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# MICROBIAL FUEL CELLS – AN OPTION FOR WASTEWATER TREATMENT

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## Abstract

The Microbial Fuel Cell (MFC) is a promising technology for efficient wastewater treatment and recovering energy as direct electricity for onsite applications. For treatment of biodegradable organic matters in MFCs, removal efficiencies comparable with established treatment methods can be obtained. Even some of the bio-refractory compounds can be effectively removed in MFCs. Power densities higher than 2 W/m<sup>2</sup> and volumetric power of 500 W/m<sup>3</sup> are reported. However the power output varies drastically depending on the MFC configuration, substrate used, type of bacterial culture and operating conditions. The results presented so far demonstrated that electricity can be generated by exploiting microorganisms as biocatalysts, but both technical and biological optimizations are needed to maximize power output. The advantages of using MFCs for wastewater treatment, the organic matter removal efficiency and electricity generation reported recently for different MFC configurations are described in this paper. Factors affecting performance of the MFC are summarized. MFC scale-up issues and further development needs are emphasized. This information on factors affecting MFC performance and scale-up issues would be very useful tool for researchers for shifting this technology from lab-scale to pilot and full-scale applications for sustainable wastewater treatment.

*Key words:* electricity generation, factors affecting performance, MFC design, scale-up, wastewater treatment

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## 1. Introduction

The high energy requirements of conventional wastewater treatment systems are demanding for an alternative treatment technology. This treatment technology should be cost effective, requiring less energy for its efficient operation, and should generate energy in such a form that would make overall operation of wastewater treatment self sustainable. Organic matter present in the wastewater can be considered a valuable material acting as a renewable source of energy. The energy available in organic wastewaters can be harvested as electricity by using Microbial Fuel Cell (MFC). Bacteria can be used to

catalyze the conversion of organic matter into direct electricity while accomplishing the biodegradation of organic matter to carbon dioxide as an end product (Allen and Bennetto, 1993; Bond, 2003; Kim et al., 2002). Therefore, wastewater treatment and simultaneous direct electricity recovery in MFC allows this device to be used as a power source for onsite appliances (Park and Zeikus, 2000).

Application of MFC for wastewater treatment (Liu et al., 2004) has several advantages, such as a high efficiency for energy conversion of the organic matter into electricity, even working at lower mesophilic temperatures, and the absence of any toxic products. In addition a wide diversity of organic

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compounds present in wastewaters can be used as substrates in MFC to produce electricity and compensate the cost of treatment (Davila et al., 2008). MFCs, if used for wastewater treatment, can provide clean and safe energy for people, apart from effective treatment of the wastewaters with and low noise and emissions.

The property of using bacteria or enzymes as a catalyst in electrochemical reactions opens up several potential applications for this technology. MFC is an emerging technology which holds promise towards sustainable power generation and wastewater treatment along with applications in broad areas of life sciences. The MFCs will have potential applications in the following areas: (a) wastewater treatment and energy recovery (Erable et al., 2010; Liu et al., 2004); (b) renewable energy generation from biomass (Rittmann, 2008; Strik et al., 2008; Venkata Mohan et al., 2010b); (c) onsite power generation in remote areas and power supply for sensors using indigenous biodegradable fuels (Fan et al., 2007); (d) biosensors for detection of various oxidizable compounds (Karube, 1985); (e) rapid estimation of bacterial food contamination (Patchett et al., 1988); (f) detection of microbial cell population in polluted water streams (Maoyu and Zhang, 1989); (g) bio-hydrogen production (Chae et al., 2008); and (h) bioremediation of petroleum contaminants in the groundwater (Morris and Jin, 2008).

This review is structured in five parts. The working principle of MFC is followed by the discussion on potential applications of the MFC for wastewater treatment and power generation reported. The different factors affecting the MFC performance are discussed followed by a discussion of the outlook of MFC.

## 2. Working principle of MFC

The schematic representation of the two chambered, MFC functionality is presented in Fig. 1. An anode and a cathode are each placed in aqueous solutions in two chambers separated by a Proton Exchange Membrane (PEM). Microbes in the anode chamber oxidize fuel (electron donor) generating electrons and protons. Current generation is due to the nature of microorganisms, as they transfer electrons from a reduced electron donor to an electron acceptor at a higher electrochemical potential. Anode Respiring Bacteria (ARB) in an anode biofilm carry out an oxidation half-reaction of organic matter, producing electrons from renewable biomass, including wastes, and producing one proton for every electron (Torres et al., 2008).

Carbon dioxide is eventually produced as an oxidation product. Electrons are transferred to the cathode through the external circuit, powering the external device, and protons are transferred internally through the membrane. Electrons and protons are consumed on the cathode, reducing oxygen to water and generating electricity. Unless the species in the anode chamber are anodophiles, the microbes are

incapable of transferring electrons directly to the anode (Du et al., 2007).

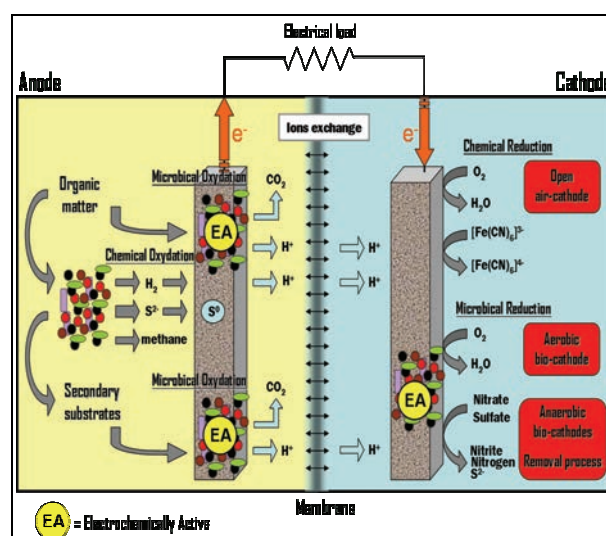


Fig. 1. Schematic representation of microbial fuel cell working principle

Hence to enhance power output of the device, electron mediators are sometimes used in the MFCs to accelerate the electron transfer, particularly when it is aimed at onsite power generation. Mediators like neutral red, methylene blue, thionine, Fe(III)EDTA are used in the anodic chamber for this purpose (Davis and Higson, 2007). Mediators in an oxidized state are reduced by accepting electrons. These electrons are released to the anode and mediators are oxidized again in bulk solution in the anode chamber (Du et al., 2007). This cyclic process accelerates the electron transfer and enhances the power output of the MFC.

### 2.1. Mediator-less MFC

Studies have shown (Gil et al., 2003; Kaufmann, 2001) that complex microbial communities used in MFCs treating wastewater produce soluble redox mediators, e.g., pyocyanin (Rabaey et al., 2004). It has been shown that certain metal-reducing bacteria, belonging primarily to the family *Geobacteraceae* can directly transfer electrons to electrodes using electrochemically active redox enzymes, such as cytochromes, on their outer membrane (Kaufmann, 2001). Furthermore, *Geobacter sulfurreducens* is known to transfer electrons beyond cell surfaces to electrodes through membrane proteins (Bond, 2003; Chaudhuri, 2003) or nanowires (Reguera, 2005). The electron transfer between the electrode and *E. coli* cells is reported to be carried out by soluble compounds in the culture (Zhang et al., 2008c). *E. coli* cells evolved under electrochemical tension in a MFC pose direct electrochemical behavior due to excretion of hydroquinone derivatives through a highly permeable outer membrane (Qiao et al., 2008). In addition to these species, metabolites produced by *Pseudomonas*

*sp.* enable gram-positive bacteria to achieve extracellular electron transfer (Pham et al., 2008). The *Shewanella oneidensis* culture is also reported to be useful as an anodic bio-film in a miniature MFC, where they are reported to metabolize lactate solution and produce higher power (Ringeisen et al., 2006). Several other anodophilic bacteria have been identified in recent research. MFCs containing such Electrochemically Active Bacteria (EAB) do not need mediators for electron transfer to electrodes and are called mediator-less MFCs. Mediator-less MFCs are considered to have more commercial potential, because mediators are expensive and can be toxic to the microorganisms (Bond and Lovely, 2003).

## 2.2. Membrane-less MFC

The MFC will receive limited acceptance for wastewater treatment if an expensive membrane is used for its fabrication. Proton transfer through the membrane may be a limiting factor, especially with fouling from suspended solids and soluble contaminants in a large scale wastewater treatment process, a likely issue. Hence, to make MFC economically competitive, it is essential to find a low cost alternative membrane or design the cell to eliminate the membrane.

To reduce the fabrication cost the MFC can be fabricated without using membrane. Such membrane-less MFCs are reported to be successful in converting organic contaminants to electricity (Ghangrekar and Shinde, 2007; Jang et al., 2004). However, the membrane-less MFC design causes a large quantity of oxygen to diffuse towards the anode and reduces the Coulombic Efficiency (CE). Higher power density of 346 mW/m<sup>2</sup> is reported in mediator-less and membrane-less MFC using plastic sieves rather than PEM (Zhan et al., 2008). A maximum power of 49 W/m<sup>3</sup> (215 A/m<sup>3</sup>) is reported for membrane-less MFC (You et al., 2008). A baffled membrane-less MFC was developed using anaerobic thick sludge near the cathode, with minimum mixing (Hu, 2008). A CE more than 30% is reported in this baffled MFC using glucose as substrate. Effectiveness of J-cloth (Associated Brands LP, as reported by authors) as a membrane (separator between the anode and cathode), instead of PEM, was evaluated. Due to the significant reduction of oxygen diffusion with two layers of J-Cloth, over 100% increase in CE was demonstrated in comparison with those without (Fan et al., 2007). Using a cloth electrode assembly (cloth sandwiched between anode and cathode), reduced the internal resistance and resulted in a power density of 627 W/m<sup>3</sup> in fed-batch mode and 1010 W/m<sup>3</sup> in continuous-flow mode (Fan et al., 2007). This power production is among the highest reported powers for the MFCs.

Behera et al. (2010a) have demonstrated the performance of a low cost MFC, made of earthen pot without employing the commercially available expensive membrane. Maximum power output of 16.8 W/m<sup>3</sup> is reported in this earthen pot MFC during

synthetic wastewater treatment. Total production cost for the anode chamber less than 1.0 US\$ is reported for this MFC. This MFC demonstrated competitive performance compared to MFCs with polymer membrane and MFCs provided with expensive cathode catalyst (Behera et al., 2010a). However, the stability of clay material in large scale reactor may be an issue and successful design of the MFC on commercial scale seems unlikely.

## 3. Wastewater treatment using MFC

### 3.1. Organic matter removal in MFC

#### 3.1.1. Treatment of easily biodegradable organic matter

MFCs have been operated successfully on a variety of organic matters represented by pure chemicals to complex wastes. Wide varieties of substrates have been tested, such as glucose, acetate, butyrate (Liu et al., 2005), cysteine (Logan et al., 2005), proteins (Heilmann and Logan, 2006), and lignocellulose (Rismani-Yazdi et al., 2007). They have been developed to generate electricity directly from complex organic wastewater such as food processing wastewater (Oh and Logan, 2005; Wang et al., 2008b), brewery wastewater (Wang et al., 2008b), domestic wastewater (Ghangrekar and Shinde, 2008; Min and Logan, 2004; Rodrigo et al., 2007; You et al., 2006b), chemical wastewater (Venkata Mohan et al., 2008a; Venkata Mohan et al., 2008b), starch wastewater (Lu et al., 2009), swine manure slurry (Jung et al., 2008; Min et al., 2005), manure waste (Scott and Murano, 2007b), landfill leachate (You et al., 2006c), and meatpacking wastewater (Heilmann and Logan, 2006). The advantages of use of MFC for treatment of various industrial wastewaters have been stated by many researchers in the recent time. These industrial wastewaters include rice mill wastewater (Behera et al., 2010b), distillery wastewater (Mohanakrishna et al., 2010; Zhang et al., 2009), palm oil mill effluent (Cheng et al., 2010), cheese whey (Antonopoulou et al., 2010), dairy wastewater (Venkata Mohan et al., 2010a), and composite vegetable waste (Venkata Mohan et al., 2010b).

While treating swine wastewater in a dual chambered MFC, 86% removal of Chemical Oxygen Demand (COD) and 83% removal of NH<sub>4</sub><sup>+</sup>-N were achieved with the maximum power density of 45 mW/m<sup>2</sup> (Min et al., 2005). In another study, treating swine wastewater in the single chamber MFC, 84% COD removal is reported with maximum power density of 228 mW/m<sup>2</sup> (Jung et al., 2008). A single chamber MFC demonstrated successful treatment of full-strength brewery wastewater (2,239 mg COD/L) producing maximum power density of 483 mW/m<sup>2</sup> (12 W/m<sup>3</sup>) at 30°C and 435 mW/m<sup>2</sup> (11 W/m<sup>3</sup>) at 20°C (Wang et al., 2008b). During treatment of sewage in a single-chamber MFC, the maximum power density of 26 mW/m<sup>2</sup> and 80% COD removal was reported (Liu et al., 2004). In another study treating sewage, maximum power density of 25

mW/m<sup>2</sup> was reported, further stating that the presence of even small oxygen concentration in the anodic chamber rapidly leads to the deterioration of performance (Rodrigo et al., 2007).

While treating chemical industry wastewater a COD removal efficiency of 63% is reported at the Organic Loading Rate (OLR) of 1.4 kg COD/m<sup>3</sup>.d, producing current density of 863 mA/m<sup>2</sup> and power of 0.198 W/kg COD removed at 100 Ω external resistance (Venkata Mohan et al., 2008a). A meat packing wastewater, diluted to COD of 1420 mg/L, produced 80 mW/m<sup>2</sup> power density and Biochemical Oxygen Demand (BOD) removal efficiency greater than 86% (Heilmann and Logan, 2006). Power was increased by 33% by addition of salt (300 mg/L sodium chloride) due to increase in solution conductivity.

Electricity generation from landfill leachate was examined by using both a dual-chamber and a single chamber MFC (You et al., 2006c). Maximum power densities of 2.06 W/m<sup>3</sup> in the dual-chamber MFC and 6.82 W/m<sup>3</sup> in the single chamber MFC were reported. The difference in internal resistance of the two MFC systems was the main reason for the differences in power generation. In another study using upflow air-cathode membrane-free MFC treating original leachate, continuous electricity generation was demonstrated to produce a maximum power of 12.8 W/m<sup>3</sup> at a current density of 41 A/m<sup>3</sup> (Zhang et al., 2008a). NH<sub>4</sub><sup>+</sup>-N elimination from the leachate was reported to be a consequence of electrochemical-independent oxidation in the MFC.

Stable performance of the MFC is reported using manure sludge waste as a carbon source at the anode (Scott and Murano, 2007a). Using carbon cloth as both anode and cathode in this MFC, a peak power of the order of 5 mW/m<sup>2</sup> is reported; whereas, platinised carbon cathode doubled the power density (Scott and Murano, 2007b). Using manure sludge in a tubular MFC anode, a maximum power density of 30 mW/m<sup>2</sup> is reported, demonstrating it as a power supply device for remote applications (Scott et al., 2007). These studies have demonstrated that the energy-efficient treatment of wastewater is one of the most promising applications of MFCs. Under different operating conditions and with various reactor types used, COD removal ranging from 60% to 90% is reported in the literature (Table 1).

Most of the MFC configurations are reported to be capable of giving COD removal efficiencies ranging from 80 to 95 % while treating different wastewaters; demonstrating the utility of MFC as a wastewater treatment system. This efficiency is comparable with the popularly used anaerobic process, such as Upflow Anaerobic Sludge Blanket (UASB) reactor.

Synthetic wastewater generally gives higher organic matter removal and CE compared to actual wastewaters (Ghangrekar and Shinde, 2008). This behavior is due to a more complex nature of the organic matter present in actual wastewater than

synthetic wastewater, where usually a single carbon source is used by the researchers.

### 3.1.2. Treatment of cellulose containing wastewater

Apart from the treatment of soluble organic matter, it is interesting that MFCs can be used for the treatment of cellulose containing wastewater to generate electricity. Unlike typical soluble substrates that have been used as electron donors in MFCs, cellulose is unique because it requires a microbial consortium that can metabolize both an insoluble electron donor (cellulose) and electron acceptor (electrode). Successful electricity generation from cellulose-fed MFC is reported using a defined co-culture of *Clostridium cellulolyticum* and *Geobacter sulfurreducens* (Ren et al., 2007). The co-culture achieved maximum power densities of 143 mW/m<sup>2</sup> and 59.2 mW/m<sup>2</sup> from 1 g/L carboxymethyl cellulose and MN301 cellulose, respectively (Ren et al., 2007). The pure culture alone could not produce any electricity from these substrates.

While treating paper recycling plant wastewater the treatment efficiency was reported to be limited by conductivity (Huang and Logan, 2008a). When only wastewater (conductivity 0.8 mS/cm) was used as feed the power density of 144 mW/m<sup>2</sup> was produced with total COD, soluble COD, and cellulose removals of approximately 29%, 51%, and 16% (for 350-h batch cycle), respectively. When a 50 mM phosphate buffer solution (PBS, conductivity of 5.9 mS/cm) was added to the wastewater, power densities reached to 501 mW/m<sup>2</sup> (CE of 16%), with efficient removal of soluble COD (73%) and slightly greater total COD removal (76%) over a 500-h batch cycle. Cellulose was removed up to 96% during treatment. Further increasing the conductivity increased the power. These results demonstrate limitations of conductivity of actual wastewater to power production (Huang and Logan, 2008a).

Lignocellulose is the most abundant plant cell wall component of the biosphere and the most voluminous waste produced by our society. Lignocellulosic biomass-derived monosaccharides might be a suitable resource for electricity generation using MFC technology. Direct generation of electricity from monosaccharides of lignocellulosic biomass was examined using air cathode MFCs (Catal et al., 2008). The mixed bacterial culture, enriched using acetate as a carbon source is well adapted to all carbon sources tested. The maximum power density obtained from these carbon sources ranged from 1.24 to 2.77 W/m<sup>2</sup> at a current density range of 0.76 to 1.18 mA/cm<sup>2</sup>. d-Mannose resulted in the lowest maximum power density, whereas d-glucuronic acid generated the highest power density, with different adaptation time. The CE was reported to be in the range of 21 to 37%, at COD removal over 80% for all carbon sources tested (Catal et al., 2008).

**Table 1.** Performance of microbial fuel cell treating different wastewaters

Sl. No.	MFC Configuration, volume	Substrate	COD (g/L)	HRT (h)	pH	COD Removal (%)	Current density	Power Density (mW/m <sup>2</sup> )	Power / unit vol. (W/m <sup>3</sup> )	Reference
1	Single chamber, air cathode, 425 mL	Starch processing wastewater	4.852	--	7.0 ± 0.1	98.0	0.89 A/m <sup>2</sup>	2239	--	Lu et al., 2009
2	Dual chamber MFC, 0.75 L	Wastewater from bulk drugs, chemical intermediates, dye and dye intermediates, pesticides	12.1	--	7.82	~62	0.416 A/m <sup>2</sup>	65.82	--	Raghavulu et al., 2009
3	Air cathode single chamber, 0.9 L	Confectionery wastewater	1.00	--	7.0	>92	0.552 A/m <sup>2</sup>	373	1.495	Sun et al., 2009
4	Tubular MFC with air cathode, 200 mL	Acetate (40 mM)	--	--	7.0	--	--	--	6.1	Kim et al., 2009
5	Double cell design, anode volume – 450 mL	Diesel contaminated wastewater, range organics -C8 to C25	0.300 g diesel/L	--	3.0 (Cathode)	82	--	32	--	Morris et al., 2009
6	Double cell design, anode volume 300 mL	Synthetic wastewater	0.812 g/L of glucose	96	--	85 % (TOC)	0.76 mA	143	--	Zhu and Ni, 2009
7	Dual chamber fuel cell with total volume of 600 mL	Filtrated wastewater plus acetate (glucose or xylose)	1.13 g/L	--	7.6	--	0.55 A/m <sup>2</sup> (for acetate)	130 ± 5 (for acetate)	--	Thygesen et al., 2009
8	An overflow-type wetted-wall MFC (30 mL anode)	Acetate	1	--	--	--	42.08 A/m <sup>3</sup>	--	18.82 W/m <sup>3</sup>	Li et al., 2009
9	Dual chamber mediator-less MFC (240 mL anode and 240 mL cathode)	Domestic wastewater and glucose	0.50 – 0.60	--	7.0	--	0.6 A/m <sup>2</sup>	--	9.3	Wang et al., 2009
10	Dual chamber MFC, 1310 mL	Synthetic wastewater	0.47 – 0.51	48	7.2 – 7.6	90	0.071 A/m <sup>2</sup>	--	--	Jadhav and Ghangrekar, 2009
11	Single chamber air cathode, 1000 mL	Synthetic: starch, peptone, and fish extract	2.9	--	7 - 8	95 - 93	--	797 – 899	117 - 129	Shimoyama et al., 2008
12	Dual chamber, 200 mL anode and cathode	Sodium acetate in anode and Electroplating waste in cathode	0.204 g/L of Cr <sup>6+</sup>	25	2.0 in cathode	99.5 and 66.2% for Cr <sup>6+</sup> and total chromium	--	1600	--	Li et al., 2008b
13	Single chamber, down-flow, 900 mL	Landfill Leachate	0.468-0.630 (BOD)	4.7	anode 7.0, cathode 7.5	57% (BOD)	0.003 A/m <sup>2</sup>	0.19	--	Greenman et al., 2009
14	Graphite-granule anode, tubular air-cathode MFC (GTMFC) (95 mL)	Glucose	1.00	2.3	-	-	216 A/m <sup>3</sup>	-	50.2	You et al., 2007
15	Single chamber membrane free MFC with carbon cloth anode and cathode	Acetate	0.80	4.1 11.3 16.0	- - -	52 - 90 (acetate)	--	--	17 22 20	Liu et al., 2008
16	Up flow air cathode MFC (95 mL)	glucose	1.00	3.96	-	-	215 A/m <sup>3</sup>	--	49	You et al., 2008

17	Single Chamber MFC (SCMFC, 388 mL)	Domestic wastewater	0.22	3.0 6.0 12.0 33.0	7.3-7.6	40 - 50-70 80	-- 0.125 A/m <sup>2</sup> -- --	-- 26 12 --	-	Liu et al., 2004
18	Membrane-less MFC (MLMFC)	Glucose and glutamate	0.30	24.0	7.0	90	--	1.3	-	Jang et al., 2004
19	Dual-chambered MFC (310 mL)	Diluted cereal wastewater	0.595	-	6.0	95	--	81±7	-	Oh and Logan, 2005
20	Single-chambered air cathode MFC	Swine wastewater (i) non-diluted (ii) diluted (1:10)	8.32 0.832 g	44.0 72.0	- -	27 92	--	261 110	- -	Min et al., 2005
21	Flat plate MFC (FPMFC) with carbon paper anode and carbon cloth cathode (22 mL)	Domestic wastewater	1.00	1.1 4.0	7.0	42 79	--	72 43	- -	Min and Logan, 2004
22	Air-cathode single chamber MFC using PEM (28 mL)	Domestic wastewater Glucose	0.20-0.30 0.60	-	7.3-7.6 -	--	--	28 262	-	Liu and Logan, 2004
23	Dual-chambered MFC (400 mL anode and 400 mL cathode)	Cellulose	-	300	6.8	--	--	55	--	Rismani-Yazdi et al., 2007
24	Single chamber air-cathode MFC (26 mL) Graphite brush anode	Acetate	1.00	330	--	--	8.2 A/m <sup>2</sup>	2400 (of cathode area)	73	Logan et al., 2007b
25	Air cathode MFC	Settled sewage	0.07-0.20	1	-	33	--	2	--	Andresen and Hu, 2007
26	Dual chamber MFC (400 mL anode)	Rice mill wastewater	1.100-1.125	--	8.0	96.5	--	--	2.3	Behera et al., 2010b
27	Open air cathode (anode volume of 500 mL)	Distillery wastewater	0.0162	--	6.0	72.84	--	--	1.74	Mohanakrishna et al., 2010
28	USAB-MFC-BAF system	Strength molasses wastewater	0.127	--	--	53.2	4.95 A/m <sup>2</sup>	1410.2	--	Zhang et al., 2009
29	MFC-USAB mixed system	Palm oil mill effluent	8.0-10.0	48	--	95	0.273 A/m <sup>2</sup>	44.6	--	Cheng et al., 2010
30	Dual chamber, mediator less MFC (310 mL anode, 310 mL cathode)	Cheese whey	0.73	50	--	100	0.080 A/m <sup>2</sup>	18.4	--	Antonopoulou et al., 2010
31	Single chamber MFC (total volum of 550 mL)	Dairy wastewater	0.004	--	--	95.49	--	--	1.10	Venkata Mohan et al., 2010a
32	Single chamber mediatorless MFC	Composite vegetable waste	0.0007	--	--	62.86	0.240 A/m <sup>2</sup>	26.41	0.057	Venkata Mohan et al., 2010b

The results presented so far on the treatment of cellulose and power generation in MFC demonstrated that electricity can be generated from cellulose by exploiting microorganisms as biocatalysts, but both technical and biological optimizations are needed to maximize power output (Rismani-Yazdi et al., 2007).

### 3.1.3. Treatment of xylose

Xylose can also be used in the MFC as a substrate for electricity production. In a 0.77 L air cathode MFC, 83.5% xylose removal was reported

producing a power density of 13 W/m<sup>3</sup> (673 mW/m<sup>2</sup>) (Huang and Logan, 2008b). Rapid removal of xylose is reported within 8 h of the 60 h fed batch cycle. Increase in power under continuous flow mode is reported at a Hydraulic Retention Time (HRT) of 20 h (20 W/m<sup>3</sup>), with 66 % COD removal. Pentose and Humic Acids (HA) are the main components of hydrolysates, the liquid fraction produced during thermo-hydrolysis of lignocellulosic material.

Xylose (typical pentose) degradation as well as the effect of HA on electricity production in MFCs

was examined by Huang and Angelidaki (Huang and Angelidaki, 2008). In the absence of HA a power density of 83 mW/m<sup>2</sup> at a xylose concentration of 30 mM is reported. With addition of HA an increase of power density and CE up to 67.4% and 92.6%, respectively, is reported. Presence of digested manure wastewater was reported to increase the CE due to the contents of natural humic acid.

#### 3.1.4. Treatment of glycerol

The side stream generated during biodiesel production containing glycerol could be effectively used for anode oxidation in MFC. Thus, further energy recovery is possible from the biodiesel production wastewater. During glycerol oxidation the current production of 111 A/m<sup>3</sup> and power production of 23 W/m<sup>3</sup> is reported in the MFC (Clauwaert et al., 2008b).

### 3.2. Removal of other contaminants

#### 3.2.1. Chromium removal from wastewater

Apart from removal of organic matter, the MFC can also be used for the treatment and removal of other compounds which can participate in the redox reactions. One of the critical pollution problems arising from the electroplating industry is the generation of wastewater containing chromium. Hexavalent chromium usually occurs as highly soluble and highly toxic chromate, and is a suspected carcinogen and mutagen (Bulgariu et al., 2008; Coheci et al., 2009).

Electroplating wastewater containing Cr<sup>6+</sup> can be treated using MFC (Li, 2008). A novel approach to Cr(VI)-contaminated wastewater treatment in the cathode chamber was investigated, producing a maximum power density of 150 mW/m<sup>2</sup> (0.04 mA/cm<sup>2</sup>) and a maximum open circuit voltage of 0.91 V with a Cr(VI) concentration of 200 mg/l as electron acceptor (Wang et al., 2008a).

#### 3.2.2. Nitrification and denitrification

MFC have also demonstrated the capability of simultaneous organic matter removal and nitrification and denitrification facilitating nutrient removal (Clauwaert et al., 2007a).

At the cathode nitrified wastewater can accept electrons and achieve denitrification. Removal rates of up to 2 kg COD/m<sup>3</sup>.d and 0.41 kg NO<sub>3</sub><sup>-</sup>-N/m<sup>3</sup>.d were achieved in the anode and cathode compartments, respectively; whilst producing a maximum power and current of 34.6 W/m<sup>3</sup> and 133.3 A/m<sup>3</sup> of cathode volume, respectively (Viridis et al., 2008). A denitrification rate in cathode up to 0.146 kg NO<sub>3</sub><sup>-</sup>-N/m<sup>3</sup>.d is reported. The highest power output in the denitrification system was 8 W/m<sup>3</sup> of cathode volume with a cell voltage of 0.214 V and a current density of 35 A/m<sup>3</sup>. The denitrification and power production rates were reported to be limited by the cathodic microorganisms, which significantly participated in denitrification at a cathodic electrode

potential below 0 V (vs. standard hydrogen electrode, SHE).

The ammonia removal mechanism in a MFC was investigated by Kim et al. (2008). For the air-cathode system, the results suggested that nitrogen losses during electricity generation were increased due to ammonia volatilization, with conversion of ammonium ion to the more volatile ammonia species, as a result of an elevated pH near the cathode where protons are consumed.

In a two-chamber MFC, nitrogen losses were primarily due to ammonium ion diffusion through the membrane. This loss was higher with electricity generation as the rate of ammonium transport was increased by charge transfer across the membrane. Very little ammonia loss was reported due to biological nitrification and denitrification. In another study, removal of ammonium-nitrogen was not observed in the single chamber MFC while treating leachate (You et al., 2006c).

However, in a membrane-less MFC treating actual sewage, nitrogen removal of 59% is reported mainly due to nitrification and denitrification (Ghangrekar and Shinde, 2008). Thus, the results mainly indicate that nitrogen removal is favored in the cathodic side of two chambered MFC due to diffusion of ammonium-nitrogen from anode to cathode, through membrane or along with the wastewater in membrane-less MFC, followed by nitrification and denitrification in the cathode chamber.

#### 3.2.3. Treatment of acid mine drainage

The MFC concept can also be effectively used for the treatment of acid mine drainage and recovery of metals. While treating synthetic acid mine drainage in MFC, operated in fed-batch mode, a maximum power density of 290 mW/m<sup>2</sup> was reported at a CE greater than 97% (Cheng et al., 2007). Electricity generation was reported to be abiotic in nature. Ferrous iron was completely removed through oxidation to insoluble Fe(III), forming a precipitate at the bottom of the anode chamber and on the anode. Optimum conditions were reported at a pH of 6.3 and a ferrous iron concentration above 0.0036 M.

#### 3.2.4. Treatment of phenols and chlorophenol-containing wastewater

The MFC can be effective for treatment of wastewater containing phenol and other organic matter in the anode chamber (Bebeselea et al., 2009). A lower cell voltage is reported during treatment of phenol containing wastewater as compared to glucose as a carbon source (Luo et al., 2007). Chlorophenol (CP) containing wastewater can be used as an oxidant in the cathode chamber of the MFC. Thus, this bio-refractory compound can be treated simultaneously with the treatment of organic wastewater in the anode chamber. When 4-CP was used as an oxidant in the cathode chamber, maximum power density of 12.4 mW/m<sup>2</sup> and CE of 22.7% is documented (Gu et al., 2007). The 60 mg/L of 4-CP was completely



dechlorinated within 45 h in the MFC. The p-nitrophenol was completely degraded after 12 h in the cathode chamber of a MFC producing a maximum power density of 143 mW/m<sup>2</sup> (Zhu and Ni, 2009). Removal of p-nitrophenol was attributed to in situ generation of H<sub>2</sub>O<sub>2</sub> in the cathodic chamber acting as an oxidizing agent.

#### 4. Power generation

The major limitations for implementation of MFCs for electricity generation during wastewater treatment are relatively low power density and the fact that the technology is only in the laboratory phase, demanding proper methodology to scale-up for full scale application. Based on the potential difference  $\Delta E$  between the electron donor and acceptor, a maximum potential of nearly 1 V can be expected in MFCs, which is not much greater than about 0.8 V that is currently being reported by many researchers. However, by linking several MFCs together, the voltage can be increased. Power densities, varying in the wide range, from 20 mW/m<sup>2</sup> to more than 2 W/m<sup>2</sup> of anode surface area, are reported in literature for individual cell (Table 1). The power reduction while treating actual wastewater could be attributed to the presence of complex organic matter in the real wastewater, which is different than the synthetic organic matter to which the anodophilic cells are adapted.

Apart from technical variables like the anode or fuel cell design, the paths and mechanisms of the bioelectrochemical energy conversion decisively determine the MFC power and energy output. Electron transfer from the microbial cell to anode, as a process that links microbiology and electrochemistry, represents a key factor that defines the theoretical limits of the energy conversion (Schroder, 2007). With continuous research efforts on identifying more and more electrochemically active cells with multiple substrates acceptance; the MFC may soon evolve as a net power generating device while efficiently treating wastewater.

A maximum power density of 5850 mW/m<sup>2</sup> is reported in a two-chamber MFC using a complex electrode system consisting of tungsten carbide containing anode and graphite foil coated with pyrolyzed iron(III) phthalocyanine/ polytetra-fluoroethylene as a cathode (Rosenbaum et al., 2006). Selection of the correct electrode material and configuration plays an important role in obtaining maximum power from the MFC.

By using nano-crystalline platinum anchored carbon nanotubes based electrodes, nearly 6-fold increase in the power density (2470 mW/m<sup>2</sup>), as compared to graphite electrodes (386 mW/m<sup>2</sup>), is reported (Sharma et al., 2008). However, power densities greater than 100 mW/m<sup>2</sup> and close to 2 W/m<sup>2</sup> have been recently reported by many researchers with different modifications in MFC design and materials, and also by enriching proper anodophilic consortia.

The main disadvantage of a two chamber MFC is that the cathode solution must be aerated to provide oxygen to the cathode (Liu and Logan, 2004). The power output of an MFC can be improved by increasing the efficiency of the cathode, e.g. power is increased by adding ferricyanide to the cathode chamber (Park and Zeikus, 2003). It is possible to design a MFC that does not require the cathodes to be placed in water. Like hydrogen fuel cells, the cathode can be bonded directly to the PEM so that air oxygen can directly react at the electrode. This technique was successfully used to produce electricity from wastewater in a single chamber MFC (Liu et al., 2004).

Considerable difference in the power production per unit volume is reported in the literature. MFCs are reported to produce power per unit volume ranging between 2 W/m<sup>3</sup> and 102 W/m<sup>3</sup> depending upon the reactor configuration, the type of anodophilic culture and the substrates used (Kim et al., 2007a). Highest power per unit volume of 2.15 kW/m<sup>3</sup> is reported using *Geobacter sulfurreducens* in the anode (Nevin et al., 2008). With miniature MFC using *Shewanella oneidensis* strain and lactate as feed, power production of 500 W/m<sup>3</sup> is reported (Ringeisen et al., 2006). A decrease in overall energy recovery is reported with increase in current density (Liu et al., 2005).

It is evident from the literature that, smaller MFCs are likely to generate more power by effectively harvesting the electron than the larger size MFCs. It was reported that enlargement of the 0.183 L MFC reactor by a factor 2.9-3.8 reduced the volumetric power output by 60-67% (Clauwaert et al., 2007b). The maximum power production of the smaller MFC (0.183 L) was reported to be 83 W/m<sup>3</sup> for batch-fed systems (20-40% CE) and 65 W/m<sup>3</sup> for a continuous system, at an acetate loading rate of 1.5 kg COD/m<sup>3</sup>.d at 90 % CE. The reported power recovery varies considerably due to different configurations of the reactor used, materials used for the electrodes, and the anodophilic species used, as well as operating conditions. However, continuous improvement in the power density is being reported with advancement of the materials used for the electrodes and improved understanding of the process design and operating parameters.

#### 5. Factors affecting MFC performance

##### 5.1. Inoculum used in MFC

In the past, most researchers have used pure culture as inoculum in the anode chamber of the MFC. Facultative anaerobic bacterium, *Aeromonas hydrophila*, was reported to be electrochemically active and useful in the anode chamber of MFC (Pham et al., 2003). The facultative anaerobe *Enterobacter aerogenes* grows rapidly under aerobic conditions, consuming oxygen to oxidize organic substrates, and also grow under anaerobic conditions, degrading substrates into hydrogen and a residue.

Due to the property of H<sub>2</sub> production and O<sub>2</sub> consumption, they are very suitable for a MFC (Tanisho et al., 1989). A fairly large current density (ca. 600 mA/m<sup>2</sup>) was reported by using glucose as a substrate and a stainless-steel net electrode plated with platinum black. *Ochrobactrum anthropi* YZ-1 also demonstrated the ability to produce current using a wide range of substrates, including acetate, lactate, propionate, butyrate, glucose, sucrose, cellobiose, glycerol and ethanol (Zuo et al., 2008). A *Klebsiella pneumoniae* strain L17 biofilm developed on an anode also showed the ability to degrade starch and glucose to generate electricity (Zhang et al., 2008b). *K. pneumoniae* biofilm cells showed direct electron transfer from fuels to electrode.

Bacteria of *Shewanella* type are known for diversity of terminal electron acceptors they can reduce. This allows them to couple the oxidation of organic matter to the reduction of the various terminal electron acceptors that they encounter in their stratified environments, and are one of the primary families of bacteria used in MFCs (Logan et al., 2006). *Shewanella oneidensis* (originally known as *Shewanella putrefaciens*) is a nonfermenting, motile, facultative anaerobic bacterium found in suboxic sediments (Biffinger et al., 2008b). *Shewanella oneidensis* MR-1 is the wild type strain while *S. oneidensis* DSP10 is a spontaneous rifampin-resistant mutant more recently used in MFCs (Ringeisen et al., 2006). By increasing the acidity, the *S. oneidensis* MR-1 culture increases the current output (Biffinger et al., 2008b). The ability of *S. oneidensis* to grow under anaerobic and aerobic conditions, to use a wide variety of electron acceptors and to secrete mediators to aid in electron transfer, makes *S. oneidensis* a provocative choice for a significantly wider variety of power applications in aerobic or microaerophilic environments (Biffinger et al., 2008a). However, to date, only a limited number of carbon containing electron donors (lactate, formate, pyruvate, amino acids) have supported metal reduction by *S. oneidensis* under anaerobic conditions. *S. oneidensis* grown with glucose in the presence of oxygen can generate more power than under strictly anaerobic conditions, where the elimination of oxygen should typically increase the fuel cell efficiency and increase power output (Biffinger et al., 2008a). A power increase with oxygen exposure is an indication that aerobic *S. oneidensis* can effectively utilize complex carbon sources as electron donors in MFCs.

Using *Geobacter sulfurreducens* with acetate as fuel in a continuous flow 'ministack' system, higher current (4.56 A/m<sup>2</sup>) and power densities (1.88 W/m<sup>2</sup>, 2.15 kW/m<sup>3</sup>) are reported as compared to the power output when mixed anaerobic sludge is used as inoculum (Nevin et al., 2008). Phototrophic purple nonsulfur bacterium (*Rhodospseudomonas palustris* DX-1) can efficiently generate electricity by direct electron transfer in MFCs using wide range of substrate (volatile acids, yeast extract, and thiosulfate) making it another highly useful culture for very high power generation (2720 mW/m<sup>2</sup>) compared to mixed

culture in MFCs (Xing et al., 2008). *Acidiphilium sp.* strains, isolated from an extreme acidic environment, are reported to be able to colonize graphite felt electrodes. These bacterial electrodes were able to produce high-density electrocatalytic currents, up to 3 A/m<sup>2</sup>, at a poised potential of + 0.15 V (versus standard calomel electrode) in the absence of redox mediators, by oxidizing glucose even with air saturated solution and at very low pH (Malki et al., 2008). Identification of such strains will be more useful in the MFC for generation of higher current density and such strains are unaffected by the presence of oxygen, which will help in solving the problem of O<sub>2</sub> diffusion from the cathode and hence can be very useful for developing MFC without membrane.

The use of mixed culture can develop higher current in the MFC due to wide acceptance of different forms of organic matter present in the real wastewaters as a substrate. Studies have shown that the MFC inoculated with mixed anaerobic sludge can also generate current density comparable with the selected pure cultures (Jadhav and Ghangrekar, 2008). Domestic wastewater can also be used as a inoculum (Zhan et al., 2008). In order to enhance power production in MFC and to reduce the start-up period of the MFC it is beneficial to use a mixed culture as inoculum with some pretreatment. For biohydrogen production heat pretreatment is widely used (Baghchehsaraee et al., 2008). Such heat treatment is also reported to be effective for pretreatment of the inoculum to enhance power production in MFC (Ghangrekar and Shinde, 2007).

Pretreatment of sludge is particularly important for suppressing the methanogens present in the mixed anaerobic culture. Electrogenic bacteria have the ability to outcompete methanogens when non-fermentable substrate is used. However, typically when the fermentable substrate is used in the MFC, *i.e.*, in the case of real wastewater treatment, methane formation is reported in the MFC during longer operation times (Clauwaert and Verstraete, 2008; Logan et al., 2008). Hence, a strategy needs to be devised to suppress the methanogens during inoculation and also intermittently during reactor operation for sustainable electrogenesis. The other inoculum pretreatment techniques which could have potential and need further exploration are pH correction to the acidic range, mild sonication of the inoculum (More and Ghangrekar, 2010), or even intermittent aeration in the anode chamber to kill strict anaerobes.

## 5.2. Operating temperature

Similar to other biological wastewater treatment processes, performance of the anode is affected by temperature variation. The operating temperature of 35°C is reported to be optimum (Zhan et al., 2008). A lag phase of 30 h was reported for operation at 30°C, which was half than that at 22°C (Min et al., 2008). The maximum power density at

30°C was 70 mW/m<sup>2</sup> and at 22°C it was 43 mW/m<sup>2</sup>. Reduction in CE and COD removal efficiency is also reported with reduction in operating temperature from 30 to 20°C (Feng et al., 2008). Thermophilic operation of MFC at 55°C for over 100 days is reported to produce power density of 37 mW/m<sup>2</sup> at a CE of 89% (Wrighton et al., 2008). In MFC generating electricity from marine sediments, the operation at 60°C was reported to produce ten times more power as compared to operation at 22°C (Mathis et al., 2008). Successful current production is also reported in the MFC operated at 50°C (Jong et al., 2006).

At 15°C, no successful operation was reported even for a long period of operation and resulted anode potential (OCV 25 mV) is much higher than the one noticed at higher temperature (22 and 30°C) where an OCV of -320 mV was reported (Min et al., 2008). However, with the change in operating temperature no change in the OCV of the cathode was reported, and it was around 400 mV at all operating temperatures. In another study MFC is reported to be working even at the temperature as low as 4°C for treatment of diluted brewery wastewater (Larrosa-Guerrero et al., in press).

Increasing operating temperature also reduces the internal resistance of the cell. A reduction in internal resistance from 1000 Ω (at 22°C) to 430 Ω at 30°C is reported (Min et al., 2008). Also, CE can be increased at higher temperature (43% at 30°C) as compared to only 8% at 22°C (Min et al., 2008). With increase in temperature biochemical reaction rate increases, and hence results in an increase of biomass growth rate due to increase in the substrate utilization rate. Higher growth rate would also result in faster microbial attachment on the electrode. Conductivity of anolyte and catholyte will increase with increasing temperature, reducing internal resistance of the cell and enhance power output (Min et al., 2008). Overall, it can be said that the MFC performs well in the mesophilic temperature range and the optimum performance can be obtained at around 35°C.

### 5.3. Operating pH

The enrichment of electrochemically active bacterial culture in the anode chamber of the MFC depends on the operating pH range. MFCs are typically operated at pH values between 6 and 8 in the anode chamber and neutral or little higher pH in the cathode chamber. The anodic microbial process prefers around neutral pH and microbial activity decreases at higher or lower pH. An anode operating pH between 7 and 8 is reported to produce maximum CE and current (Gil et al., 2003). Reduction in current and CE is reported at pH 6 and 9. It is reported that, the current increases significantly with increase in pH from 6 to 9 (especially from 7.5 to 8.0) and current decrease sharply at pH values above 9.0 (Timur et al., 2007).

The acidity of electrolyte has a pronounced influence on both bacterial metabolism as well as

cathodic oxygen reduction reaction (ORR) rates. Increasing the acidity of anode will increase the driving force for cathodic oxygen reduction by 59 mV/pH unit as long as catalytic activity remains high (Biffinger et al., 2008b). The higher current and voltage with higher electrochemical activity results in high pH difference across the membrane; hence, higher pH difference between anodic and cathodic electrolyte was reported to favor higher current and voltage (Jadhav and Ghangrekar, 2009). Also, it is reported that at an anodic pH of 6.5 the MFC gave maximum current. Acidophilic pH (6.0) in anodic chamber was reported to be effective with respect to power output as compared to the corresponding neutral (7.0) and alkaline pH (8.0) (Raghavulu et al., 2009). However, substrate degradation was observed to be higher at neutral pH, followed by alkaline and acidophilic operation. It is reported that the MFC could tolerate an initial (feed solution) pH as high as 10 (He et al., 2008) with optimal initial pH between 8 and 10 to produce higher current. The bacterial metabolism exhibited a buffer effect and changed the electrolyte pH.

The results presented so far suggest that, the operational pH between 6 and 7 may give optimum power production from the MFC. However, operation of MFC at feed pH up to 10 is possible. Higher pH in the anode chamber favors higher COD removal but reduces power. Higher pH difference between anode and cathode appears to improve power output of the MFC. The favorable pH and difference of pH between anode and cathode depends on the type of species used in anode, the electron donor used as substrate, catholyte used and proton flux through the membrane.

### 5.4. Effect of applied loading rates, hydraulic retention time and wastewater concentration

The applied OLRs will have a marked influence on both power yield and substrate degradation rate in the MFC. OLRs in the range of 0.05 to 2.0 kg COD/m<sup>3</sup>.d are typically used by researchers to achieve maximum power from the MFC. The OLRs used in the anode chamber of the MFC by researchers are comparable with those used in activated sludge process. However, these are only comparable with the OLRs adopted for sewage treatment in high rate anaerobic processes, such as UASB reactor and anaerobic filters, and far less than the OLRs used in case of industrial wastewater treatment in UASB reactors.

While treating wastewater a maximum power yield (274 mW/g COD) was reported at OLR of 0.574 kg COD/m<sup>3</sup>.d (Venkata Mohan et al., 2007). Operation of the MFC at the higher OLR is reported to reduce the CE. While treating leachate, increasing OLR from 0.65 to 5.2 kg COD/m<sup>3</sup>.d resulted in a decrease of overall CE from 14.4% to 1.2% (Zhang et al., 2008a). Hence, it can be said that depending on the configuration of the MFC used and the wastewater being treated there is an optimum range of

OLR to obtain maximum COD removal efficiency and harvest maximum power.

The hydraulic retention time, which is related to the loading rate, is a key factor in the design of a wastewater treatment plant. The HRT can affect the opportunity for contact between the substrates and microorganisms. From the literature it is evident that higher HRT in the anode chamber favors higher treatment efficiency and higher power production. Increase in power density with increase in HRT up to 15.5 h and with further increase in HRT reduction in power density is reported (Li et al., 2008a). The optimum HRT depends on the type of organic matter being treated apart from the reactor geometry and strength of the wastewater. The favorable HRTs reported in the literature are a little higher than the HRTs generally adopted for established wastewater treatment systems such as the UASB reactor. Hence, in order to make volume of MFC comparable with other already established treatment processes, it is required to modify configuration of MFC to handle more OLR at lower HRT.

Non-fermentable substrate, such as acetate, gives higher power density and energy conversion efficiency as compared to fermentable substrates such as glucose (Lee et al., 2008). Ethanol can be effectively used as a substrate in the MFC to produce higher power; however, use of methanol as a substrate is not effective and did not result in appreciable electricity generation (Kim et al., 2007b). When the effect of different forms of organic matters such as, acetate, glucose and xylose was evaluated with humic acid (HA) as mediator in two chambered MFC, acetate produced higher power due to a simpler metabolism than glucose and xylose (Thygesen et al., 2009). In the presence of HA the power increased by 84% and 30%, for glucose and xylose respectively, due to the mediating effect of HA. Lesser increment in power after mediator addition with xylose indicates better electrogens development in the cell during xylose decomposition. No specific effect of HA addition was reported for acetate, demonstrating excellent ability of the microbes developed in the anode chamber for electron transfer (Thygesen et al., 2009). With external mediator addition increase in power output during fermentable substrate degradation indicates limited electron transfer ability of the microbes developed in the cell.

When the effect of influent COD concentration in the wastewater was studied by varying COD from 129 mg/L to 1124 mg/L, the maximum power density obtained with a fixed external resistance (100  $\Omega$ ) showed a saturation-type relationship with respect to wastewater concentrations (Li et al., 2008a). The maximum power density was  $P_{\max} = 164 \text{ mW/m}^2$ , with a half-saturation concentration of 259 mg/L. Most researchers have found saturation-type relationship between substrate concentration and generated power or voltage (Min et al., 2005). At low COD concentration, electricity generation was limited by the anode due to kinetic limitations; whilst at high concentration, the cathode was shown to have a more

significant effect on electricity generation than the anode (You et al., 2006c).

Conductivity of the wastewater fed in anode chamber also affects the power output by reducing the internal resistance at higher conductivity, and hence increasing the power. Increase in the power output by 85% was reported when the ionic strength of the electrolyte was increased from 100 to 400 mM by addition of NaCl (Liu and Logan, 2004).

### 5.5. Nutrient requirement

The COD/N ratio required for the MFC type wastewater treatment system is reported to be lower than the conventional treatment (Virdis et al., 2008). The effect of different forms of nitrogen on MFC performance was evaluated, and it is reported that nitrogen can be supplemented in the form of urea, ammonium sulfate, and ammonium nitrate producing similar power (Tiwari et al., 2008). However, removal of nitrogen from the feed is reported to adversely affect power production. The effect of phosphorous concentration in the feed on performance of MFC is not available so far. In general it appears that the 'P' requirement similar to anaerobic processes satisfies the requirement of electrogenic bacteria. However, detailed study is required to ascertain the exact requirement. Successful operation of MFC is reported without addition of trace metals (Min et al., 2005; Min et al., 2008). Most MFC researchers, using pure culture and synthetic wastewater, have not reported any trace metal addition as considered to be essential for methanogens in high rate anaerobic processes. The exact nutrient requirement of the MFC will depend on the type of microorganisms used in the anode for specific organic matter removal. Studies are required to establish exact macro-nutrient and micro-nutrient requirements of the electrogens to sustain their growth in the MFC.

### 5.6. Oxidants used in cathode

#### 5.6.1. Catholyte properties

Several catholyte properties have been found to limit the MFC performance due to high ohmic resistance. These restrictions include low proton concentrations at neutral pH range (Jang et al., 2004) and low ionic conductivity of catholyte solutions in dual chamber MFCs. Optimization of catholyte composition and concentration can, therefore, enhance the performance of MFCs (Zhao et al., 2006). Increasing the ionic strength of the catholyte improves the cathodic proton transfer rate and results in increased current output (Gil et al., 2003; Jang et al., 2004). Extreme pH and ionic strength of the catholyte can affect cathodic performance adversely, due to inactivation of metal-based catalysts and biocatalysts.

The most popular oxidant employed in MFC studies due to its free availability in the air (Erable et al., 2009a; Liu et al., 2005; Logan et al., 2005; Min and Logan, 2004) is oxygen. Hydrogen peroxide

(H<sub>2</sub>O<sub>2</sub>), an intermediate product obtained from the oxygen reduction, has also been studied as oxidant in cathodic compartment (Park et al., 2004). Hexacyanoferrate [Fe(CN)<sub>6</sub>]<sup>3-</sup> is commonly considered as artificial electron mediator in cathodic chamber (Rabaey et al., 2003) but it often acts as a real final electron acceptor because the reoxidation reaction rate of the product [Fe(CN)<sub>6</sub>]<sup>4-</sup> by oxygen is really slow (Rabaey et al., 2005). Permanganate can also be used as an effective cathodic electron acceptor in MFCs, e.g. five-fold more power density can be achieved using permanganate than with other electron acceptors such as hexacyanoferrate and oxygen (You et al., 2006a).

Despite their excellent performances in MFCs, hexacyanoferrate and permanganate are not considered as sustainable oxidants because they still require continuous replacement. Instead of oxygen, ferric iron can be reduced to ferrous iron (Fe<sup>2+</sup>) at the cathode. Ferric iron reduction at the cathode and simultaneous biological ferrous iron oxidation of the catholyte was demonstrated using bipolar membrane separating the anode and cathode in the MFC (Ter Heijne et al., 2007). The immobilized microorganism *Acidithiobacillus ferrooxidans* is showed to be capable of oxidizing ferrous iron to ferric iron at a rate high enough to ensure power output of 1.2 W/m<sup>2</sup> and a current of 4.4 A/m<sup>2</sup>.

#### 5.6.2. Oxidant concentration

Power output has been shown to be proportional to the oxidant concentration in the catholyte of dual chamber MFCs (Gil et al., 2003). For example, increase in power output is reported with increasing loading rate of H<sub>2</sub>O<sub>2</sub> (Tartakovsky and Guio, 2006). Increasing the dissolved O<sub>2</sub> concentration is limited by its solubility in water. Stirring and flushing the catholyte with air or pure O<sub>2</sub> and recirculation of the catholyte have been tested in attempts to enhance the oxygen flux to the cathode (Jong et al., 2006). When permanganate concentration was increased from 0.02 to 0.2 g/L in the cathodic compartment, 3-times improvement in the performance of MFC was reported (You et al., 2006a).

Similar trend of increasing power output with increase in nitrate concentration in the cathodic chamber is reported (Clauwaert et al., 2007a).

#### 5.7. Improvement of bacterial activity with imposed potential

The biological component of the MFC could be optimized by imposing potential during start-up, to favour suitable type of microbial growth on the electrode. Adaptive evolution strategies, cultivation with a solid electron donor or acceptor in order to pre-adapt bacterial metabolism, have improved efficiency of electricity generation. Studies performed during the past years on MFCs have shown that the best performance in terms of current and power generation was obtained when the anode poised potential during

the start-up was around -200 mV versus Ag/AgCl (Aelterman et al., 2008a; Aelterman et al., 2008b; Erable et al., 2009b). The imposed anode potential did not show any influence on the start-up time of the reactors (Aelterman et al., 2008a). However, unlike this observation, a decrease in start-up time from 59 days to 35 days was reported by imposing an anodic potential of +200 mV vs. Ag/AgCl compared with a control MFC operated under 1000 Ω resistance (Wang et al., 2009). After reaching steady state in both MFCs, no difference in performance was reported. In a study with *S. oneidensis* MR-1, reduction in start-up time by increasing the anode imposed potential is reported (Cho and Ellington, 2007). Overall, it is obvious that electrode potential plays a key role in start-up of MFC by regulating bacterial activity in the anodic compartment. A proper strategy needs to be worked out to have quick start-up of the MFC and to facilitate maximum power output.

#### 5.8. Effect of external load

The studies performed until now on MFCs reveal that the anode potential represents the determining element for the energy gain in case of microorganisms used as a catalyst in the anodic chamber (Aelterman et al., 2008a; Schroder, 2007). The external load used during the start-up period controls the bacterial growth rate, bacteria adhesion, and also determines the electrical energy output (Aelterman et al., 2008b). In fact, the external resistance is used in order to control and impose the anode potential and also to adjust the electrons flow between anode and cathode. The value of external resistance should be linked with substrate loading in order to enable the biocatalyst to take advantage of higher substrate concentration and to convert it in electrical energy (Aelterman et al., 2008a; Aelterman et al., 2008b). When the substrate concentration is increasing, in order to improve the current generation, the external load must decrease. Gil et al. (2003) showed that external resistance was the rate-determining factor at over 500 Ω by limiting the electron flow between anode and cathode. Also, they proved that at external load lower than 200 Ω, proton flow between anode and cathode was the main limiting factor. Slightly higher COD removal efficiency was reported in MFC when the external load was lowered (Jadhav and Ghangrekar, 2009); similar trend was reported by Gunawardena et al. (2008). Thus, the data presented in literature so far suggests that it is very important to determine and choose the right external load for each practical usage of MFC. This right load will depends on the configuration of the MFC, substrate concentration and OLR used.

#### 5.9. MFC configuration and design

The geometrical shape of the reactor, dimensions and positioning of the electrode against the membrane, the arrangement of influent and

effluent for proper distribution of substrate to the anode chamber and to avoid short-circuiting, are among the parameters that will play important role in MFC performance (Jadhav and Ghangrekar, 2008). Most of the researchers are using dual chamber MFC. A highly scalable MFC design, consisting of a series of cassette electrodes, was proposed by Shimoyama et al. (2008). This 12-chamber MFC was reported to give COD removal efficiency of 95% at an OLR of 2.9 kg COD/m<sup>3</sup>.d; giving maximum power production of 129 W/m<sup>3</sup> (anode volume) and 899 mW/m<sup>2</sup> of anode surface area. Such stack arrangement will be useful for application of MFC for wastewater treatment and onsite power generation device.

However, increased use of single chamber air cathode MFC is being observed with simple carbon or carbon modified with some pretreatment or platinum coated carbon acting as cathode electrode material. An air-cathode MFC is an efficient and sustainable configuration not requiring active aeration or addition of chemicals for cathodic reaction. Recently used air cathode MFCs demonstrated comparable power densities, similar to dual chambered MFCs and hence this single chamber MFCs can receive wide acceptance due to their lower operating cost.

The major cost component in the MFC fabrication is the requirement of PEM for separating anode and cathode. Researchers have tried alternatives for this membrane to minimize production cost of MFC by either using alternative to PEM or designing membrane-less MFCs. Still, a major drawback in membrane-less MFC is loss of substrate to aerobic oxidation because of increased contact between oxygen from the cathode chamber and organic matter in the anode chamber. This fraction of organic matter will be lost and cannot be used by the EAB for current generation.

Another issue is loss of power output when such membrane-less MFCs are connected in series. They are unable to deliver the voltage nearly equal to the sum of the individual cell voltages. Hence, further research is needed for proper geometrical arrangement of the membrane-less MFC to overcome these drawbacks and to make it compatible with membrane MFCs.

The ideal material selected for electrodes should offer a higher surface area per unit volume to maximize opportunity for direct growth of microorganisms on the anode surface. The graphite granules, felt and carbon brush or fibres can be suitable alternative for the electrodes. The electrode material offering very high surface area but very fine pore size may not be very suitable for the electrodes as it may lead to the formation of dead pockets and reduction in the MFC power output (Aelterman et al., 2008b; Erable et al., 2009a).

Graphite fiber brush anodes that have high surface areas and a porous structure can produce high power densities (1430 mW/m<sup>2</sup>, 2.3 W/m<sup>3</sup>) as compared to other carbon forms, and therefore have qualities that make them ideal for scaling up MFC systems (Logan et al., 2007b). Power density as high

as 2011 mW/m<sup>2</sup> is reported for MFC using carbon brush anode (HaoYu et al., 2007). Further emphasize is required to explore the possibility of non-noble metal catalyst coating on the electrode surface to maximize power production. Also, suitable surface area to volume ratio of anode needs to be established, which will also be dependent on the OLR applied (Jadhav and Ghangrekar, 2008).

## 6. Outlook

Although, MFCs are reported to be successful for wastewater treatment and electricity recovery, many aspects need further investigation. Full scale implementation of such bio-electrochemical wastewater treatment is not straightforward because certain microbiological, technological and economic challenges that have not previously been encountered in any other wastewater treatment system need to be resolved. Most of the studies performed have used very small volumes (less than 100 ml) for the anode and cathode chambers. However, for real applications larger reactor volumes will be used and the geometry and design of the reactor will play a crucial role during scale-up. Introducing wastewater or aqueous "fuel" in such a way to facilitate uniform substrate distribution to the entire anode surface is desirable to eliminate kinetic and mass transport limitation. For continuous feeding reactor flow operation will help mixing in the anode chamber and hence the distribution of the substrate. The cross sectional area of the anode and cathode and proper arrangement of the influent and effluent will be important. A four-fold increase of the current output, producing sustainable maximum power of 110 W/m<sup>3</sup> of cathode volume, was reported when anode effluent added to the cathode lead to the development of a cathodic biofilm (Freguia et al., 2008). Apart from increasing power, this sequential anode-cathode configuration will also provide good COD polishing at the cathode by heterotrophic bacteria. However, excessive organic loading to the cathode should be avoided, as it can reduce the long-term performance through excessive growth of the heterotrophic bacteria.

There is a wide variation in the literature on type of reactors; materials of reactor and electrodes; geometry and size of the reactor; specific surface area of the electrode required with respect to the reactor volume, volumetric ratios of anode and cathode chambers; anodophilic species type, concentration and sludge age, etc. It is stated that the maximum generated power density is not directly proportional to the surface area of the anode, instead it is proportional to the logarithm of the surface area of the anode (Dewan et al., 2008).

For designing a MFC stack, minimizing the length of external connection between the anode and cathode of the other MFC is also important. Uniform distribution of the influent equally to all the MFC units in a stack will play an important role in achieving similar performance from all cells.

Adopting similar start-up strategy for development of electrogenic bacteria on the anode surface is necessary to eliminate the problem of cell reversal. If one of the cells is not performing in the stack, it may give negative voltage and reduce overall output of the stack. Voltage reversal of one of the cell in a stack adversely affects bacteria on the anode of the affected cell. The control of voltage reversal will be crucial for long-term operation of MFCs in series. A better understanding of the long term effects of voltage reversal on power generation by MFC stacks is needed in order to efficiently increase power production (Oh and Logan, 2007; Rozendal et al., 2008).

It has been reported that in the MFC operated with fermentable substrates, competition exists between the electrogens and methanogens for the substrate. In longer operation, the methanogens replace the EAB from the anode surface, or form multilayer over the EAB on the anode, and hence limit the substrate availability for the EAB and reduce power output of the cell. This implies that the MFC should be used after a fermentation reactor so that the substrate is available in the non-fermentable reduced form (such as acetate) to minimize the substrate competition and maximize power output. Also, strategy is needed to develop a protocol to suppress methanogens growth on the anode and encourage electrogenic bacterial growth to maximise power, without losing the substrate for methanogenesis. More studies with actual wastewaters are required so that strategies can be developed for (i) improving the degradation of complex materials, and (ii) controlling the microbial reactions occurring in the system (Rozendal et al., 2008).

Scale up of the MFC still remains a critical issue. Key attributes for scale up are anodes and cathodes that have high surface areas, cathodes that allow for oxygen reduction in a non-fouling manner, and the need for non-precious metal catalysts. Recent advances have been made based on the development of new materials and configurations suitable for scale-up of these electrodes (Duteanu et al., 2010; Erable et al., 2009a; Logan et al., 2007a).

The challenge lies in proper design of the MFC to suit the stack arrangement. Replacement of the membrane, with alternative cheaper material or proper reactor design, could improve the economic feasibility of the process to treat wastewater by reducing not only the capital investment but also the operation cost for membrane maintenance and periodic replacement.

It is not known till now what will be the capital cost to develop a MFC system. The cost to build, operate and maintain such a system is a key factor in future implementation of the MFC technology. Large-scale power production and a high COD conversion rate must be achieved at a benchmark cost to make MFCs economically competitive (Clauwaert et al., 2008a). Compared to anaerobic digestion, the revenue that might be raised from the production of electricity in MFCs is unlikely

to offset their higher capital cost and to create a competitive advantage (Rozendal et al., 2008). Still, MFCs have some particular benefits over anaerobic digestion that could make them competitive under certain circumstances, such as operation on a small-scale, at low COD concentrations, at low temperatures and/or with integrated nitrogen removal (Clauwaert et al., 2007a; Ghangrekar and Shinde, 2007; Virdis et al., 2008). Harvesting energy while treating small volumes of low strength wastewater, like sewage, makes MFCs application particularly attractive. For such low strength and low volumes of wastewaters, recovering methane and using it for electricity generation is not practical. Thus, MFCs may have a future for such small scale sewage and industrial wastewater treatment. Furthermore, simultaneous nitrogen removal and removal of some recalcitrant compounds in MFC will offer an advantage over other existing technologies, offering complete treatment.

## 7. Conclusions

Research into MFC, to develop it as a wastewater treatment system, is gaining impetus day by day. Considerable improvement in the performance of the MFC has occurred in recent times. Full-scale implementation of such bio-electrochemical wastewater treatment system is not straightforward because certain microbiological, technological and economic challenges need to be resolved that have not previously been encountered in any other wastewater treatment system.

Many more improvements, as stated earlier, are necessary, before the MFC can be commercialized as wastewater treatment process. With continuous interdisciplinary research efforts involving microbiology, biotechnology, material science, chemical engineering, electrochemistry, and environmental engineering, many more improvements in the performance are expected.

It is interesting and encouraging that MFCs are not only effective in treatment of organic contaminants but they are also effective for the treatment of some bio-refractory pollutants, which cannot be treated in established biological treatment methods. The MFC technology holds promise towards wastewater treatment and sustainable energy generation with possible applications within a broad range of life sciences in the near future.

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