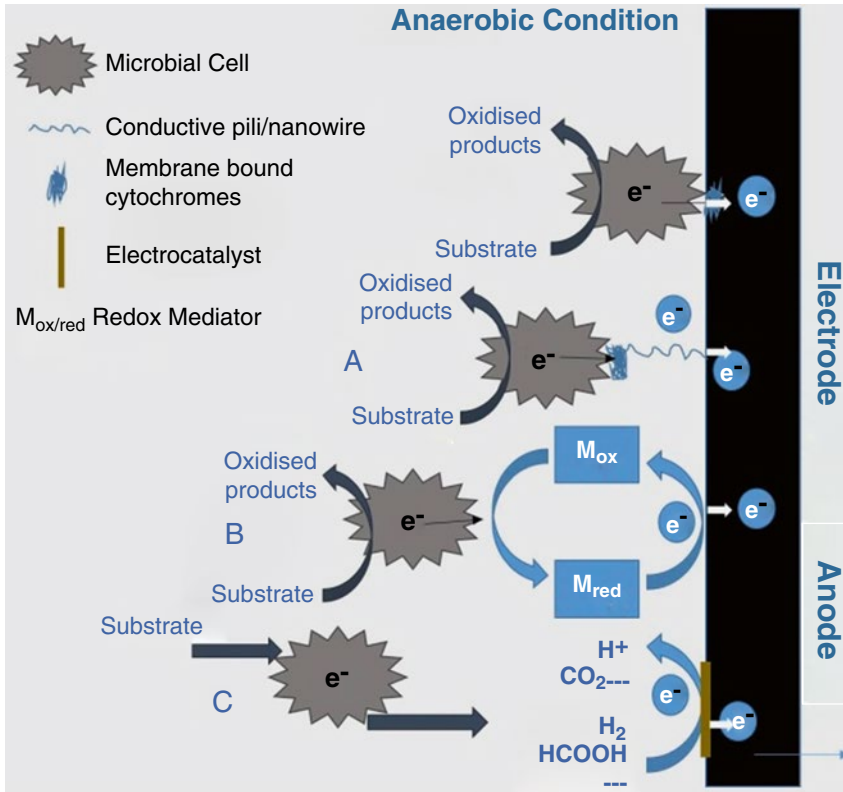
### 10.2.2 Electron-Transfer Mechanisms from Microorganisms to the Anode in MFCs

The key mechanisms involved in microbial electron transfer (ET) to the anode are illustrated in Fig. 10.2. These include the ET via (a) membrane-bound cytochromes and/or electrically conductive cell appendages such as pili or nanowires, (b) self-excreted (by microorganisms) or exogenous redox mediators, and (c) via the oxidation of reduced primary metabolites such as hydrogen (Patil et al. 2012). Broadly, these can be categorized into direct electron transfer (DET) and indirect or mediated electron-transfer (IET/MET) mechanisms.

The DET occurs when the microorganisms are attached to the electrode surface. This mechanism is prominent in two well-studied microorganisms, viz, *Geobacter sulfurreducens*

(Bond and Lovley 2003; Reguera et al. 2006) and *Shewanella oneidensis* MR-1 (Kim et al. 2002; Gorby et al. 2006; Biffinger et al. 2007). In these microbial strains, involvement of terminal reductases such as c-type outer-membrane cytochromes in ET to the anode has been well documented (Patil et al. 2012). In particular, in the case of *G. sulfurreducens*, outer-membrane cytochromes such as OmcS (Mehta et al. 2005), OmcB (Leang et al. 2003), and OmcZ are involved in the DET process. Among these, OmcZ is prominent in establishing and promoting the DET to the anodes. Similarly, in *S. oneidensis* MR-1, membrane spanning and outer-membrane cytochromes help in establishing rapid connection between cytoplasm and extracellular electron acceptor. Specifically, the role of outer-membrane MtrC-OmcA complexes in EET to anodes has been established in the case of the *S. oneidensis* MR-1 strain (Baron et al. 2009). *G. sulfurreducens* are shown to have electrically conductive pili referred to as nanowires, (Reguera et al. 2006), which assist long-range ET across anodic biofilms. Similarly, in *S. oneidensis* MR-1, the nanowires have been reported to play a role in DET to the electrodes (Gorby et al. 2006).

In the case of IET, direct contact of microbial cells to the electrode is not necessary. In one of the IET mechanisms, electrochemically or meta-



**Fig. 10.2** Electron transfer (ET) mechanisms from microorganisms to the electrode (anode) in MFCs. A. Cell-membrane-bound cytochromes and/or electrically

conductive pili (nanowires) mediated ET. B. Self-secreted (by microbes) or exogenous redox mediated ET, and CET. C. via oxidation of reduced primary metabolites

bologically produced hydrogen and formate can mediate and boost the ET to anodes. In another IET mechanism, soluble redox mediators that can be added externally (Biffinger et al. 2007; Rozendal et al. 2006; Lee and Rittman 2010) or produced by microbes (Cheng et al. 2009; Clauwaert and Verstraete 2009) facilitate the ET process. These mediators promote electrogenic activity of biofilm and are secreted specially by species of *Shewanella* and *Pseudomonas*. Flavin mononucleotide (FMN) and riboflavin are the mediators that are identified in *Shewanella* species (Rabaey et al. 2005b). The ET is mediated by compounds like phenazines in *Pseudomonas* sp. (Rabaey et al. 2005b). Riboflavin encourages efficient ET at EAB-electrode interface as it accumulates at the interface during sustained incubations (>72 h) (Marcus et al. 2011).

### 10.2.2.1 Electron Transfer Across Electro-catalytically Active Anodic Biofilms

Microorganisms are the core elements of the MFCs, which determine the performance in terms of current production by forming a slime layer on the anode surface, technically referred to as electrocatalytically active biofilm (EAB). The diffusion of wastes and nutrients to the microbes is governed by the natural chemical gradient which in turn modulates the biological activity of biofilm both spatially and temporally (Marcus et al. 2007; Logan et al. 2006). The process of ET across the biofilm is a mechanically and spatially heterogeneous pathway (Torres et al. 2010) and occurs through varied mechanisms such as DET and/or MET. The position of cells within the biofilm affects the mechanism of ET with DET dominating in those resting at electrode surface, and indirect mechanisms are required to transport the

electrons across the biofilm thickness. The cells on the outer rim of the biofilm are farther from the electrode surface and are readily exposed to the waste and nutrients, whereas the cells in direct contact with electrode surface are prone to many physical and chemical limitations. Redox-active components on the outer membrane of the bacteria like c-type cytochromes (Shi et al. 2009) assist in the DET when they come in contact with electron acceptor. Indirect mechanisms involve intermediary synthesis of either electron shuttles, redox mediators (Gralnick and Newman 2007), or appendages like nanowires (Gorby et al. 2006; Reguera et al. 2005). Additionally, IET depends either on solid conductive matrix of variable composition or produced soluble and mobile electron carriers (Torres et al. 2010).

### 10.2.3 Electrocatalytically Active Anodic Biofilms

Microorganisms are present either as planktonic cells or EABs in BESs (Borole et al. 2011). Biofilms can be monolayered or multilayered collection of microorganisms on the electrode surface which facilitate ET and subsequent power generation. Both biofilm and planktonic microorganisms coexist and work in unison to produce electricity. The EABs house both electrochemically active and inactive microorganisms with the former contributing actively to the generation of electricity from waste organics or inorganics. The latter supplement the electricity production process by degrading the complex organics through mechanisms like fermentation or utilizing other electron donors or acceptors. The electrochemically active microorganisms primarily help in efficient ET and enhance the energy output and treatment efficiency. The majority of the electroactive microbial communities are generally either enriched or adapted from mixed microbial inoculum sources before using in BESs (Borole et al. 2011). The power output depends on the activity of electrode-associated biofilms. Eliminating non-electroactive microbial communities like methanogens, nitrate reducers, hydrogen scavengers, and, potentially, aerobic organisms in EABs is critical for getting better power output with

MFCs. Therefore, flow-over or flow-through anodes are currently being preferred in BESs because high substrate concentration and pH gradients help in the washout of suspended, non-electroactive microorganisms. Operational, biological parameters and system design are the critical parameters which contribute toward high performance of a biofilm. The structure and the composition of the biofilm are dependent on the operational conditions which are well associated with electroactivity and performance of the system. The composition and activity of the biofilm depend on the type of inoculum and mode of operation.

The biological parameters which influence the formation of an efficient EAB are the source and nature of inoculum (mixed or consortia) and substrate, type (gram positive or negative), and the nature of enrichment. The inoculum affects biofilm parameters like growth and ET rates and mechanisms, abundance, film thickness, conductivity, and substrate uptake, all of which contribute to the activity of the biofilm and the performance of the system (Borole et al. 2011; Gimkiewicz and Harnisch 2013; Erable et al. 2010; Dulong et al. 2006). The use of pure or mixed culture affects the electroactivity and at the same time also influences the power output. Studies found that gram-negative bacteria generate higher current compared to gram-positive bacteria as the presence of cell envelope structures (thick cell wall) in gram-positive bacteria inhibits easy transfer of electrons from the cell to electrode (Milliken and May 2007). However, an investigation found that *Thermincola* spp., a gram-positive microbe, isolated from a thermophilic system, were able to transfer electrons directly to electrode which might be with the help of c-type cytochromes of the cell envelope (Wrighton et al. 2008). EABs are complex in nature and are susceptible to minute changes in the system (Borole et al. 2011). In waste treatment system, biofilm-forming electroactive bacteria capable of DET are crucial in generating high current densities. Formation and sustenance of a conductive biofilm matrix which can ably facilitate high ET rates between electrodes and microorganisms is the critical need for commercial and large-scale applications.

### 10.2.3.1 Pure or Mixed Culture Inoculum Sources

The nature of the microbial inoculum plays an important role in contribution toward the internal resistance of the BESs. Pure as well as consortium of microorganisms have been employed by several research groups in MFCs. Very few pure cultures of bacteria help in DET from the cell membrane to the electrode. Exoelectrogenic bacteria such as *Geobacter* spp. (Bond and Lovley 2003; Dumas et al. 2008a, b), *Shewanella* sp. (Kim et al. 1999a, b; Ringeisen et al. 2006; Biffinger et al. 2007; Liang et al. 2009; Yang et al. 2011b), and *Rhodospirillum rubrum* sp. (Liu et al. 2007a, b) showed promising ability to generate bioelectricity. The major challenge with pure cultures is the possibility of microbiological contamination and low growth rate. To overcome this problem, a wide variety of mixed consortia of bacteria or waste streams such as domestic wastewater (Min and Logan 2004), soil (Niessen et al. 2006), fresh as well as marine sediments (Zhang et al. 2006), activated sludge (Ki et al. 2008; Patil et al. 2009), and anaerobic digester sludge (Kim et al. 2004; Chae et al. 2010) have been used. The mixture of different microorganisms assists in the transfer of electrons derived from the metabolism of organic wastes in this case.

The bacteria in pure culture systems are highly substrate specific compared to their mixed culture counterpart. Studies found that the power density using mixed cultures is relatively higher than those using pure cultures in same MFC (Logan et al. 2006; Ishii et al. 2008). Mixed microbial communities are preferred mainly due to their stability, robustness, nutrient adaptability, and stress resistance. Additionally, the ease of availability and tolerance to environmental changes makes the use of mixed cultures highly promising for bulk-scale systems. The mixed culture systems adapt slowly to generate stable power output which is evident from the reports that the start-up time ranges from a few days to 3 months. The use of complex substrates such as wastewaters and mixed inoculum sources leads to the growth of a diverse group of microbes at anode and in bulk of MFCs (Min et al. 2005b; Venkata Mohan et al. 2007).

### 10.2.4 MFC Configurations

A wide variety of MFC designs and configurations have been employed by several research groups for simultaneous waste treatment and bioelectricity generation. Based on the architecture and operation, they are broadly classified into double-chambered, single-chambered air-cathode, up-flow, and stack MFCs.

#### 10.2.4.1 Two- or Double-Chambered MFC

A typical double-chambered MFC comprises of anodic and cathodic chambers separated by a cation or proton exchange membrane (CEM or PEM). These membranes facilitate the flow of cations or protons to the cathode chamber and limit the diffusion of oxygen or other oxidants to anode chamber. The two-chambered MFCs can have various practical shapes. H-type MFC is the most extensively used MFC configuration, which consists of two bottles or units connected by a tube containing a PEM as separator (Min et al. 2005b; Oh and Logan 2006; Hou et al. 2009; Picot et al. 2011). The power generated in this system is quite low due to high internal resistance (Logan et al. 2006). This configuration primarily finds its application in basic research such as evaluating power generation using new electrode or separator materials or for microbial community analysis that develops during the degradation of specific pollutants (Sevda et al. 2013b). Nowadays, parallel-plate configurations are more frequently used. These offer better membrane to working volume ratio, low resistance, and better symmetry (Fuentes-Albarrán et al. 2012).

#### 10.2.4.2 Single-Chambered Air-Cathode MFC

The scale-up of double-chambered MFCs has been found to be tough task due to its complex design. Hence, single-chambered MFCs are developed to minimize the costs and construction issues. A typical single-chambered cell consists of only an anode chamber with cathode in direct contact with air widely referred to as air cathode. The cost-effective single-chambered air-cathode MFCs have been found to be more advantageous

over the double-chambered MFCs (Park and zeikus 2003; Liu and Logan 2004; Sukkasem et al. 2008; Lorenzo et al. 2009; Tugtast et al. 2011; Zhang et al. 2011a). This is mainly due to following reasons: (1) no aeration in cathode chamber is needed and passive air can be used; (2) ease of operation, no recycling, or chemical regeneration of catholyte is required; and (3) higher volumetric power density can be obtained because of smaller cell volume (Fan et al. 2007). In this configuration, the PEM is bonded with the cathode material into a single entity.

In order to further minimize the costs, membrane-less MFCs have been developed. These MFCs were easier to construct and generated relatively high power density (Liu and Logan 2004). However, before the columbic efficiency was much lower than the system with membrane mainly due to the consumption of substrate by the oxygen diffused across the cathode (Liu and Logan, 2004). Other major challenge in this system is the distance between the anode and the cathode. It is confined to range of 1–2 cm because of higher risk of short circuit and potential negative effect of oxygen on the activity of biocatalysts on the anode (Liu et al. 2005; Cheng et al. 2006a). Researchers have tried many configurations in order to overcome these obstacles and generate high current density (Min et al. 2005b; Oh and Logan 2006; Hou et al. 2009; Picot et al. 2011).

#### 10.2.4.3 Up-Flow MFC

In the initial attempts to scale up MFC technology, up-flow MFCs (UMFCs) seemed to be a promising configuration for bulk-scale wastewater treatment and simultaneous electricity generation (Jang et al. 2004). This hybrid design combining the features of MFC and up-flow anaerobic sludge blanket (UASB) reactor minimizes the power consumption during agitation/mixing. In this design, increased rate of electrochemical reactions and quick biofilm formation is well facilitated due to nonmechanical mixing or agitation. When the reactor is fed from the bottom of the anodic chamber with anolyte along with simultaneous discharge of effluent from cathodic chamber to anodic chamber, an up-flow

hydraulic pattern is created. This pattern ensures proper mixing of the anolyte. To avoid any biogas accumulation, the PEM in UMFC is inclined at an angle of 15° to the horizontal plane. Being a low-power consuming and continuously fed MFC, UMFC is considered to be an encouraging design for large-scale treatment of wastewaters. Scalable and commercial UMFCs – multiphase UMFC and U-shaped cathode UMFC – have been developed by researchers showcasing the ability of MFCs to generate high power output (Yang et al. 2011a).

#### 10.2.4.4 Stack MFC (Scalable MFCs)

The voltage or current output can be enhanced using a uniquely structured MFC architecture known as stack MFCs. In this system, several MFCs are connected either in series or parallel based on the operational requirements. The MFCs are connected head-to-tail using insulated pipes. The current gets summed up when the cells are connected in parallel and the voltage remains same. While in series connection, common current flows through the cells and the voltage gets added (Larminie and Dicks 2000). In both series and parallel connections, the performance of individual cells is interdependent on each other. A study found that current production in series connection is six times lower compared to that in parallel connection when operated at same volumetric flow rate. Due to relatively high short-circuit current in parallel connection, high rate of biochemical reaction is achieved than fuel cells in series (Aelterman et al. 2006). Stack MFC with parallel connection is the most appropriate configuration for rapid substrate degradation and high current densities. Electrode separators are essential in this type of configuration limiting their use in open environment (Kim et al. 2012; Cheng and Logan 2007).

### 10.2.5 Factors Affecting the MFC Performance

In self-sustaining systems like MFCs, the research focus has been always on enhancing the efficiency of waste treatment and optimizing the

bioelectrocatalytic performance of these systems. Several critical parameters such as microbial inoculum and its concentration, substrate composition and concentration, pH of the feed, feeding rate, temperature, electrode materials, ion exchange separators, and reactor configuration influence the performance of MFCs. In general, mixed microbial communities offer to be better biocatalysts for electricity generation with wastewaters. Loading pH affects current density and coulombic efficiency in a waste treatment system. Metabolic activities like proton translocation, amino acid degradation, adaptation to acidic or basic conditions, and virulence (Olson 1993) are dependent on the pH of the system. The influent pH affects the start-up time of biofilm formation and also the maximum current outputs (Patil et al. 2011). Higher current density and coulombic efficiency were observed in acidophilic conditions. Effective electron discharge at higher resistance was observed in acidic conditions compared to neutral and alkaline conditions (Veer Raghavulu et al. 2009). In small-scale systems, the pH gradients across the electrode hinder the growth of microorganisms and lead to reduced performance of microorganisms in contact with electrode surface. At low pH, microorganisms are prone to higher stress levels. Investigations found that enriched bacteria have improved pH tolerance compared to normal cultures (Borole et al. 2011). Acidic pH facilitates efficient proton transfer to the cathode chamber and at the same time also minimizes the proton gradient. A study found acidic pH of 6.0 proved to be ideal for mixed consortia to form biofilm with simultaneous electricity generation (Veer Raghavulu et al. 2009).

The impact of temperature on the MFC performance is crucial for long-term and commercial operations. The growth and electrocatalytic properties of the biofilm vary with temperature. In tropical weather conditions, the performance of bacteria enriched at higher temperatures showed great promise in MFC applications. In such cases high current density is observed at temperature of 40 °C (Liu et al. 2010). Additionally, the temperature used during the enrichment phase also affects the bioelectrocata-

lytic performance of the system (Patil et al. 2010). Bacteria enriched at lower temperatures produced higher current densities when operated at low temperatures. The thermophilic bacteria are found to be generating higher current densities at high temperatures like 60 °C. Substrate concentrations and loading also affect the MFC performance. The metabolism might shift toward other metabolic pathways like acetogenesis or methanogenesis when there is excess of substrate and absence of low-resistance path to an electron sink. Further, the performance of MFCs depends on many other factors like electrode spacing, anolyte conductivity, and membrane type (Liu et al. 2005; Cheng et al. 2006b).

Electrode materials and their properties are the key factors which influence the performance of MFCs. High electrical conductivity, biocompatible surface, chemical stability, inert nature (non-oxidative), non-self-destructive and electrocatalytic activity, and sustainability of its properties with time are some of the important properties of the electrodes, which need to be considered (Srikanth et al. 2011; Rosenbaum et al. 2007; Guo et al. 2014b). Both electron propagation and electron-transfer characteristics vary with properties of electrode (Aelterman et al. 2008; Larrosa-Guerrero et al. 2010; Liu et al. 2010). In open circuit condition, the biofilm formation is affected by nature of electrode but not affected in closed conditions (Larrosa-Guerrero et al. 2010). Current densities vary with surface roughness or microbially accessible surface of the electrode (Dumas et al. 2008a). Biofilm growth and diffusion of substrate is maximized by either increasing the pore properties or nano-modification of electrodes. This modification maximizes the true surface area for swift electron exchange. The influence of substrate composition, waste, and wastewaters on the production of bioelectricity will be explained in the upcoming sections.

### 10.2.6 Electrode Materials Used in MFCs

A wide variety of materials have been investigated to function as electrodes over the past few



decades. Several noble metals like Pt, Au, Ag, and Pd and other metals like Rh, Ir, Ni, and Cu have been used mainly due to their properties like high conductivity, broad working potential range, and specificity for sensing and detection applications (Kumar et al. 2013). But high costs and weak adhesion of inoculated bacteria restrict the utility of these electrodes in MFCs. Later on, researchers turned to other materials like, stainless steel, aluminum, and carbon based materials to function as anodes (Ouitrakul et al. 2007). High ohmic and activation losses were reported when nickel was used and weaker adhesion of inoculated bacteria on stainless steel limited the application of these materials as anodes.

Several advantages associated with carbon-based electrodes prompted researchers to use these materials as a potential substitute to previously employed metal-based electrode materials. Many forms of carbonaceous materials with/without modifications have been tried as anode materials in MFCs. These include mainly carbon cloth (Liu et al. 2005), carbon felt (Logan et al. 2007), carbon foam (Chaudhuri 2003), reticulated vitreous carbon (RVC) (He et al. 2005), graphite sheets (Srikanth et al. 2011; Venkata Mohan et al. 2007, 2009a, b), graphite rods (Rabaey et al. 2004), graphite granules (Rabaey et al. 2005a), graphite fiber brushes (Logan et al. 2007; Zou et al. 2010; Liu et al. 2005; Cheng et al. 2006b), and carbon fiber mats (Chen et al. 2011; Patil et al. 2013). Relatively high physical strength, enhanced conductivity, eco-friendly nature, low cost, roughness, biocompatibility, etc. made carbon-based materials more suitable as anodes.

These carbonaceous electrodes are grouped broadly into flat, packed, and brush electrodes based on their configuration. Materials like carbon cloth and paper, graphite plates, glassy carbon, carbon mesh, and fibers fall under the category of flat electrodes, whereas carbon felt, reticulated vitreous carbon, granular activated carbon, granular graphite, and graphite disks fall under the stuffed electrodes. Graphite fiber, a brush electrode, possesses fibrils which are structures formed by winding finely cut slices of carbon fibers in the form a brush. These fibrils enhance the sustenance of microorganisms on the surface of anodes. Fiber

brush electrodes have higher surface area compared to flat and stuffed configurations (Kumar et al. 2013). Carbon nanostructures are being used in several studies because they exhibit excellent electron-transfer characteristics with a high surface area to volume ratio and also provide a viable support for biofilm growth (Sharma et al. 2008). Further, impregnated and immobilized nanostructures are being extensively explored due to their positive impact on conductivity and charge transfer (Wei et al. 2011).

Generally, the cathode material is the same as that of anode. In wastewater-fed MFCs, carbon fibers linked with conductive and noncorrosive materials like nickel and titanium proved to function as good cathodes (Hasvold et al. 1997, 1999). Previously, precious metal like pt has been used as a catalyst when oxygen is used as the electron acceptor. But recent advancements in electrode development found new cathodes where pt is held on the electrode supporting material using a binder like Nafion (perfluorosulfonic acid) or polytetrafluoroethylene (PTFE). Studies found that though density of pt loading can be reduced to minimize the costs, cheaper alternates like cobalt- and iron-organic mixture catalysts should be used (Cheng et al. 2006b; Zhao et al. 2005) mainly due to the high costs incurred in electrode development. Materials like carbon paper and graphite rods are not quite suitable for scale-up because of their inherent lack of durability, structural strength, and high costs. Design of new electrodes like activated carbon air cathodes is quite essential for large scale and longer use of MFCs for wastewater treatment (Zhang et al. 2011a, c, 2014; Pant et al. 2010b).

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## 10.3 Potential Waste and Wastewater Feedstocks for MFCs

### 10.3.1 Potential of Wastes and Wastewaters as Substrates for MFCs

A diverse array of waste and wastewaters offers to be a rich and renewable substrate for bioenergy, biofuels, and value-added chemical genera-

tion (Rozendal et al. 2008a, b). The use of negative or low-value waste streams helps in simultaneous tackling of globally and environmentally critical issues like sustainable energy sources, pollution reduction, and wastewater treatment (Pant et al. 2012). Abundance, cheaper costs, and sustainability of wastes make them an economic commodity to be used as a potential substrate source for MFC technology for the production of sustainable, renewable, and eco-friendly power with simultaneous accomplishment of waste treatment. Major constituents of wastes/wastewaters act as active electron donors to promote growth, metabolic activity, and functioning of electrogenic bacteria.

### 10.3.2 Influence of Wastewater Nature or Composition on the Performance of MFCs

The substrate is the most integral component in any biological system principally because it serves as carbon (nutrient) and/or energy source (Pant et al. 2012). The composition, nature, and characteristics of the wastes are the driving factors which determine the efficiency and commercial viability of the waste to energy conversion systems. The concentration of individual components of waste/wastewaters that can be transformed into energy is of special interest in BESs (Angenent and Wrenn 2008). The composition of the microbial assemblage and its integrity on the electrode surface as a biofilm varies drastically with the nature of the waste stream. Equally, critical performance parameters like coulombic efficiency, power density and treatment efficiency, or COD removal of waste treating MFCs depend on the influent constituents and concentration (Chae et al. 2009).

### 10.3.3 Types of Wastes Feedstocks

The primitive/first usage of wastewaters in MFCs for bioelectricity generation dates back to 2004 (ElMekawy et al. 2015). Since then, a broad

spectrum of soluble or dissolved complex organic wastes/wastewaters and renewable biomass emerging from domestic to industrial sectors have been employed for simultaneous bioenergy generation and waste remediation (Pant et al. 2012; ElMekawy et al. 2015). Several solid wastes like food wastes, cattle manure, wheat straw, corn stover, etc. and various domestic, industrial, and agricultural wastewaters have been studied for bioelectricity generation. Tables 10.1 and 10.2 showcases an overview of the performance of MFCs fed with various wastes and wastewaters.

## 10.4 Electricity Production and Waste/Wastewater Treatment Using MFCs

The wastes and wastewaters are the most obvious potential substrates to operate MFCs due to their high organic content. Various electroactive and non-electroactive microorganisms aid in transforming the chemical energy stored in chemical compounds in biomass or wastes to electrical energy. Due to direct conversion of chemical energy into electricity instead of heat in MFCs, Carnot cycle with a limited thermal efficiency is avoided and theoretically a higher conversion efficiency system (>70 %) can be developed, similar to a conventional fuel cell (Du et al. 2007). Besides renewable production of electricity, biofilms of electroactive bacteria in MFCs facilitate proficient removal of organic carbon from wastewaters (Pant et al. 2012). By doing so, MFCs potentially reduce the energy requirement by over 50 % compared to the energy required for conventional treatment technologies where huge amount of energy is spent on aerating the activated sludge (Du et al. 2007). Comparatively, they produce 50–90 % lesser disposable solids during the treatment process (Holzman 2005). Most importantly, they enhance and sustain the growth of bioelectrochemically active microbes during the treatment ensuring operational stability (Du et al. 2007). The most striking advantage of bioelectricity over bioproducts production using BESs is that it can be utilized in situ or on

**Table 10.1** An overview of performance of MFCs with different wastes

Feedstock	MFC configuration	Microbial inoculum source	Maximum power density (mW/m <sup>2</sup> )*	Treatment efficiency	Energy recovery OR coulombic efficiency	References
Vegetable waste	Single chamber	Enriched mixed culture	172.86	COD – 62.86 %	COD- 144.83 J/Kg	Venkata Mohan et al. (2010)
Cattle manure	Three chambers (dual anode)	Enriched <i>E. coli</i> and manure leachate culture	93	**	49 KJ/Kg of dry manure CE-5.2 %	Zheng and Nirmalakhandan (2010)
Corn stover hydrolysate	Single-chambered air cathode	Enriched wastewater	331	**	CE-20-30 %	Wang et al. (2009b)
Wheat straw	Two chambers	Enriched wastewater	123	**	CE-37.1 %	Zhang et al. (2009c)
Blue green algae	Single chamber	Pre-enriched microbial community from waste water	PD-144 CD-550 mA/m <sup>2</sup>	COD – 78.9 %	CE-28.2 %	Yuan et al. (2011)
Food wastes	Two chambers	Anerobic fermentor effluent	240.3	**	**	Choi et al. (2011)
Food wastes	Two chambers	Ostrich dung enriched with acetate	101	**	**	Choi et al. (2011)
Marine sediments	Two chambers	<i>Desulfuromonas acetoxidans</i>	16	**	**	Bond et al. (2002)
Lignocellulosic biomass	Single-chambered air cathode	Sequentially enriched mixed culture	**	COD-83 %	CE-21 %	Catal et al. (2011)
Yogurt waste	Two chambers	Lixiviated composite leachate waste	CD - 1450 mA/m <sup>2</sup>	**	**	Cercado-Quezada et al. (2010)
Potato waste	Three chambers with central cathodic chamber	Methanogenic activated sludge	**	COD-87 % COD-91 % (Anaerobic treatment + MFC)	0.3 % 7.6 % (Anaerobic treatment + MFC)	Durruty et al. (2012)

*PD* Power density, *CD* Current density *CE* Coulombic efficiency

\*with respect to the projected surface area of the anode

\*\*not reported

**Table 10.2** A comparative overview of performance of MFCs with different wastewaters

Feedstock	MFC configuration	Microbial inoculum source	Power density (mW/m <sup>2</sup> )*	Treatment efficiency	Energy recovery or coulombic efficiency	References
Chemical wastewater	Two chambers	Anaerobic mixed consortia	CD – 747.96 mA/ m <sup>2</sup>	62.90 %	**	Venkata Mohan et al. (2007)
Synthetic wastewater	Two chambers	Selectively enriched anaerobic mixed consortia	222.59 mA/ m <sup>2</sup>	74.20 %	**	Venkata Mohan et al. (2007)
Chemical wastewater	Two chambers	Selectively enriched anaerobic mixed consortia	67.48 mW/ m <sup>2</sup>	61 %	**	Venkata Mohan et al. (2007)
Agricultural wastewater	Single chamber	Mixed culture	0.015 mW/cm <sup>2</sup>	2.9 %	***	Nimje et al. (2012)
Domestic wastewater	Single chamber (air cathode)	Enriched mixed culture	422 mW/ m <sup>2</sup>	25.80 %	**	Ahn and Logan (2010)
Winery wastewater	Four single-chambered, cubic-shaped MFC	Wastewater served as both inoculum and substrate	**	65 ± 7 %	18 ± 4 %	Cusick et al. (2010)
Urine	Two chambers	Microflora from activated sludge	8 mA/ m <sup>2</sup>	22-30 %	***	Ieropoulos et al. (2012)
Domestic wastewater	Single chamber	Anaerobic sludge	300 mW/ m <sup>2</sup>	**	***	Liu et al. (2011a)
Urban wastewater	Single chamber (air cathode)	Effluent from a parent MFC treating synthetic wastewater	1.42 W/m <sup>3</sup>	80 %	***	Puig et al. (2011)
Mixed volatile fatty acids	Single chamber	Anaerobic sludge collected from a local wastewater treatment plant	PD=0.69 W/m <sup>3</sup> CD=2.62 A/m <sup>3</sup>	**	20~39 %	Teng et al. (2010)
Bad wine	Two chambers	Mixed culture	3.82 W/m <sup>3</sup>	**	45 %	Rengasamy and Berchmans (2012)
Palm oil mill effluent (POME)	Two chambers	Mixed culture	622 mW/ m <sup>2</sup>	23 ± 1 %	32 %	Jong et al. (2011)
Beer brewery wastewater	Single chamber	Anaerobic mixed consortia	264 mW/ m <sup>2</sup>	40-43 %	19.75 %	Wen et al. (2009)

Swine wastewater	Single/two chamber(s)	Wastewater was used as the inoculum	Two chambers: 45 mW/ m <sup>2</sup> Single chamber: 261 mW/ m <sup>2</sup>	92 %	8 %	Min et al. (2005a)
Chemical wastewater	Two chambers	Selectively enriched mixed consortia	222.59 mA/ m <sup>2</sup>	74.2 %	**	Venkata Mohan et al. (2007)
Domestic wastewater	Single chamber	Anaerobic mixed consortia	325.51 mA/ m <sup>2</sup>	**	**	Venkata Mohan et al. (2009c)
Chocolate industry wastewater	Two chambers	Activated sludge	CD 3020 mA/m <sup>2</sup>	COD – 75 %	**	Patil et al. (2009)

*PD* Power density, *CD* Current density

\*with respect to the projected surface area of the anode

\*\*not reported

site without any purification or isolation steps (Kang et al. 2010). Both solid wastes and liquid waste streams can be potentially treated using MFCs as further elaborated in subsequent sections.

#### 10.4.1 Solid Wastes

The origin of various solid waste feedstocks is dispersed over many domains ranging from marine environment (Bond et al. 2002) to agriculture and domestic sectors (Pant et al. 2010a; ElMekawy et al. 2015). Agricultural residues like corn stover, cattle manure, wheat straw, etc. have been tried as substrate in BESs. The carbon and nitrogen compounds present in cattle manure help in proliferation of microbial communities in MFCs (ElMekawy et al. 2015). Agricultural particulate matter like wheat straw and corn stover is majorly composed of cellulose and hemicellulose which can be actively utilized for bioelectricity generation. The challenge of using such lignocellulosic biomass rests on the inability of the electroactive microorganisms to degrade them directly. Conversion of cellulose into monosaccharides or other low-molecular-weight compounds through hydrolysis (Ren et al. 2007) and hemicellulose into soluble sugars using cellulolytic enzyme treatment or steam explosion process (Zuo et al. 2006) becomes a necessary step to boost the degradation and activity of microorganisms in this case. These hydrolyzed compounds are ideal substrates to support bioelectricity generation. Microbial communities with both cellulolytic and exoelectrogenic activities are necessary to maximize the power output with such agricultural wastes (Rezaei et al. 2009b).

Highly biodegradable food wastes in the form of vegetable waste, yogurt waste, and other edibles are available in surplus due to daily routine of mankind. These can be readily used to tap bioelectrochemical energy due to their rich organic content (Digman and Kim 2008; Li and Yu 2013). Pre-fermentation of these food wastes before feeding them in MFCs can lead to better performances. Studies performed under different oper-

ational and experimental conditions using multiple solid residual wastes highlight their promising use in MFCs (Table 10.1). The power densities achieved with such wastes vary from 16 to 331 mW/m<sup>2</sup> accompanied by COD removal efficiencies lying between 62 % and 91 %.

#### 10.4.2 Wastewater Sources

##### 10.4.2.1 Industrial Wastewaters

The effluents from slaughter houses, chemical, brewery, food processing, and other industries are the most sought out substrates in BESs (Katuri et al. 2012; Li et al. 2013a, b). The ease of availability and the necessity to treat these high organic matter-containing high strength effluents have made these wastewaters an ideal fuel source to generate bioelectrochemical energy. Wastewater streams from food processing and beverage industries like brewery, winery, dairy, vegetable, meat, and other food-processing industries are abundant in availability, rich in organic content, and possess high biodegradability (Digman and Kim 2008; Li and Yu 2013; Guo et al. 2014a). The absence of microbial growth inhibiting agents in these wastewaters adds up to an additional advantage. In the frequently used wastewaters in MFCs, COD concentration ranges from 3000 to 5000 mg/L (Zhang et al. 2013a, b; Zhuang et al. 2012). Integrated treatment systems coupled with MFCs have also been employed to treat wastewaters such as palm oil mill effluents to pull down the costs incurred in conventional treatment of the mill wastewaters (Ahmad et al. 2011; Cheng et al. 2010; Leño et al. 2012). MFCs have been proved to be better treatment systems for animal and chemical industrial wastewaters with COD removal efficiencies ranging from 65 to 92 % (Table 10.2).

##### 10.4.2.2 Domestic and Agricultural Wastewaters

The domestic and agricultural wastewaters are relatively less strong in terms of organic content compared to industrial counterparts (Pant et al. 2010a). The necessity to treat household and sanitary let-offs led researchers and public environ-

mental bodies to focus on treatment systems like BESs. These low-strength wastewaters have been well exploited by several research groups to obtain better energy output than industrial wastewaters. Manure wash water and agricultural effluents are more efficient than agricultural particulate and residual wastes for electricity production in MFCs (Zheng and Nirmalakhandan 2010). Power densities obtained using domestic wastewaters are greater than agricultural and industrial counterparts (Table 10.2). However, the treatment efficiencies obtained using these wastewaters are relatively lower due to lesser COD levels. Table 10.2 gives a comparative overview of the most commonly used wastewaters employed for bioenergy generation in MFCs.

## 10.5 Challenges of Employing MFCs for Waste/Wastewater Treatment

Though MFC technology seems to be a promising bioprocess system, its utility is limited by various operational and economic challenges. From application's point of view, power density of about 1 kW/m<sup>3</sup> or equivalent current density of 5000 A/m<sup>3</sup> of total anolyte volume or 50 A/m<sup>2</sup> of projected anode surface area, if an average voltage output of 0.2 V is expected to be reachable under load conditions, would be sufficient for long-term and commercially viable applications (Clauwaert et al. 2008). Thus far, maximum current densities ranging from 10 to 25 A/m<sup>2</sup> for milliliter-scale systems and 6 A/m<sup>2</sup> or lower for liter- or higher-scale systems have been achieved with wastewater-fed MFCs (Rabaey et al. 2010a). The challenges associated with the use of MFCs for wastewater treatment are discussed in the upcoming sections.

### 10.5.1 Scale-Up

The commercialization of bioelectricity production using MFCs has always been a curious and challenging attempt for many research groups. The notable attempts of pilot testing of MFCs

were made by three research groups during the last decade. A reactor with total volume of 1 m<sup>3</sup> comprising of 12 modules, each 3 m high, was tested at Foster's brewery in Yatala, Queensland (Australia), by the Advanced Water Management Center at the University of Queensland (Logan 2010). This MFC generated maximum current of 2A/cell at 400 mV voltage with power density of 0.5 W/m<sup>2</sup> of membrane area and 8.5 W/m<sup>3</sup> of reactor volume. Additionally, COD removal of 0.2 kg COD/(m<sup>3</sup> d) was reported in this pilot study (Keller and Rabaey 2011). Researchers at University of Connecticut and their collaborators (Fuss and O'Neill and Hydroqual Inc.) set up a system at a site in the USA (Jiang and Li 2009) treating wastewater, removing up to 80 % of the chemical oxygen demand present at 300–600 mg/L. A large-scale setup for biohydrogen production using MEC technology was constructed at the Napa Wine Company, in Oakville, CA, USA, by Penn State researchers with engineering services by Brown and Caldwell (Walnut Creek, CA, USA). It consisted of 24 modules, each with six pairs of electrodes, and is approximately treating 1 m<sup>3</sup> of wastewater (Logan 2010).

The scale-up of this technology is limited by many factors such as the cost of electrodes, low power densities, and potential losses in long-term operation. Extensive tests including pilot-scale studies are necessary to know the performance of materials at larger scale and their longevity, and at the same time examination of BESs with variations in fuel (wastewater) composition, temperature, and as a function of maintenance (e.g., to control fouling on electrodes) are highly critical (Logan 2010). The economic and operational limitations in bulk-scale systems are discussed in the forthcoming sections. Stacks cells are found to be useful in enhancing the performance, but the problem of voltage reversal due to differences in resistances between stack cells and substrate starvation in cells during operation (Oh and Logan 2007) limits their chance of operating on large scale. It has been found that the voltage reversal can be minimized by avoiding low substrate concentrations (that occur in fed-batch cycling) using continuous flow and by closely matching internal resistances among cells in the stack (Logan 2010).

### 10.5.2 Operational Limitations

The major operational limitations of pilot-scale MFCs include operating under natural environment; exposure to sun, wind, rain, and insects; low temperature during night time; uneven flow and composition of wastewater; clogging of feed line due to biofilm growth; and lastly difficulty in online potentiometric measurement at large scales (Keller and Rabaey 2011). Partial utilization or degradation of waste in large-scale continuous reactors is another major point of concern. The growth of excessive and unwanted biomass in cathode chambers and biofouling on cathode also affects the long-term performance in pilot-scale MFCs.

### 10.5.3 Economic Limitations

The major obstacle in bulk-scale production systems is the high costs of electrodes, installation, and operation. Though introduction of current collectors into electrodes (Zhang et al. 2009a; Zuo et al. 2008), chemical treatments, and use of precious metals (Cheng and Logan 2007; Liu et al. 2007b) enhance the power output, the economic constraints restrict their utility. For example, fuel cell grade materials can cost approximately \$1,000/m<sup>2</sup> which is quite expensive (Logan 2010). Cheaper electrode treatment techniques like simple heat treatment of the carbon mesh offer to be economical and sufficient for good energy generation (Wang et al. 2009a) compared to expensive high-temperature ammonia gas treatment which facilitates bacterial adhesion and increases power densities (Cheng and Logan 2007). For scale-up, graphite fiber brush anodes (Feng et al. 2010; Logan et al. 2007; Nielsen et al. 2007) are promising electrode materials. In waste treatment systems, aeration in cathode chamber is a costly affair. Alternate materials like activated carbon with metal mesh current collector are used for oxygen reduction. Cathodes impregnated with metals like iron and nickel displayed power densities ranging from 23 W/m<sup>3</sup> to 36 W/m<sup>3</sup> (Aelterman et al. 2009; Zhang et al. 2009a). But usage of cheaper metals like stainless steel and cheaper binders protects the

cathode from corrosion and at the same time improves power densities in bulk-scale systems. Interestingly, biocathode research is catching pace to help developing BESs into large-scale energy-producing units. In attempts to pull the cost further down, removal of membrane separators improved the performance in treatment systems. But, the use of membrane separator is beneficial in scale-up systems as it allows closer electrode spacing and prevents short circuiting which in turn improves power densities on a volumetric basis (Logan 2010).

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## 10.6 MFCs Toward a Sustainable Technology Development

Some strategies that can be used to improve the performance of MFCs are discussed below.

### 10.6.1 Waste/Wastewater Pretreatment

The nature of substrate and applied organic load affects power generation as well as substrate degradation in MFCs. Majority of solid wastes are highly heterogeneous in nature which hinder rapid metabolic degradation by electroactive microorganisms. Pretreated wastes/wastewaters generated either through fermentation or hydrolysis offer optimum organic content compared to raw substrates. Pretreatment minimizes the activation losses which further enhances the bioelectrochemical activity of the biocatalyst and the process efficiency. It has been reported that pre-fermented food wastes show high catalytic activity and decent current density with added advantage of effective electron transfer. With pre-fermented waste, 47 % higher current density has been obtained than that with untreated waste (Goud and Mohan 2011).

### 10.6.2 Bioaugmentation

Bioaugmentation majorly finds its application in treatment systems as it accelerates the treatment efficiency of hazardous waste sites or bioreactors for the effective removal of undesired compounds.



Studies found that bioaugmentation was beneficial in improving the start-up of a bioreactor (Wilderer et al. 1991), to boost reactor performance (Stephenson and Stephenson 1992), to protect the existing microbial community against adverse effects (Venkata Mohan et al. 2009a), to accelerate the onset of degradation process (Bathe et al. 2005; Hu et al. 2008; Park et al. 2008), or to compensate for organic or hydraulic overloading (Chong et al. 1997). It offers a promising strategy to improvise the working of wastewater treating MFCs. It spins around the concept that the active inter-species interactions in a biological system like MFC could aid in efficient electron transfer (Lovley 2006) and consequently enhance the bioelectricity generation. Augmentation with robust and catabolically relevant organisms having specialized and desired characteristics improves the bioprocess efficiency. Nowadays, indigenous wild type or genetically modified organisms are employed as augmenting catalysts (Veer Raghavulu et al. 2012). The alliance between *Brevibacillus* sp. and *Pseudomonas* sp. enhanced the energy outcome and highlighted the higher and effective electron transfer (Pham et al. 2008). The synthesis of mediators by *Pseudomonas* sp. helped its counterpart to achieve extracellular electron transfer. On similar grounds, *Shewanella* sp. has been identified to function as an augmenting agent (Veer Raghavulu et al. 2012) under diverse environmental conditions to assist electron transfer due to its ability to synthesize redox mediators (Fredrickson et al. 2008; Richter et al. 2007; Lower et al. 2007). A stable and higher electrogenic activity throughout the operation was reported in a system augmented with *S. haliotis* (Veer Raghavulu et al. 2012). High potential difference is maintained for a longer period enabling higher electron discharge and reduction in activation losses. Augmented systems have greater functioning than those using individual and mixed consortia (Veer Raghavulu et al. 2012). Syntrophically associated bioaugmented systems can be commercially viable mainly due to its ability to supplement performance parameters like higher power output for longer periods, stable electron discharge throughout operation, and high substrate degradation.

### 10.6.3 Bioprocess Integration

For a sustainable technology development, neutral-energy operation, cost-effective process, stable performance, high effluent quality to meet water reclamation and reuse requirement, less resource consumption, a low environmental footprint, and good social equity are quite essential (Muga and Mihelcic 2008; Levine and Asano 2004). In the present technological scenario, it is quite challenging to achieve these traits concurrently. Bioprocess integrations offer a fascinating concept to visualize an efficient and sustainable technology for electricity generation and simultaneous waste treatment. Attempts to integrate MFC technology with other bioprocesses generated higher current densities compared to conventional reactors. Incorporating processes like forward osmosis (Zhang et al. 2011b) and activated sludge process (Liu et al. 2011b) with MFC showcased better performance in terms of power/current densities. The use of forward osmosis membrane separator facilitates better proton diffusion with water flux and more electricity. This technology helps in simultaneous wastewater treatment, water extraction from wastewater, and bioelectricity generation. Development of a sophisticated reactor design like anaerobic fluidized bed MFC and bioelectrochemical membrane reactor holds great promise for sustainable and green energy recovery and waste treatment process. Simultaneous integration of multiple treatment processes like an up-flow anaerobic sludge blanket reactor–MFC biological aerated filter (UASB–MFC–BAF) highlights the commercial ability of integrated MFC technology (Zhang et al. 2009a).

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## 10.7 Microbial Electrocatalysis: Latest Advancements and Other Applications

Over the past few years, MFC technology paved way for developing advanced and alternate bioprocesses. Several research groups showed keen interest in investigating its possible integration with other processes mainly due to its innovative features and environmental benefits (Logan et al.

2006; Rabaey and Verstraete 2005; Rozendal et al. 2009). Microbial electrocatalysis has been explored to develop applications for the production of hydrogen (Logan et al. 2008) and other chemicals (Rozendal et al. 2009), resource recovery (Xie et al. 2014), desalination (ElMekawy et al. 2014a), and bioelectrochemical treatment. A brief discussion explaining these advancements is given in the upcoming sections.

### 10.7.1 Microbial Electrolysis Cells: H<sub>2</sub> Production

Biohydrogen is projected to be crucial player in the nonfossil fuel-based future economy. This green fuel was initially produced using two bioprocesses: converting carbohydrates by fermentative bacteria (dark fermentation) and converting organic acids by photosynthetic bacteria (photofermentation) (Liu et al. 2010). Microbial electrolysis cells (MECs) are developed to curtail the limitations and challenges of biohydrogen production using these two processes. In this modified MFC system, hydrogen is produced by electrohydrogenesis from acetate or fermentation end products. Bacteria referred as exoelectrogens help in the oxidation of substrate to transfer electrons to anode. The basic difference between MFC and MEC lies in the cathodic reaction. In a MFC, current is produced by the oxygen reduction under aerobic condition at cathode, whereas in a MEC, due to anaerobic condition at cathode, no spontaneous generation of current is possible. Current is spontaneously produced in MFCs due to the higher redox potential of oxygen compared to that of a microbial anode which facilitates easy flow of electrons from anode to cathode. But in MECs, there is no spontaneous flow of electrons because the redox potential of hydrogen reduction, protons to hydrogen, at cathode is lower compared to that of reaction at anode. Thus, a small external voltage is required to the circuit for the reaction to proceed (Logan et al. 2006). MECs were initially referred to as bioelectrochemically assisted microbial reactors (BEAMR) (Logan et al. 2006). Owing to higher hydrogen recovery and wider substrate diversity, biohydro-

gen production through MECs gained a lot of interest compared to that of the fermentative counterparts. But, the production has been low with domestic wastewaters feeds (Ditzig et al. 2007; Wagner et al. 2009). Simultaneous production of methane is one of the major limiting factors in extensive use of MECs for hydrogen production. Several studies have focused on evaluating the simultaneous wastewater treatment capacity of MECs. Treatment efficiencies ranging from 19 to 72 % have been reported when swine wastewaters were used as substrate (Wagner et al. 2009). Reported pilot-scale studies using winery wastewaters displayed 44 % lesser performance compared to lab-scale setups (Cusick et al. 2011). This shows the need for further improvements in developing efficient MEC technology.

### 10.7.2 Microbial Electrosynthesis

Besides electricity generation and waste treatment, BES has garnered great interest in the field of microbial electrosynthesis. This concept aims at reducing carbon dioxide or waste gases and organic substrates to multicarbon compounds using different terminal electron acceptors (Nevin et al. 2010). The first report of reducing carbon dioxide to acetate and 2-oxobutyrate was exhibited by biofilms of *Sporomusa ovata* growing on graphite cathode surfaces. This field addresses the use of microorganisms to function as biocatalysts on cathodes (i.e., biocathodes) to perform electricity-driven synthesis of chemicals and fuels compounds (Rabaey et al. 2010b; Sharma et al. 2013). Other hydrocarbons such as methane and ethanol have been synthesized using this mechanism (Pant et al. 2012). Extensive research is yet to be done to establish this field on lab and then pilot to commercial scales.

### 10.7.3 Microbial Desalination

The major limiting factors in large-scale treatment of wastewaters using MFCs are (1) lower conductivity (1–2 mS/cm) and alkalinity (100–

300 mg CaCO<sub>3</sub>/L) of wastewaters (Rozendal et al. 2008a; Ter Heijne et al. 2006; WEF 2007) and (2) pH variations during operation. The main reason for the pH drop is the relative slower diffusion of protons compared to transfer of electrons which subsequently inhibits microbial activity (Luo et al. 2012). Recent advancements found a way to curtail these limiting factors in the form of a microbial desalination cell (MDC). MDC is a modified version of a MFC with a central desalination chamber separated from anode and cathode chambers with the help of an ion exchange membrane. In MDC, a potential gradient is generated due to typical anodic and cathodic reactions. This gradient generated by the bacteria helps in the diffusion of ions from the central chamber to the adjoining cathode and anode chambers (Cao et al. 2009) thereby increasing the ionic strength and the conductivity of the wastewater. For example, the effluents of oil and gas production industries are a rich source of bicarbonate ions (Benko and Drewes 2008). The transfer of these bicarbonate ions during desalination to anode chamber increases the alkalinity of wastewater which further enhances the treatment efficiency and bioelectricity production. A study found that an MDC can improve the power density by four times, COD removal by 52 %, and coulombic efficiency by 131 % (Luo et al. 2012) clearly highlighting an integrative and promising approach for wastewater treatment with simultaneous energy production and desalination.

#### 10.7.4 Bioelectrochemical Treatment of Pollutants

In an advancing approach, BESs are being explored for bioelectrochemical treatment of various organic, inorganic, and aromatic compounds alongside conventional COD reduction.

The shift of focus toward these systems from conventional treatment methodologies is primarily attributed to the synthesis of toxic by-products, operational, and economic constraints of existing physicochemical remediation approaches. Moreover, biological treatment systems are relatively 5–20 and 3–10 times cheaper in terms of

capital and operational costs, respectively, than advanced oxidation methods (Marco et al. 1997). In these systems, several chemotrophic and heterotrophic species, primarily present in mixed culture, actively degrade pollutants and environmentally hazardous compounds by both cathodic reduction and anodic oxidation reactions (Mohanakrishna et al. 2015). The anaerobic treatment at cathode requires an organic co-substrate (electron donor) to create reductive conditions in the cathodic chamber. The resultant-reduced products are found to be eco-friendly and harmless. Several investigations showcased the ability of BESs to treat perchlorates (Thrash et al. 2007), sulfides (Rabaey et al. 2006), nitrates (Clauwaert et al. 2007; Virdis et al. 2008), nitrobenzene (Mu et al. 2009a), azo dyes (Mu et al. 2009b; Ding et al. 2010), and chlorinated organic compounds (Aulenta et al. 2007). These compounds, in the absence of oxygen, perform the role of electron acceptors to accomplish terminal electron reduction which further facilitates their remediation in BESs (Mohanakrishna et al. 2015). Other compounds like sulfur and estrogens are treated at the anode (Chandrasekhar and Venkata Mohan 2012; Kiran Kumar et al. 2012). Nitrogen-rich effluents are treated using simultaneous nitrification-denitrification technique (Zhang and He 2012). In azo dye degradation process, the thick color is removed due to the formation of colorless amines (Frijters et al. 2006).

### 10.8 Conclusions and Future Prospects

Waste to bioenergy conversion offers a promising way to tackle the energy sustainability and waste management issues. This chapter summarized the ability of BESs such as MFCs to generate bioelectricity from different wastes and wastewaters with simultaneous waste treatment. Though the technology seems advantageous in terms of waste treatment, the magnitude of energy recovery is still the major point of concern. It is challenged by various constraints and limitations for large-scale applications. Investigations aimed at enriching desirable electroactive microbial com-

munities could help developing MFCs into a competitive technology. Complexity of wastes, expensive electrode materials, and complex reactor architectures are the domains which seek further technological advancements for better outcome. Waste pretreatment, bioaugmentation, and bioprocess integration are viable options for improvising wastewater treatment using MFCs. To achieve a commercially viable and eco-friendly technology, research should be carried on integrating MFCs with other bioprocess like fermentation, desalination, bio-product recovery, and metal recovery. Research focuses in the direction of operating MFCs at higher loading rates with cheaper electrode materials, and simplified reactor designs are important in order to realize the practical applications of MFCs for tapping energy from the wastes and wastewaters. The future for BESs seems promising in wastewater treatment sector as some of these technologies are currently under trial or operational at larger scales. These include production of methane from wastewater using MECs (Cambrian Innovation Inc., 2013) and energy-efficient wastewater treatment with MFCs ([www.emefcy.com](http://www.emefcy.com)).

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**Jai Sankar Seelam** Jai Sankar Seelam (B.Tech, 2014) graduated with a Bachelor's degree in Biotechnology and Biochemical Engineering from the Indian Institute of Technology (I.I.T), Kharagpur. He is currently enrolled in MSc – Water Technology (joint degree) at Wetsus Academy, Leeuwarden, the Netherlands for the academic session 2015–2017. He worked as a guest researcher at VITO NV, Belgium, in summers of 2013 and 2014. His research interests include wastewater treatment and energy recovery from wastes and wastewaters.

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**Deepak Pant** Deepak Pant (Ph.D., Environmental Biotechnology, 2007) is a senior scientist at the Flemish Institute for Technological Research (VITO), Belgium, currently working on bioenergy, specifically, the design and optimization of bioelectrochemical systems for energy recovery from wastewater and microbial electrosynthesis for production of value-added chemicals and fuels through electrochemically driven bioprocesses. He has one book (published by Springer), 52 peer-reviewed publications with 2300 citations (h-index 24), and 15 book chapters to his credit. More details: [be.linkedin.com/pub/deepak-pant/b/b44/942/](https://be.linkedin.com/pub/deepak-pant/b/b44/942/)

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**Sunil A. Patil** Sunil A. Patil (PhD, 2011) is currently working as a post-doctoral researcher at the Laboratory of Microbial Ecology and Technology (LabMET), Ghent University, Belgium. His main research areas include microbial bioelectrochemical systems for energy recovery from wastewater, microbe-electrode interactions, and electricity-driven bioproduction of value-added chemicals and fuels from CO<sub>2</sub>. He has 24 peer-reviewed publications and five book chapters to his credit.

recovery from wastewater, microbe-electrode interactions, and electricity-driven bioproduction of value-added chemicals and fuels from CO<sub>2</sub>. He has 24 peer-reviewed publications and five book chapters to his credit.



**Balasaheb P. Kapadnis** Balasaheb P. Kapadnis (PhD, 1981) is currently working as an emeritus professor at the Department of Microbiology, Savitribai Phule Pune University, Pune, India. His main research areas include environmental microbiology with reference to biological management of pathogens and value addition to waste. He has 75 peer-reviewed publications and 10 book chapters to his credit.

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