Chapter 17
Sediment Microbial Fuel Cell and Constructed Wetland Assisted with It: Challenges and Future Prospects

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17.1 Introduction

In recent years, the research work focus in energy sector has been shifted towards the renewable energy due to continuous depletion of conventional energy sources. On the other hand, exponentially increasing pollution in water reserves has stimulated phenomenal debates among researchers, pollution control agencies, and stakeholders in search of sustainable solution to remediate it. Sediment microbial fuel cell (SMFC) is one of the most promising approaches to address these two highly recognized problems together (Sajana et al. 2013b). In addition, SMFCs can offer distinctive opportunity to understand the flow of energy through electrochemically active bacteria, energy collection efficiency from natural systems, and the role of SMFCs for power generation and *in situ* bioremediation in the natural environment (Sajana et al. 2013a). SMFCs comprise two electrically conductive electrodes as anode and cathode placed 5–10 cm beneath the free surface of sediment and free water surface, respectively (Fig. 17.1a). Chemical energy associated with organic matter present in the sediment and water gets converted to electron and proton during oxidation catalyzed by microorganisms, working as biocatalyst on anode surface. Sediment permits the flow of protons from anode to cathode side serving as proton permeable natural medium. The anode collects extracellular electrons and transfer them to the cathode through an external circuit. On cathode, oxygen or other chemical oxidant (like nitrate) serve as terminal

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D. Das (ed.), *Microbial Fuel Cell*,
https://doi.org/10.1007/978-3-319-66793-5_17

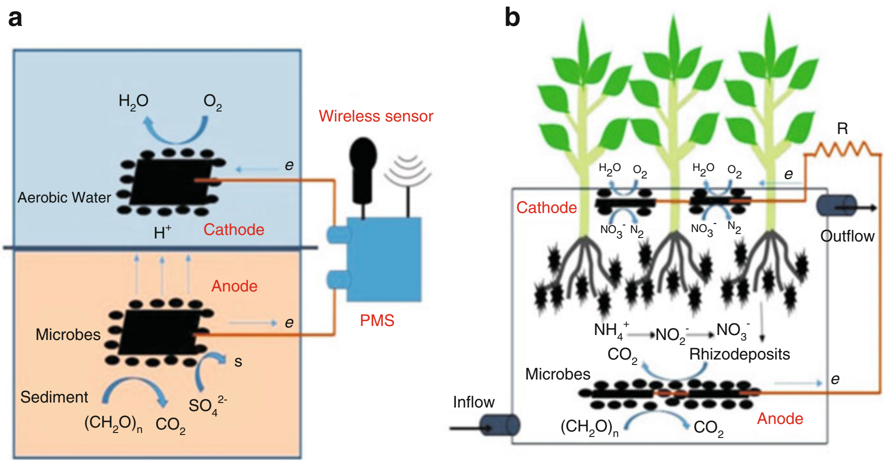

Fig. 17.1 Schematic diagram of (**a**) Sediment microbial fuel cell; and (**b**) Constructed wetland microbial fuel cell

electro acceptor (TEA), which combines with electron and proton and produce water or other reduced product (Rismani-Yazdi et al. 2008). In addition, anions and cations can be used for charge balanced in the SMFCs based on their concentration in the fluid (Kim et al. 2007). Natural phenomenon of redox charge gradient have been used for development of SMFCs. Table 17.1 shows the brief summary of half-cell equations (anodic and cathodic) which can take place on anode and cathode during bioconversion of organic matter to electricity.

In last decade, application of various types of SMFCs in different environment have been demonstrated for wastewater treatment (Fang et al. 2013), bioremediation of aquaculture sediment (Sajana et al. 2013b), and powering remote sensors (Ewing et al. 2014). All these have been shown to be of great interest of research in order to seek sustainable solution to mitigate pollution threat and power recovery. However, the lacuna of the SMFCs lie in poor power production and recovery of electrons from substrate (coulombic efficiency) due to deprived electrode kinetics. The performance of SMFCs has been remedied by various modifications in the SMFC in recent times, rendering it as an alternative for aquatic sediment bioremediation and source of bioenergy that has found its niche.

The constructed wetland (CW) and microbial fuel cell (MFC) are two different biological systems which are capable of degrading organic matter in distinct way. CWs depend upon ecological functions similar to natural wetland and are largely based on plant interactions, but it is still unknown that which plant population can enhance the treatment performance of CWs. However, some researchers manifested the relation between plant root canopy and density and functional performance of microbial population on the treatment performance of CWs. However the relationship lacks adequate scientific evidence (Hammer 1989; Reed et al. 1995). On the other hand, an MFC provides controllable option for wastewater treatment and power recovery (Tiwari et al. 2016). Kinetics of anode and cathode can be enhanced by manipulation of

Table 17.1 Anodic and cathodic half-cell reactions in MFCs and corresponding standard potentials (E^0) vs. Standard Hydrogen Electrode (SHE)

Anodic reactions	E^0 (V)	Cathodic reactions	E^0 (V)
$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$	−0.43	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$H_2 \rightarrow 2H^+ + 2e$	−0.4	$MnO_2(s) + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O$	1.23
$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^-$	−0.28	$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.5
$H_2S \rightarrow S^o + 2H^+ + 2e$	−0.28	$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$	0.361
$H_2S + 4H_2O \rightarrow SO_4^{2-} + 6H^+ + 8e$	−0.22	$Fe^{3+} + e \rightarrow Fe^{2+}$	0.77
$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e$	−0.24	Fumarate + H^+ + e → Succinate	0.03
$NADH \rightarrow NAD^+ + H^+ + 2e$	−0.32	$2NO_3^- + 12H^+ + 10e \rightarrow N_2 + 6H_2O$	0.74
		$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O$	0.433

Source: He and Angenent (2006)

microbial consortia using physical and chemical treatment (Rajesh et al. 2014; Tiwari and Ghangrekar 2015); whereas using oxygen reduction catalyst the cathode kinetics can be enhanced (Noori et al. 2016a). The similarity of substrate degradation characteristics of both biological system using microorganisms led to the concept of combination of CWs and MFCs, which resulted in a most promising approach of CW-MFC for wastewater treatment and renewable energy tapping. The very first report on performance of CW-MFC was documented by Yadav et al. (2012) which was used to treat synthetic wastewater containing azo dye. CW-MFCs or SMFCs possess narrow difference in terms of system architecture. The difference of these two systems could be pointed out based on their feed uptake mechanism by electricigens. SMFCs allow electricigens to take feed from the rhizodeposits, exudates and secondary metabolites of aquatic animals, whereas rhizodeposits and wastewater serves as substrate medium for electricigens in CW-MFC (Strik et al. 2008). It is reported that the root of living plants can increase the substrate to the electricigens, which may result in as much as 18-times higher power as compared to the fresh water SMFCs (Timmers et al. 2012).

This chapter addresses the SMFC and CW-MFC to develop better understanding of the parameters influencing performance of these. A brief summary of previous research has also been included which deals with the application of SMFCs as power source for operating wire-less sensors. With limited researches performed in the past, the aspects of CW-MFCs are discussed for summarizing the current trends, application potential and future research needs to improve the performance.

17.2 Fundamentals of SMFCs and CW-MFCs

SMFCs have added advantage for field application because they require less attention for operation and maintenance, can power remote sensors (Gong et al. 2011) and also can provide *in situ* remediation of aquaculture ponds for maintaining healthy aquatic environment (Sajana et al. 2013a). A SMFC can be easily fabricated and installed by inserting an anode in sediment up to a depth of 5–10 cm from sediment-water interface in which degradation of organic matter and collection of electrons occurs. A cathode should be placed just below the air-water interface, on which reduction of TEA (mostly O_2) occurs by combining electrons and protons. The anode and cathode should be connected through corrosion resistant conductive materials (such as copper and aluminum) across an external load as shown in Fig. 17.1a.

There are three possible mechanisms reported for electron transfer from micro-organisms to anode: (1) Direct contact of *c*-type cytochromes; (2) Nanowires (conductive pili); and (3) Redox mediators or electron shuttle (Sajana et al. 2013a). The losses during oxidation of organic matter to generate electron and proton and subsequent reduction in cathode are considered as bottlenecks of these systems. These losses can be listed as thermodynamic loss, activation loss, ohmic loss and concentration loss and can be seen during polarization study. Many studies in past few years have successfully identified the parameters affecting the performance of SMFCs and CW-MFCs. These parameters include the electrode material (Dumas et al. 2007), distance between the electrodes and pH (Sajana et al. 2013b), temperature (Liu et al. 2005), dissolved oxygen (DO) near the cathode (Saravanan et al. 2010), organic matter in the sediment (Sajana et al. 2014) etc. In successive sections, brief description on the parameters affecting the performance of SMFCs and CW-MFCs is presented.

Though the concept of CW-MFC is new for wastewater treatment and simultaneous recovery of bio-electricity, these two distinctive systems, CWs and MFCs, have been explored widely for wastewater treatment. CW-MFCs are subclass of SMFCs and between them the feeding mechanism to the electricigens are possibly the main distinction. CWs possess anaerobic and aerobic strata throughout their soil depth and the water column (Yadav et al. 2012); hence a CW-MFC can be developed by embedding an anode in the deep layer of soil and a cathode on the water column (soil surface) or in rhizosphere (Fig. 17.1b). The incorporation of plants in SMFC creates system similar to the CW-MFC. Therefore, in some literatures both the technologies were placed in the same category (Xu et al. 2015).

17.3 Factors Affecting the Performance of SMFCs and CW-MFCs

17.3.1 Electrode Materials

Power generation in SMFCs is truly based on the characteristics of electrode materials and it was found limited by kinetics of anode and cathode. As for example, an anode should possess biocompatibility for bacterial cell adhesion, it should be highly conductive and super hydrophilic (Wu et al. 2015); whereas a better cathode material with excellent catalytic activity and high electronic conductivity can enhance oxygen reduction reaction (ORR) (Noori et al. 2016b). Numerous kinds of electrode materials such as stainless steel wire mesh (Song et al. 2011), graphite plates (Mohan et al. 2009) and carbon cloth (Des Jarlais et al. 2013) have been investigated in SMFCs. The electrode material used should be corrosion resistant, since it has to survive in highly exhaustive environment. Due to chances of high corrosion, the SS wire mesh has limited application in marine environment over carbon based electrode materials. Graphite granules with graphite rod as anode demonstrated ever highest power density of 380 mW m^{-2} till date (Nielsen et al. 2007). Song et al. (2012) reported power density of 75 mW m^{-2} using activated carbon felt as anode in fresh water SMFC.

Like SMFCs, the electrode materials affect the performance of CW-MFC. Due to high corrosion potential of iron-based electrodes in water logged medium (soil and sediments) they are susceptible to corrosion and cannot be used for prolonged period. Therefore, carbon based electrodes are always preferred for such applications since they can offer long term sustainability, high electrical conductivity and non-oxidative in nature and moreover they can facilitate large surface area for microbial attachment for biomass growth. Dordio and Carvalho (2013) reported enhanced COD removal by biosorption process from CWs using carbon granules. Granular activated carbon (GAC) as biocathode material for CW-MFC was found to be the most suitable with a power density of 55.05 mW m^{-2} as compared to the other tested materials, for instance carbon cloth (28.9 mW m^{-2}) and stainless steel (1.76 mW m^{-2}) (Liu et al. 2014). The enhanced performance using GAC in CW-MFC was attributed to its higher surface area to support ORR and the rational utilization of capillary action. Furthermore, the size of carbon granules was also observed to have influence on the performance of SMFCs, with smaller size of graphite granules between 0.25 mm and 0.5 mm, the current density was found to be 77.7 mA m^{-2} as compared to the lower value of 37.9 mA m^{-2} with large granule size between 1 and 5 mm (Arends et al. 2012).

In spite of electrode materials, the shape and architecture also have depicted profound effect on the performance of SMFCs. A better geometry of electrode with high surface area can facilitate better substrate diffusion resulting in high redox kinetics, thereby, enhancing the power recovery from SMFCs. Various shape of carbon-based electrode materials have been tested to evaluate its effect on the performance of SMFCs. Graphite rod anode in SMFC containing acetate enriched sediment recovered a power density of 19.57 mW m^{-2} as compared to the lower value of 8.72 mW m^{-2} with graphite disk anode (Sacco et al. 2012). Li et al. (2009) demonstrated that the SMFC with solid column graphite anode could be a better anode as compared to the graphite disk anode material due to enhanced surface area. The power density obtained from SMFC using graphite column anode was found to be 20.2 mW m^{-2}, which was 1.35-times higher than the SMFC using graphite disk anode (14.9 mW m^{-2}). Higher power density with graphite column anode can be attributed to the less diffusion hindrance of substrate due to large surface area.

17.3.2 Electrode Spacing and External Resistance

Distance between the electrodes can regulate internal resistance of SMFCs by regulating ohmic overpotential loss. Loss in potential energy experienced by MFCs during movement of proton and electron via natural voltage gradient between anode and cathode causes ohmic overpotential loss (Singh et al. 2010). The ohmic overpotential losses are proportional to the current and behaves linearly as current increases (Rismani-Yazdi et al. 2008). It can be calculated by measuring the gradient of linear portion of voltage vs. current curve. A reduced spacing in electrodes in MFCs can decrease ohmic overpotential loss by reducing proton transfer energy from anode to cathode (Krishnaraj and Jong Sung 2015). Current density obtained from the SMFC was observed to be a function of electrode distance; as the distance between anode and cathode was increased from 12 cm to 100 cm, the current density decreased from 11.5 A m^{-2} to 2.11 A m^{-2} (Hong et al. 2009). Sajana et al. (2013b) reported similarly on the reduction of power density of 3.1 mW m^{-2} with an electrode spacing of 100 cm as compared to the electrode spacing of 50 cm (4.29 mW m^{-2}). However, the chemical oxygen demand (COD) and total nitrogen (TN) removal efficiency was noticed higher in SMFC with 100 cm electrode spacing as compared to the 50 cm.

According to the Ohm's law, $I = V/R_{ex}$ (where I is current generation, V is voltage and R_{ex} is external resistance), the sustainable I from an MFC and SMFC is a function of R_{ex}. The effect of R_{ex} on the performance of MFC has been demonstrated in earlier studies (Del Campo et al. 2014; Pinto et al. 2011). Increase in R_{ex} from 100 Ω to 1000 Ω drove positive effect on voltage generation from SMFC with substantial increase in operating voltage from 20 mV to 550–600 mV (Song et al. 2010a). Power density obtained from SMFC with varied R_{ex} was found to be enhanced from 0.064 mW m^{-2} when SMFC was operated with R_{ex} of 10 Ω to 0.413 mW m^{-2} (at R_{ex} of 100 Ω) and to 2.4 mW m^{-2} at R_{ex} of 1000 Ω (Hong et al. 2009). Song et al. (2010a) observed similar trend of power production of 0.0, 0.73, 1.66, 2.81 and 3.15 mW m^{-2} corresponding to the applied R_{ex} of 0, 100, 400, 800 and 1000 Ω in fresh water SMFC. This could be attributed to the fact that as the external resistance approached close to internal resistance the power production increases, and the internal resistance of SMFCs is generally higher. However, among all R_{ex} tested, higher organic matter removal efficiency of 29% at external resistance of 100 Ω was obtained in SMFC, whereas lower organic matter removal efficiency of 10.3% was obtained at R_{ex} of 1000 Ω.

17.3.3 Effect of Catalysts and Mediators

Role of catalysts in MFCs had been well documented and most of the results showed significantly higher power output as compared to the SMFCs provided without catalyzed cathode or anode. As for example, results have proven that the complex substrates such as cellulose and molasses can be effectively used in MFCs as substrate in presence of *Clostridium* biocatalysts (Niessen et al. 2005). Moreover, it has been observed that the sufficient availability of H_2 in anode could increase the methanogenic activity (Conrad 2002) and reduces the performance of SMFCs. Anode coated with platinum-poly (3,4-ethylenedioxythiophene) (PtPEDOT) bilayer composite biocatalysts can oxidize H_2 at anode, which decrease the methanogenic activity on anode of SMFC and improves the performance (Rosenbaum et al. 2005). An anode modified with mediators such as anthraquinone-1, 6-disulphonic acid (AQDS) and 1, 4-napthoquinonone (NQ) had enhanced the power density of SMFCs. A fivefold higher power density of 98 mW m^{-2} in SMFC was obtained using AQDS modified graphite plate as compared to the SMFC using plane graphite plate without any modification (Reimers et al. 2001).

Oxygen is the most feasible and sustainable TEA for the application of SMFCs due to high reduction potential and abundant availability in pond and marine environment in dissolved form. However, slow-moving ORR and high overpotential losses had been a bottleneck to achieve considerable power from the SMFCs (Noori et al. 2016c). Therefore, the cathode reduction kinetics need to speed-up using suitable catalysts. Platinum (Pt) catalyzed cathodes demonstrated promising results when used in MFCs and SMFCs due to reduced activation energy barrier to accomplish ORR. He et al. (2007) reported power density of 49 mW m^{-2} using Pt catalyzed carbon cloth cathode in SMFC. A platinum (Pt) modified carbon felt cathode could produce 207 mW m^{-2} from marine SMFC (Mathis et al. 2008). Though Pt catalyzed cathode delivered attractive results, its high cost and acute poisoning due to presence of H_2S could be a challenging task to implement in SMFCs, especially in marine environment. Hence, low-cost iron-cobalt based catalyst was developed to replace Pt. Cathode mounted on carbon paper with iron doped tetramethoxyphenyl porphyrin (Fe-CoTMPP) catalyst noted almost 300-times higher power density of 62 mW m^{-2} as compared to plain carbon paper (0.2 mW.m^{-2}) (Scott et al. 2008).

Natural water bodies containing diverse microorganism population are capable of performing catalytic activity for ORR (He and Angenent 2006). Later, this distinctive property of microorganisms shaped the opportunity of biocathode development. Hasvold et al. (1997) observed enhance ORR due to formation of biofilm on cathode which reveals that the cathode biofilm can function as biocatalyst. Application of biocathodes in SMFCs can be advantageous for several reasons. First, the cost of construction and operation of SMFCs may be lowered. Second, metal catalysts or artificial electron mediators could be poisoned by pollutants present in natural water. Third, microorganisms can function as catalysts to assist the electron transfer. Maximum power density of 1 W m^{-3} was observed using floating foam box reinforced carbon cloth biocathode in marine SMFC (Wang et al. 2012). Algal biocathode has been seen to produce oxygen in cathode, which could be an added benefit to overcome oxygen depletion in cathode (Mohan et al. 2014). Berk and Canfield (1964) reported maximum open circuit potential of 0.96 V with short circuit current of 750 mA m^{-2} using blue-green marine algae in the cathode of MFC. An algae assisted cathode could produce maximum power density of 21 mW m^{-2} and could be further enhanced to 38 mW m^{-2} using carbon nanotube coated cathode (Wang et al. 2014). Due to chances of acute poisoning of metal-based catalyst in aquatic environment, thermodynamic overpotential loss occurs, thereby, reducing the power output. Hence, the use of biocathodes has been advocated as sustainable solution for SMFCs.

17.3.4 Effect of pH, Dissolved Oxygen and Temperature

The pH of water and sediment plays an important role in the performance of MFCs and SMFCs, a mid-range alkaline pH range between 7 and 8 was suggested to obtain high current (He et al. 2008). Under alkaline range (pH 9), the biofilm attached to the anode was found to be more electrochemically active as compared to the acidic pH 5. At pH <6, reduction in power generation was also reported (Behera and Ghangrekar 2009). However, acidophilic pH around 6 or less may impart positive affect on the metabolism of microorganisms, which results in releasing additional electrons and protons (Mohan et al. 2009). In a different study with acidic pH <3, the SMFC demonstrated sustainable power density and current density of 0.3 W m^{-2} and 3.5 A m^{-2}, respectively (García-Muñoz et al. 2011). Sajana et al. (2013b) reported slight reduction in COD removal efficiency when pH of feed was increased from 6.5 (79%) to 8.5 (77%). Moreover, at pH 8.5 SMFC produced higher power density of 4.29 mW m^{-2} as compared to the power density of 3.5 mW m^{-2} obtained at pH of 6.5. The effect of pH on the performance of SMFCs is still confusing and no clear concluding remarks can be drawn from the previous experiments possibly due to the dynamic behaviour of biological system. However, a better performance can be expected in the pH ranging between 6 and 9.

The dissolved oxygen (DO) concentration at the cathode reaction interface greatly affects power recovery of SMFC and should be high enough to maintain the ORR (An et al. 2011). The DO concentration in natural aquatic environment fluctuates by microbial activity due to presence of organic matter (Zhang et al. 2009) as well as with fluctuations in temperature (Manasrah et al. 2006). For example, growth of microorganisms on cathode consume oxygen during respiration and if the re-oxygenation rate is lower than consumption rate, the water becomes oxygen depleted (Nguyen et al. 2006). An et al. (2011) developed bi-functional anti-microbial and catalytic cathode using silver nanoparticle (Ag-NPs) to overcome the problem of oxygen depletion. Results showed that after getting stable OCV of 0.67 V on 9th day in SMFC using plain graphite cathode the OCV was observed to be declining during consecutive days of operation until 50 d due to microbial growth of biomass (9.69 g of cell protein/g of electrode). As compared to the plain graphite cathode, less microbial growth in Ag-NPs treated cathode (5.3 g of cell protein/g of electrode) prevented to deplete DO concentration, which resulted in maintaining consistent cell voltage. Furthermore, when the DO concentration was increased from 3 to 7 mg/l, the current density obtained from SMFC was enhanced from 23 mA m^{-2} to 25.5 mA m^{-2} (Hong et al. 2009).

The performance of SMFC is found to be greatly influenced by temperature due to uneven fluctuation in DO and effect on microbial activity. Though at low temperature, the DO concentration would be high in water but most of the anaerobic microorganisms to be developed on anode show their activity in the mid temperature range of 20–25 °C excluding *Geobacteraceae,* which can grow at 4 °C. The current density was found to be increased from 15.6 mA m^{-2} to 52.6 mA m^{-2} when the operating temperature was increased from 10 to 35 °C (Hong et al. 2009). Schamphelaire et al. (2008) also observed reduction in power density from 231 mW m^{-2} to 157 mW m^{-2} when the temperature was decreased from 20 °C to 13.2 °C in rice field soil SMFC. Renslow et al. (2011) observed that the performance of freshwater SMFC decreased linearly with decrease in the temperature. The decrease temperature can reduce the microbial activity, resulting in high electrode resistance and less power recovery. Huang et al. (2012) reported disrupted anode kinetics due to seasonal change in environmental temperature.

17.3.5 Plants

The plant interactions regulate the ecological function of CWs similar to the natural wetland. However, it is still unclear that which plant types can enhance the performance of CWs. The relation between plants root canopy and density as a function of microbial population and its effect on the treatment performance of CWs was attempted to establish, but unfortunately the relationship has not resulted in sound evidence (Reed et al. 1995). Perhaps to use the locally available plants in study area of CW-MFCs would be a better solution (Xu et al. 2015). It would be of great interest to understand the effect of density and canopy of plants on the microbial growth and on the electrode kinetics. Plants can influence the distribution of electron donor/ acceptor by increasing the oxygen concentration due to their physical effect on water flow. Plants also have number of other functions such as creating surface area from bacterial attachment and biofilm formation, supplying carbon to the microorganism, up taking of some contaminants etc. Inclusion of plant roots of *Ipomoea aquatica* at the cathode was reported to improve the power generation of CW-MFCs by 142% as compared to the unplanted and rhizosphere-anode CW-MFCs (Liu et al. 2013). As shown in Table 17.2, *Ipomoea aquatica* and *Phragmites austrails* are the two major species of plant which have been majorly investigated in the CW-MFCs for phytoremediation of wastewater.

Table 17.2 Performance comparison of CW-MFCs under different substrate flow pattern and aquatic plant

Wastewater	Flow pattern	Plant	COD removal (%)	CE (%)	Power density (mW m^{-3a})	References
Swine	Vertical	*Phragmites australis*	76.5	0.1–0.6	42	Zhao et al. (2013)
Synthetic	Batch mode	*Canna indica*	75	75	0.05–0.06 mW m^{-2}	Yadav et al. (2012)
Synthetic	Vertical subsurface	*Ipomoea aquatica*	95	2.8–3.9	44.63 mW m^{-2}	Liu et al. (2014)
Synthetic	Vertical	*Ipomoea aquatica*	94.8	0.39–1.29	12.42 mW m^{-2}	Liu et al. (2013)
Swine	Vertical	*Phragmites australis*	80		268	Doherty et al. (2015b)
Synthetic	Vertical	*Ipomoea aquatica*	85.7	0.5	852	Fang et al. (2015)
Synthetic	Vertical	*Ipomoea aquatica*	85.7	0.58–1.71	5.62 mW.m^{-2}	Fang et al. (2013)
Municipal	Horizontal	*Phragmites australis*	81.6	–	< 1	Corbella et al. (2014)
Synthetic	Horizontal	*Phragmites australis*	95	0.3–0.5	94	Villasenor et al. (2013)

[a]Otherwise stated; *CE* coulombic efficiency

17.3.6 Operating Conditions

For developing the natural redox gradient, which is an obligatory parameter for producing current from bio-electrochemical systems, most of the CW-MFCs were operated under up-flow regime of feeding (Fang et al. 2015; Liu et al. 2013). This type of feeding arrangement can minimize the DO concentration at anode and ensure higher substrate availability while maximizing DO at cathode. However, the up-flow regime to maintain natural redox gradient results in large electrode distance and subsequently contributes higher ohmic resistance to the system (Doherty et al. 2015a). For example, the internal resistance of 500 Ω obtained from CW-MFC (Doherty et al. 2015a) was found higher than 33 Ω for a multi-electrode MFC with separator electrode assembly (Ahn and Logan 2012).

Doherty et al. (2015b) proposed a design to minimize electrode separation and enhancing the power recovery by 70% wherein anode and cathode were separated with glass wool and combined flow, up-flow at anode and down-flow at cathode, was adopted simultaneously. However, long term operation of this design of CW-MFC resulted in clogging problem for the plants roots, hence not allowing them to penetrate the wetland soil subsurface (Doherty et al. 2015b). The performance of CW-MFC was enhanced by using bentonite layer as a separator and recirculating the flow of substrate from bottom to top of the wetland. However, the electricity recovery was compromised at higher organic loading because the anode was not capable to fully oxidize the organics (Villasenor et al. 2013).

17.4 Electricity Generation as a Function of Wastewater Treatment

Constructed wetlands are being considered as low-cost solution for wastewater treatment from past few decades (Hammer 1989). Lots of research have been conducted to enhance the performance of CWs by improvising different design, including different species of plants, manipulating soil characteristics and integrating other biological system such as MFCs. The very first report in integrated CW and MFC system demonstrated 75% COD removal efficiency (Yadav et al. 2012). CW-MFC planted with *Ipomoea aquatic*a demonstrated slightly higher COD removal efficiency of 94.8% than that obtained from unplanted CW-MFC (92.1%) (Liu et al. 2013). Unlike the COD removal, a substantial difference in total nitrogen efficiency was observed in planted CW-MFC (90.8%) and unplanted CW-MFC (54.4%) possibly due to assimilation of nitrogen in plants. Furthermore, planted CW-MFC showed enhanced power density of 12.42 mW m^{-2} as compared to the unplanted CW-MFC (5.13 mW m^{-2}).

Furthermore, CW-MFCs were also found to be capable of removing specific compounds such as azo dye from wastewater. Fang et al. (2013) obtained 91.1% removal efficiency of azo dye active brilliant red X-3 (ABRX3) and power density of 0.3 W m^{-3} when a CW-MFC was operated under 3 d HRT. Discolouration efficiency was also found to be affected by the operation modes such as close circuit and open circuit. As for example, in the same study, a 15% higher discolouration was observed when CW-MFC was operated under current generation mode (close circuit mode) than that of open circuit mode. CW-MFC treating high strength synthetic wastewater containing 500 mg/l of methylene blue dye demonstrated 93.1% discolouration rate with power density of 15.73 mW m^{-2} after 48 h of contact time (Yadav et al. 2012). Anode acts as an insoluble terminal electron acceptor while promoting the degradation of dye thereby increasing the metabolic rate of anaerobic microorganism and enhancing the substrate consumption, which eventually facilitates more electrons to accelerate discolouration rate from wastewater.

Though the inclusion of MFCs in CWs improves the COD removal efficiency (Doherty and Zhao 2015), only 0.05% to 3.9% of COD removal could be converted into electricity (Doherty et al. 2015a). Most of the researchers have reported low coulombic efficiency (CE) in SMFC, up to 3.9% (Table 17.2), suggesting that very little amount of electricity would be possible to convert from degradation of bulk organic compounds.

17.5 Scaling Up of SMFCs and Operating Wireless Sensors

SMFC is a promising alternative renewable energy source which can generate electricity for powering remote sensors, requires low maintenance and can provide alternate wastewater treatment option at low cost. Scaling-up of this technology is quite difficult with a specific configuration. However, researchers have claimed that Watt-level of power density could be obtained from MFCs and SMFCs. For example, Song et al. (2010b) demonstrated an MFC with energy generating capacity of 100 W m^{-3}, whereas a 30 ml MFC could generate a power density of 4.3 W m^{-2} (Fan et al. 2012). However, these normalized power densities were estimated based on the results obtained from laboratory scale MFCs. In the initial stage of development of SMFCs, it was expected that the power output from a SMFC would improve proportionally with increase in electrode size, but practically the power density does not depend on the surface area of the current limiting electrode (Ewing et al. 2014). A study revealed that for enhancing the power density from MFCs up to two-fold, the electrode surface area should be increased by 100-times (Dewan et al. 2008). This way of enhancing power from SMFCs or MFC for real time application does not seem feasible solution at all, since a huge electrode area would be problematic to bury in sediment in remote location. Moreover, it would be implacable to install such a huge SMFC to operate a single remote sensor. However, providing a power management system coupled with charge pumps and supercapacitors may be a feasible solution (Gong et al. 2011; Tang et al. 2015).

Ewing et al. (2014) developed a strategy to operate 2.5 W remote sensor using power obtained from MFC by intermittent harvesting and storing in supercapacitors. Multiple small-size electrodes with parallel connection rather than using a big single electrode may be a good solution for getting applicable power to operate wire-less sensors (Ewing et al. 2014). SMFCs fabricated with four anodes of 0.36 m^2 surface area (0.09 m^2 each) connected in parallel provided the power of 2.3 mW vs. 0.64 mW, where the latter was obtained from the SMFC using a single anode with surface area of 0.36 m^2. This power obtained was used to operate a wire-less temperature sensor using customized power management system (PMS). A 18 mW metrological buoy has been set-up by Naval Research Laboratory, USA (NRL, USA) powered by benthic attended generators (BUGs) for remotely monitoring air-temperature, water-temperature, pressure and relative humidity (Tender et al. 2008). To remotely monitor environmental parameters and military tactical surveillance via wire-less sensors are the foremost promising applications of SMFCs. As far as SMFC is concerned, a wire-less sensor cannot be operated with power generated from SMFC due to inconsistent and low output voltage. Therefore, a PMS was developed to store sufficient energy in supercapacitors for intermittent use and to boost the voltage using DC-DC convertor up to the requirement of sensors (in most of the cases 5 V). Bandyopadhyay et al. (2013) propelled an underwater 25 W bio-robot vehicle for 165 s at a time using power recovered from SMFC. Furthermore, movement of fish and other aquatic life has been monitored using ultrasonic sensor powered by SMFC (Donovan et al. 2013). From the above discussion, it can be concluded that the SMFC could be a promising renewable source of energy, but certain controllable parameters such as electrode materials, electrode spacing, shape, external resistance etc. need further attention to improve performance. Moreover, to operate wire-less sensors, an optimized PMS could provide a long-term solution. Unfortunately, to the best of our knowledge, there is no research available which had used CW-MFC as renewable power source to operate wire-less sensors.

17.6 Conclusion

Various issues, challenges and opportunities of SMFCs and CW-MFCs have been reviewed. In the present situation, the pollution threats in fresh water bodies and depleting conventional sources of energy are the two main brainstorming concerns across the globe. Development of SMFCs is expected to provide solution to these problems. In near future SMFCs might take niche of many available treatment technologies to offer sustainable solution to sediment and water remediation and energy harvesting. However, the challenges related to fabrication, installation and performance optimization are still under development stage. Corrosion-free carbon-based materials such as carbon cloth, carbon/graphite felt, graphite plates/disc/column etc. should be used in SMFCs or CW-MFCs due to their appreciable performance and prolonged stability in exhaustive environment. The electrodes offer large surface area for biofilm development/to accomplish higher ORR. However, this is found to have noticeable effect on the wastewater treatment and electricity recovery. To obtain high electrical current, comprehensive strategy on the operating parameters including optimized electrode spacing, external resistance, plant type, pH, temperature and DO need to be explored while maintaining natural redox gradient, substrate availability and required condition to trigger ORR in the system. Finally, an efficient PMS would provide opportunity to utilize the power generated by SMFCs for wire-less sensor operation for tactical surveillance, metrological monitoring etc.

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