

REVIEW

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Microbial fuel cell: a green approach for the utilization of waste for the generation of bioelectricity

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Abstract

Today we are witnessing a global energy crisis due to huge energy demands and limited resources. Non-renewable energy sources are depleting and renewable energy sources are not properly utilized. There is an immediate need for search of alternate routes for energy generation. Microbial fuel cell (MFC) technology, which uses microorganisms to transform chemical energy of organic compounds into electricity is considered a promising alternative. Extensive studies have corroborated new insights into MFC, which show that a wide array of carbon sources including wastes can be employed using a variety of microbes. Consequently, microbial transformation of wastes using novel bioremediation strategies such as MFC for energy generation is considered as an efficient and environmentally benign approach. This paper deals with critical review of different classes of xenobiotics and wastes that can be employed for bioenergy generation, microorganisms involved, power output, major benefits, challenges and pit holes of MFC technology.

Keywords: Microbial fuel cell (MFC), Electricity, Technology, Waste, Pollutant, Xenobiotic

Background

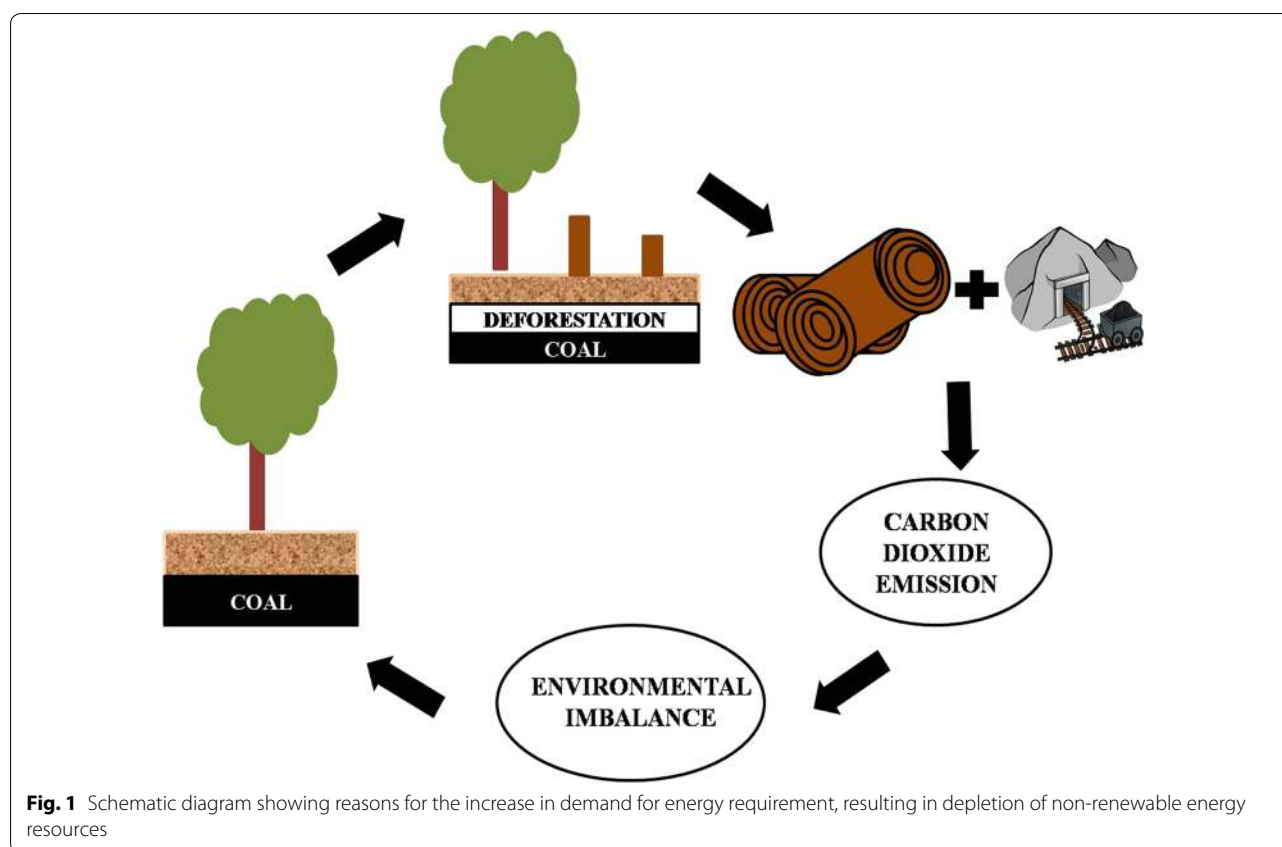
Energy requirement is ever increasing throughout the world. In this regard, fossil fuels have catered to a major portion of the total energy requirement, in one way or another. This has subsequently resulted in tremendous depletion of fossil fuel resources and is bringing about an ecological imbalance. In addition, combustion of fossil fuels generates a lot of carbon dioxide, which is a major green house gas and has shown alarming consequences on the environment. Therefore, search for alternate sources of energy generation that are cheap and eco-friendly have become a prime necessity (Logan 2004). Microbial fuel cells (MFC) technology, which harnesses energy from metabolism of microorganisms, seems to be attractive to warrant energy generation (Logan 2004; Rabaey et al. 2003; Venkata Mohan et al. 2008) (Fig. 1). The use of MFC as an alternative source for power generation is considered as a reliable, clean, efficient process,

which utilizes renewable methods and does not generate any toxic by-product. Therefore, in recent years, MFCs have shown to be a potent technology for recovery and in situ conversion of chemical energy into electricity (Logan 2004).

An MFC is a system in which microbes convert chemical energy produced by the oxidation of organic/inorganic compounds into ATP by sequential reactions in which electrons are transferred to a terminal electron acceptor to generate an electrical current (Torres et al. 2009). A typical MFC consists of anode and cathode compartments, which are separated by a cationic membrane. Microbes reside in the anode compartment, where they metabolize organic compounds such as glucose which act as electron donor. The metabolism of these organic compounds generates electrons and protons. Electrons are then transferred to the anode surface. From anode, the electrons move to cathode through the electrical circuit, while the protons migrate through the electrolyte and then through the cationic membrane. Electrons and protons are consumed in the cathode by reduction of soluble electron acceptor, such as oxygen or hexacyanoferrate

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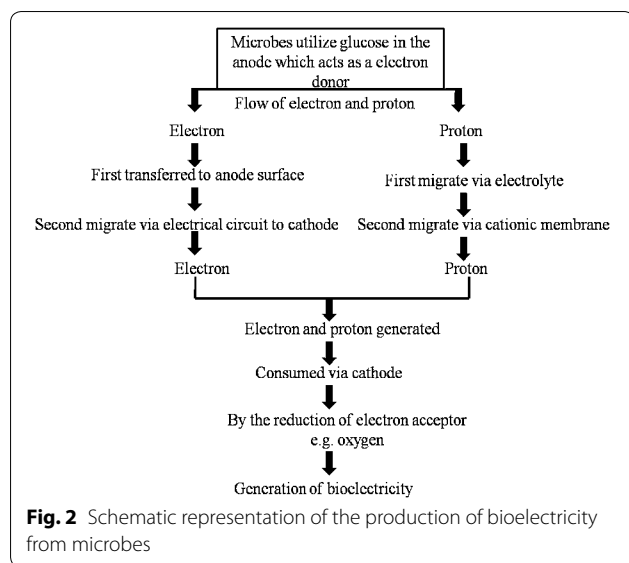


(Rabaey et al. 2004) and acidic permanganate (You et al. 2006). Electrical power is harnessed by placing a load between the two electrode compartments (Allen and Bennetto 1993) (Fig. 2). However, the use of oxygen could avoid the potential environmental pollution resulted from the use of liquid-state electron acceptors. To accelerate the oxygen reduction on the surface of the cathode, platinum is commonly used because of its excellent catalytic ability. However, the high cost of platinum is a major limitation to MFC application and economic viability. Replacement of platinum with alternative cheap metals, such as manganese dioxide (Li et al. 2010), iron(II) and cobalt-based materials (Cheng et al. 2006a, b; Ter Heijne et al. 2007), could also improve the oxygen reduction rate with cost saving. Metal-based materials, however, are generally susceptible to the adverse environmental conditions that may occur in MFCs and cause inactivation (Sun et al. 2011a, b). Recent development of biocathode that uses microorganisms as catalysts to assist electron transfer is a promising way to improve cathode performance without the use of noble metal. Many compounds other than oxygen could be also used as terminal electron acceptors in biocathode, such as nitrate, sulfate, iron, manganese, selenate, arsenate, urinate, fumarate, carbon dioxide and hexavalent chromium (Stams et al. 2006;

Wang et al. 2008). This provides a potential approach for wastewater treatment using biocathode due to its variety of terminal electron acceptors such as recalcitrant wastes like azo dyes (Sun et al. 2011a, b).

On the basis of design, MFC can be divided into two main types: single chambered and dual chambered. The MFC described above containing separate cathodic and anodic chambers is called dual-chambered MFC, whereas, the one which contains both cathode and anode in a single chamber is single-chambered MFC (Fig. 3a, b).

A wide variety of substrates have been employed in MFC. The substrates not only influence the integral composition of the bacterial community in the anode biofilm, but also the MFC performance including the power density (PD) and Coulombic efficiency (CE) (Chae et al. 2009). During development of this technology, low molecular weight substrates were employed as substrates, i.e., carbohydrates such as glucose, fructose, xylose, sucrose, maltose and trehalose (Chaudhuri and Lovley 2003; Kim et al. 2000a, b), organic acids such as acetate, propionate, butyrate, lactate, succinate and malate (Bond and Lovley 2005; Holmes et al. 2004a, b; Min and Logan 2004), alcohols such as ethanol and methanol (Kim et al. 2007) and inorganic compounds such as sulfate (Rabaey et al. 2006). Later, complex substrates such as starch, cellulose, dextran, molasses, chitin



and pectin (Niessen et al. 2005, 2006; Rezaei et al. 2007) were also employed. In addition, complex carbon sources present in wastewaters from different sources were also tested for bioenergy production (Liu et al. 2004; Rabaey et al. 2005a, b). Many studies have been performed, which have utilized wastewaters from different sources such as

starch processing (Gil et al. 2003) and wastewaters coming from the meat packing industry (Heilmann and Logan 2006), swine farms (Min et al. 2005) and food processing (Oh and Logan 2005) and potato-producing units (Rabaey et al. 2005a, b). Solid agricultural wastes such as corn stover (Zuo et al. 2006) and carbohydrates (Scott and Murano 2007) have also been tested as fuel after being pretreated. Studies have demonstrated that these organic sources affect the power output of MFCs and the power density usually varies from 1 to 3600 mW/m², with most values lying between 10 and 1000 mW/m². Table 1 depicts various substrates that are utilized for electricity production in an MFC, and their power output. Similarly a wide variety of microorganisms have been used for electricity generation in MFC. Potter (1911), for the first time employed *Saccharomyces cerevisiae* and bacteria such as *Escherichia coli* for power generation in MFC. Studies have demonstrated that pure microbial cultures have limitations for technical application because of necessity for sterile conditions, which leads to high cost, whereas mixed cultures or microbial consortia have been shown to be robust and more productive than pure strains. In addition, extraction can be easily achieved from natural sources (Ha et al. 2008). Table 2 shows the list of microorganisms commonly employed for electricity generation in the MFC.

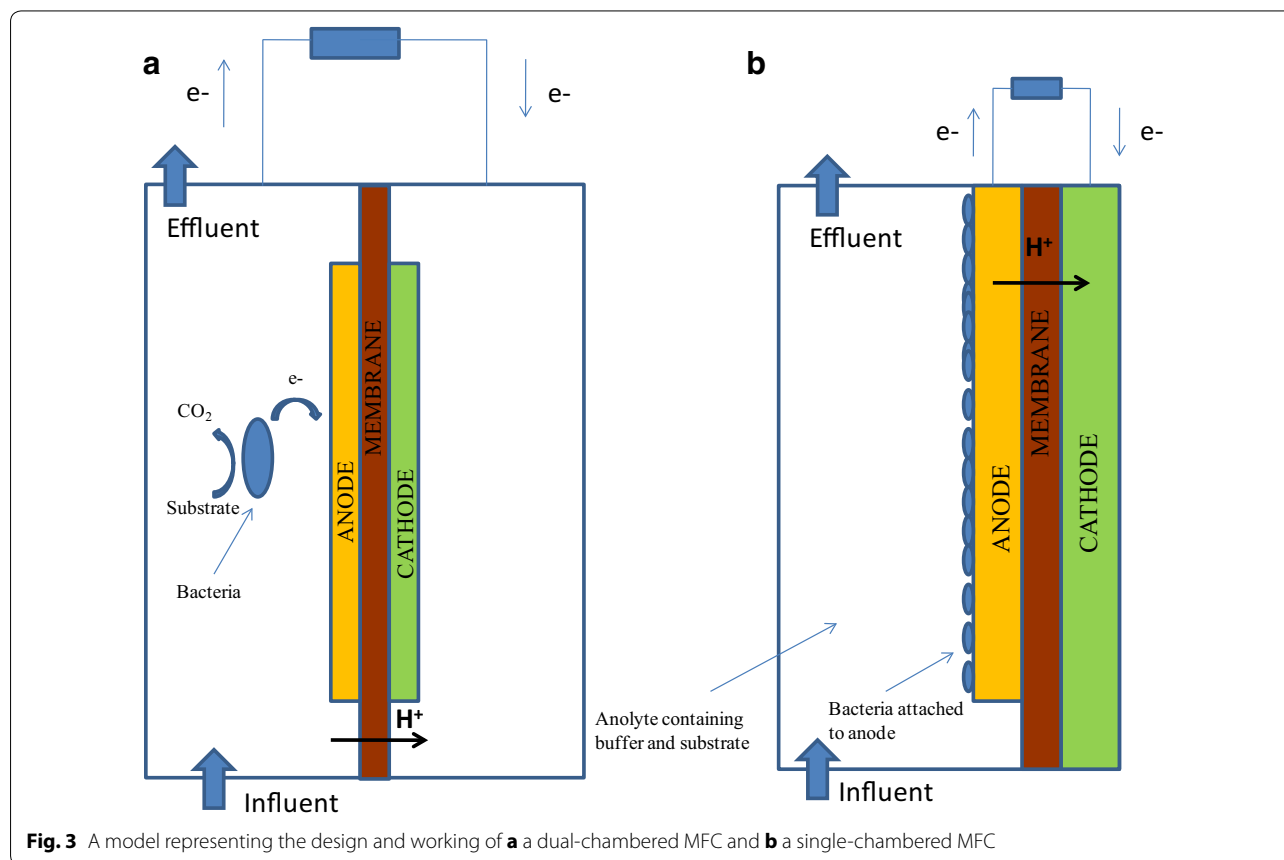


Table 1 A list of substrates used in MFCs

S. no.	Substrates	Concentration	Microorganism	Current density (mA/cm ²)	Reference
1	Cellulose	4 g/L	Pure culture of <i>Enterobacter cloacae</i>	0.02	Rezaei et al. (2009)
2	1,2-Dichloroethane	99 mg/L	Microbial consortia from acetate enriched MFC	0.008	Pham et al. (2009)
3	Furfural	6.8 mM	Pre-acclimated bacteria from anode of a ferricyanide-cathode MFC	0.17	Luo et al. (2010)
4	Lactate	18 mM	Pure culture of <i>S. oneidensis</i> MR-1	0.005	Manohar and Mansfeld (2009)
5	Landfill leachate	6000 mg/L	Leachate and sludge	0.0004	Greenman et al. (2009)
6	Phenol	400 mg/L	Mixed aerobic activated sludge and anaerobic sludge (1:1, v/v)	0.1	Luo et al. (2009)
7	Sucrose	2674 mg/L	Anaerobic sludge from septic tank	0.19	Behera and Ghangrekar (2009)
8.	Beer brewery wastewater	600 mg/L	Anaerobic mixed consortia	0.18	Wen et al. (2009)
9	Chocolate industry waste-water	1459 mg/L COD	Activated sludge	0.302	Patil et al. (2009)
10	Domestic wastewater	600 mg/L	Anaerobic sludge	0.06	Wang et al. (2009)
11	Protein-rich wastewater	1.75 g/L COD	Mesophilic anaerobic sludge	0.008	Liu et al. (2009a, b)
12	Starch processing waste-water	4852 mg/L COD	Starch processing wastewater	0.09	Lu et al. (2009)
13	Synthetic wastewater	16 g COD/day	Granular sludge from an upflow anaerobic sludge blanket reactor	0.017	Aldrovandi et al. (2009)
14	Synthetic wastewater	510 mg/L	Anaerobic culture from a preexisting MFC	0.008	Jadhav and Ghangrekar (2009)
15	Food-industry wastes	8169 CO mg/L	Aerobic sludge	0.025	Quezada et al. (2010)
16	Vegetable based waste	0.98 kg COD/m ³ -day	Anaerobic acidogenic mixed consortia	0.0329	Mohanakrishna et al. (2010)
17	Swine wastewater	60 CO gm/L	paddy field soil	0.700	Ichihashi and Hirooka (2012)
18	Slaughterhouse wastewater	900 COD mg/L	Granular anaerobic sludge inoculum	0.130	Katuri et al. (2012)
19	Food waste	16 g/L	Anaerobic culture	0.045	Choi et al. (2011)
20	Rice straw hydrolysate	400 mg/mL	<i>Desulfohalobus</i> and <i>Clostridium</i>	137.6	Wang (2014)

Use of waste/xenobiotics for electricity generation

The functioning and efficiency of MFC largely depends upon the type of materials employed for metabolism by microbes (Logan and Regan 2006a, b). Many workers have reported utilization of simple and complex organic/inorganic sources present in wastewaters from different origin as a substrate for electricity production. The use of wastewater as a source of substrate has a dual advantage; first, the electricity produced is cheap, and second, it leads treatment of wastewater. Extensive research has shown that these complex substrates such as agro wastes are oxidized by different group of microorganisms and cause generation of electricity. In this section, we have discussed some uncommon wastes and pollutants, which are utilized in MFC for electricity generation.

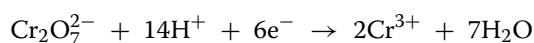
Hexavalent chromium

Microbial fuel cells (MFCs) are considered as an efficient technology which effectively utilizes wastewater for energy generation (Logan and Regan 2006a, b).

Chromium is widely used in number of industrial applications such as leather tanning, metallurgy, electroplating, and as a wood preservatives. Chromium exists in the aqueous solution either as hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)], in which Cr(VI) is more hazardous due to its mutagenic and carcinogenic properties (Humphries et al. 2004). Therefore, there is a need for detoxification of hexavalent chromium [Cr(VI)]. Studies have shown that chemical or electrochemical reduction of hexavalent chromium [Cr(VI)] into non-toxic trivalent chromium [Cr(III)] is the most preferred method for removing its toxicity. Other approaches such as ion exchange resins, filtration and direct chemical reduction are also employed (Kurniawan et al. 2006). A major drawback of utilizing these technologies is that these technologies require high-energy inputs and cause production of by-products, which itself are pollutants. Many reports have shown that acidic hexavalent chromium [Cr(VI)] can also be possibly applied as the cathodic electron acceptor in the MFC through the reaction:

Table 2 Microorganism employed for bioelectricity generation in MFC

S.no.	Microorganism	Substrate/co-substrate	Power density (mW/m ²)	Mediator	References
1	<i>Shewanella oneidensis</i> strain 14063	Sodium pyruvate	>40 at acid orange 7(AO7) initial conc. is 70 mg/l	1-amino-2 Naphthol, one of the metabolites of AO7 reductive decolourisation.	Fernando et al. (2012)
2	<i>Shewanella oneidensis</i>	Lactate	24	Anthraquinone-2,6-disulfonate (AQDS)	Ringeisen et al. (2006)
3	<i>Klebsiella pneumoniae</i>	Glucose	NA	HNQ as mediator biomineralized manganese as electron acceptor	Menicucci et al. (2006)
4	<i>Rhodoferrax ferrireducens</i>	Glucose, xylose sucrose, maltose	158	Mediator-less MFC	Liu et al. (2006)
5	<i>Klebsiella pneumoniae</i> strain L17	Glucose	34.77	Mediator-less MFC	Liu et al. (2009a, b)
6	<i>Nocardiopsis</i> sp. KNU (S strain)	CMC	162	Mediator-less MFC	Sedky et al. (2012)
7	<i>Streptomyces enissocaesilis</i> KNU (K strains)	CMC	145	Mediator-less MFC	Sedky et al. (2012)
8	<i>Pseudomonas</i> species	Luria–Bertani (LB) medium	NA	phenazine-1- carboxamide	Pham et al. (2008)
9	<i>Pseudomonas</i> sp.	Peptone	979	Methylene blue	Daniel et al. (2009)
10	<i>Rhodoferrax ferrireducens</i>	Glucose	NA	Mediator-less MFC	Vet and Rutgers (2007)
11	<i>Escherichia coli</i> strain K-12	Sucrose	215	Mediator-less MFC	Zheng and Nirmalakhandan (2010)



Under standard conditions (i.e., pH = 7), the above half-cell reaction has a redox potential (E_0) of 1.33 V showing that the overall reaction in the MFC for power generation is thermodynamically favorable. Therefore, reduction of hexavalent chromium can be coupled with electricity generation using MFC and can be applied in Cr(VI) wastewater treatment (Tandukar et al. 2009). In this study, reduction of Cr(VI) in the cathode of an MFC was performed. Also putative Cr(VI) reducing microorganisms were identified, which belong to *Trichococcus pasteurii* and *Pseudomonas aeruginosa*. The MFC was continuously monitored for Cr(VI) reduction and power generation. Acetate was provided to the anode compartment as substrate and bicarbonate was added to the cathode compartment as the sole external carbon source. The contribution of biomass decay and abiotic processes on Cr(VI) reduction was minimal, confirming that most of the Cr(VI) reduction was assisted by microbial activity in the cathode, which utilizes electrons and protons generated from the oxidation of acetate in the anode compartment. Relatively fast Cr(VI) reduction was observed at initial Cr(VI) concentrations below 80 mg/L. However, at 80 mg Cr(VI)/L, Cr(VI) reduction was extremely slow. A maximum Cr(VI) reduction rate of 0.46 mg Cr(VI)/g VSS.h was achieved, which resulted in a current and power density of 123.4 mA/m² and 55.5 mW/m², respectively. The reduced chromium was not detectable in the

supernatant of the catholyte which indicated complete removal of chromium as Cr(OH)₃ precipitate. This study demonstrated that although the reduction of Cr(VI) took place efficiently, the power output was low in comparison with the conventional anaerobic or aerobic process (Tandukar et al. 2009; Molokwane et al. 2008), which was a drawback for using MFCs for actual bioremediation on Cr(VI)-contaminated sites. Reports have shown that by increasing cathode surface area and using small anode relative to cathode area can improve power production from MFCs (Rismani-Yazidi et al. 2008). It was anticipated that a large biocathodic surface area may allow the packing of more electrochemically active microorganisms and provide the bacteria and Cr(VI) with more reaction sites. Consequently, it will greatly enhance reactor performance by high Cr(VI) reduction rate and power production. In many studies, graphite fiber and granule graphite have been used successfully to enlarge the surface area of biocathode for O₂ reduction and has improved power production greatly (You et al. 2009). Therefore, the use of graphite granule may increase power production and Cr(VI) reduction rate. To test this hypothesis, a two-chamber MFC reactor (Wang et al. 2008) was employed for Cr(VI) reduction containing Cr(VI)-contaminated soil sole inoculum. The power generated by the MFC and the biomass was monitored for initial Cr(VI) concentrations ranging from 12.8 to 39.2 mg/L. The obtained biomass ranged from 1.9 to 2.2 g/L corresponding to Cr(VI) concentration from 12.8

to 39.2 mg/L. The maximum power production increased from 0.3 to 2.4 W/m³ with initial Cr(VI) concentrations of 12.8–39.2 mg/L, demonstrating that power production was directly relative to the initial Cr(VI) concentration. In another study, alkaline hexavalent chromium containing wastewater was successfully treated in MFC. It was observed that 10 mg/L chromium was completely reduced in 45 h with power production of 21.4 mW/m² (Gangadharan and Nambi 2015). Xafenias et al. (2015) also studied chromium reduction in the presence of anaerobic sludge, Cr(VI) at 100 mg/L was completely removed within 48 h of incubation. The maximum power density of 767.01 mW/m² (2.08 mA/m²) was achieved during this period.

Agro wastes

The waste material arising from various agricultural operations such as farming, poultry processing industries, slaughter houses, and agro industries is collectively termed as agro wastes. It is rich in COD. Some of the agro wastes used for bioelectricity generation are as follows: starch obtained from cassava is an important economic product produced by many traditional and rural agro industries situated in Southeast Asia, Africa and Central America. During production of starch from cassava, high amount of starch-rich wastewater is released, having a very high chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total solids (Peters and Ngai 2000; Kaewkannetra et al. 2009). It is also rich in cyanoglycosides. These cyanoglycosides hydrolyze to form cyanide, which is a common component of cassava wastewater. Cyanide concentrations have been reported as high as 200 mg/L from many wastewaters. Therefore, it is necessary that cassava wastewater is properly treated prior to its release into the environment (Kaewkannetra et al. 2009). Many workers have reported different techniques for treatment of cassava wastewater. However, most of the techniques are expensive. Therefore, treatment of cassava wastewater and production of electricity using MFC has been found to be suitable for this purpose (Rabaey and Verstrate 2005; Lu et al. 2009). Kaewkannetra et al. (2009) have utilized cassava wastewater for generation of electricity by employing MFC. For this process, an MFC was constructed, which utilized sludge arising from wastewater treatment plant from a cassava mill factory. The wastewater had a high organic content of 16,000 mg/L and is comparable to the organic matter present in similar large-scale starch processing industries (Kaewkannetra et al. 2009). The results of this study showed that COD removal was approximately 88 % within 120 h and maximum power generated was 1771 mW/m². In another study, it was shown that by increasing the pH of anode chamber, the production of

electricity can be increased. A single-chambered MFC was used with cassava mill wastewater having COD 1086 mg/L. The pH was increased from 5.0 to 9.0. It was observed that the maximum power density generated was 22.19 W/m³ at pH 9 (Prasertsung et al. 2012). These results clearly indicated that cassava mill wastewater has a great potential to benefit from the use of MFCs to simultaneously treat and generate electricity as it is a readily biodegradable waste source.

Many studies have shown that cellulose can also be employed for generation of electricity using MFC (Niessen et al. 2005). Rismani-Yazidi et al. (2007) have employed cellulose for bioelectricity generation using microorganisms from rumen of cattle. Ren et al. (2008) employed a dual-chambered MFC for electricity generation using a binary culture of cellulose-degrading bacteria *Clostridium cellulolyticum* and electrochemically active bacteria *Geobacter sulfurreducens*. In fed-batch mode, maximum power density obtained was 143 mW/m² with 1 g/L carboxymethyl cellulose (CMC). In a study by Rezaei et al. (2009), cellulose-degrading bacteria was first enriched in a special U-tube MFC from wastewater. The dominant bacteria in this enriched culture was *Enterobacter cloacae* strain FR. When cellulose at a concentration of 4 g/L was fed in this MFC, maximum power density of 4.9 mW/m² was obtained. Sedky et al. (2012) have utilized cellulose as substrate for electricity generation using a dual-chambered MFC. In their study, cellulose-degrading bacteria *Nocardiopsis* sp. KNU and *Streptomyces enissocaesilis* KNU were employed for cellulose degradation in anode and the cathode contained 50 mM ferricyanide. With 1 g/L cellulose, the maximum power density for the mixed culture was 188 mW/m². Use of vegetable waste for bioelectricity production was also investigated by Clauwaert et al. (2008). In their study, a single-chambered MFC containing 0.5 g COD/L clover sap was employed for electricity generation. Maximum power density obtained in this study ranged from 28 to 70 mW/m³. Recent studies have shown that cellulose from different sources such as wheat straw, rice mill wastewater, corn stover, and Canna indica could be partially degraded by electrophilic bacteria for electricity generation (Zang et al. 2010). In these studies, the biomass was pretreated to convert it into cellulose and hemicelluloses and these hydrolysates were employed for electricity generation. The tubers of *Dioscorea zingiberensis* are used to separate diosgenin, which is an important precursor for the synthesis of steroid hormone drugs. These industries produce large amounts of wastewater rich in sugars, fatty esters and N-containing compounds. In a study by Li and Ni (2011), a two-chamber MFC was used to treat this wastewater and to generate electricity. At a concentration of 3000 mg-COD/L, the maximum

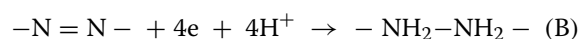
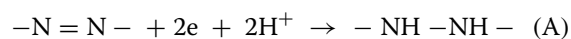
power density achieved was 175 mW/m². Brewery wastewater was used for electricity production in double-chamber MFC. Carbon fiber was used as anode and plain carbon felt with biofilm as cathode. It was observed that with hydraulic retention time (HRT) of 14.7 h, a relatively high chemical oxygen demand (COD) removal efficiency of 91.7–95.7 % was achieved under long-term stable operation. The MFC exhibited a voltage of 0.434 V and a maximum power density of 830 mW/m³ at an external resistance of 300 Ω (Wen et al. 2010). Many reports are available which use slaughter house wastewater for generation of electricity. Slaughter house wastewater contains high amount of proteins, fats and carbohydrates, which is an ideal source for generation of electricity. A dual-chambered microbial fuel cell, fed with slaughterhouse wastewater with an anaerobic mixed sludge as a source of inoculum was used. It was observed that when wastewater at a concentration of 900 mg-COD/L was fed, a maximum power density of 578 mW/m² was obtained (Katari et al. 2012).

In a different study, Chaturvedi et al. (2013), studied degradation of chicken feathers by a strain of *P. aeruginosa* with concomitant electricity production in MFC. It was observed that maximum voltage corresponding to 141 mV was observed after 14 days of incubation. Maximum power density of 1206.78 mW/m² and maximum current density of 8.6 mA/m² were observed. The results showed that chicken feathers can be successfully employed as a cheap substrate for electricity production in MFC. In a different study, rice straw hydrolysate was used for electricity production by Wang et al. (2014). In presence of 400 mg-COD/L, a power density of 137.6 ± 15.5 mW/m² was obtained. Further, it was noted that *Clostridium* and *Desulfobulbus* were the main bacteria involved in electricity generation.

Azo dyes

Many reports have confirmed that bioelectricity can also be generated using waste arising from different sources (Feng et al. 2008; He et al. 2005) and thus complex organic compounds present in waste can be removed with concomitant energy production. However, waste arising from different sources consists of a mixture of compounds, in which some are oxidisable and some are not. These contaminants cannot be degraded by oxidation at anode due to their high redox potentials. However, efficient treatment of wastewater means complete removal of contaminants. Therefore, to remove these contaminants, some modifications in MFC technology were performed. The idea emerged from reports which showed that microorganisms present in biocathode can remove nitrogen (Virdis et al. 2008; Jia et al. 2008). However, this process was not applicable because of its

demerit such as longer start up time and lower power generation (Clauwaert et al. 2007). This drawback was overcome by the use of abiotic cathode such as potassium ferricyanide-feeding cathode (Schröder et al. 2003), which was far more efficient than biocathode. But later on, it was observed that the running cost of this cathode was high and recycling of ferricyanide was difficult. It was noticed that various pollutants are present in wastewaters which have high redox potentials, such as nitro aromatic compounds, chlorinated aromatic compounds, and some metal ions (e.g., chromium (VI) (Wang et al. 2008). Therefore, these pollutants can be used as an alternative to potassium ferricyanide. In this context, it was assumed that azo dyes, which are widely used in textile industries and are one of the major pollutants in wastewaters, can be used as electron acceptors at cathode (Xu et al. 2007). All the azo dyes are characterized by the presence of the –N = N– bond, which can be employed as an electron acceptor. The reduction reactions that may be involved in the cathode chamber are described as follows (Menek and Karaman 2005), in which the –N = N– double bond was reduced to hydrazo (A) or amine (B), via the consumption of two or four electrons.



Liu et al. (2009a, b) have reported production of electricity by employing microbial fuel cells using azo dyes as the cathode oxidants and using *Klebsiella pneumoniae* strain L17 in the anode. For this study, a dual-chamber MFC was constructed, and the biocatalyst employed was *Klebsiella pneumoniae* strain L17 fed with glucose. In this study, three azo dyes namely orange I, orange II, and methyl orange were employed. The results demonstrated that the azo dyes were successfully degraded at the cathode. In addition, power output was highly dependent on the catholyte pH and the dye molecular structure. When pH was varied from 3.0 to 9.0, the maximum power density decreased from 34.77 to 1.51 mW/m². The performances of the MFC fed with different azo dyes can be ranked from good to poor as MO > orange I > orange II.

In a different study, Sun et al. (2009) investigated the removal of Congo red in a single-chambered MFC. In an air cathode single-chambered MFC, equal volumes of aerobic and anaerobic sludge were used as inoculum. The growth medium contained glucose 500 mg-COD/L and Congo red 300 mg/L. The MFC was continuously operated for more than 4 months at a fixed external resistor of 500 Ω. It was observed that MFC voltage gradually decreased over time. The cathode potential decreased rapidly, while that of the anode remained the same. This suggests that the voltage decrease in the MFC supplied

with Congo red was primarily due to the deterioration in cathode performance rather than the suppression of the metabolic activity of anodophilic bacteria. The stable anode potential also indicated that the microbial community was well acclimated. The peak potentials of the cathode decreased from 0.10 to -0.11 V. The results on degradation of Congo red showed that the anaerobic cleavage of the azo bonds of Congo red converted them to form aromatic amines. The electrons arising from glucose (electron donor) by bacteria at the anode were partly transported to the azo dye for reductive cleavage of the azo bond (Sun et al. 2011a, b; Chen et al. 2010). Thus, biological reduction of Congo red which occurred in the presence of glucose is mainly responsible for the degradation of Congo red. This degradation mechanism is similar to the mechanism, which occurs in a conventional anaerobic reactor (Dos Santos et al. 2007; Pandey et al. 2007). In addition, in this study, the microbes taking part in the reduction of Congo red were also identified by PCR-DGGE approach. The bacteria were identified as the members of the genera *Azospirillum*, *Methylobacterium*, *Rhodobacter*, *Desulfovibrio*, *Trichococcus*, and *Bacteroides* were more abundant in the presence of Congo red. Most of the bacteria were found to be aerobic or facultative bacteria, which are often highly versatile in their abilities to degrade aromatic and heterocyclic compounds (Chen et al. 1993; Barkovskii et al. 1995; Roldán et al. 1998; Song et al. 2003; Fournier et al. 2005).

Bakhshian et al. (2011) studied the enzymatic decolorization of reactive blue 221 (RB221) using laccase in a dual-chamber MFC. A dual-chamber MFC was used in which molasses was utilized as substrate in a fed-batch mode in the anode chamber, and dye decolorization catalyzed with an enzymatic reaction by laccase was evaluated simultaneously in the cathode. Results demonstrated that at dye concentration of 112.5 mg/L, maximum power density of 27.5 mW/m² was achieved. In a different study, simultaneous bioelectricity generation and dye degradation was performed with the help of a combined anaerobic–aerobic process. The anaerobic system was a typical single-chambered microbial fuel cell which utilized acid navy blue r (ANB) dye along with glucose as growth substrate to generate electricity. The dye decolorization followed pseudo first-order kinetics. It was observed that coulombic efficiency and power density were at peak values at 10.36 % and 2236 mW/m², respectively, for 200 ppm of ANB (Khan et al. 2015a, b). In a recent study, a new device called microbial fuel cell-coupled constructed wetland (CW-MFC) was constructed to treat the wastewater and produce energy. In this study, degradation of recalcitrant dye reactive brilliant red X-3B (ABRX3) was decolorized. It was observed that decolorization rate and the electricity production increased to a

peak value of 95.6 % and 0.852 W/m³, respectively, when the COD concentration was 300 mg/L while the ABRX3 proportion was 30 % (Fang et al 2015).

Selenite

Selenium and its various derivatives such as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are widely used in industries such as glass manufacturing and electronic industries. Thus, wastewater arising from these industries contains high amounts of selenium and its derivatives. Many studies have shown that selenite is more toxic than selenate to aquatic invertebrates and fishes (Hamilton 2004) and it is readily accumulated by aquatic plants and thus causes bioaccumulation in higher organisms (Riedel et al. 1991). Selenium also comes into environment through sewage sludge, fly ash from coal-fired power plants, oil refineries, and mining of metal ores (Hamilton 2004; Lemly 1997). Studies have confirmed that moderately high concentrations of Se cause both acute and chronic toxicity in aquatic organisms (Catal et al. 2008; Kashiwa et al. 2000; Rovira et al. 2008). Therefore, several methods have been developed for removal of selenium from environment (Banuelos and Lin 2005). Few reports have shown that selenium compounds can be converted to elemental selenium by various microbes, which is less toxic (Fujita et al. 2002; Kashiwa et al. 2000). Catal et al. (2009) have investigated the application of MFC technology in reduction of selenium and production of electricity using selenium-containing waste. In their study, a single-chamber air cathode MFC was constructed. Sodium acetate (2 g/L) or glucose (1.2 g/L) was employed as carbon source. Artificial wastewater was created by dissolving sodium selenite in minimal medium solution containing either acetate or glucose. The MFCs were inoculated with a mixed bacterial culture. Results showed that a voltage of 0.54 V was produced using Se-free medium solution, corresponding to an anodic power density of 2900 mW/m². In addition, it was observed that the power output was not affected when the medium solution was replaced with solutions containing 1–25 mg/L. However, further increase of selenite to 50 mg/L resulted in a 13–17 % decrease in voltage output. When selenite was increased to 75 mg/L, the voltage and power density decreased to 0.41 V and 2200 mW/m², respectively.

Nitrate

The presence of nitrate in water is increasing tremendously due to excessive use of nitrate-based fertilizers and through animal waste (Chebotareva and Nyokong 1997). Nitrate being a non-toxic compound can be easily transformed to Nitrite (NO_2^-) in human body, which causes a disease namely “blue baby syndrome”, which is normally observed in infants. Nitrate can be converted

into N-nitroso compounds which are carcinogenic in humans (Claudio 2005). Therefore, many methods have been designed to treat nitrate-contaminated water. Some of the commonly employed methods are electrochemical treatment, ion exchange (IE), reverse osmosis (RO), electrodialysis (ED), and heterogeneous catalysis (HC) (Park and Yoo 2009). A major drawback of these methods is that most of them are expensive (Till et al. 1998). Recently, use of MFC technology for removal of nitrate has gained importance due to ease and feasibility of this process. Several studies have been carried out for reduction of nitrate to nitrite or nitrogen gas at cathode, few workers have employed a metal catalyst (Polatides and Kyriacou 2005) or microorganisms as catalysts on cathode electrode (He and Angenent 2006). In these studies, the anode was employed as a power source (Fang et al. 2011) or in some studies external power supply was used, (Dima et al. 2005) or cathode, which served as electron donor (Lovley 2011). In few studies, electrochemical denitrification process to remove nitrate ions was employed at cathode chamber of bioelectrochemical denitrification system (Kondaveeti and Min 2012). Three different cathodes of Pt-coated electrode, biocathode, and plain carbon were used to investigate their performance in nitrate removal. An H-type two-chambered bioelectrochemical denitrification system was employed. The results showed that biocathode showed a higher removal percentage (82.4 %) followed by a platinum (80.4 %) and carbon cathode (67.8 %). The biocathode and platinum achieved a higher removal rate of 0.183 mg NO₃/cm² in comparison with plain carbon (0.151 mg NO₃/cm²). In other studies, denitrification with biocathode in cathode chamber using an bioanode as the electron donor source was carried out and could achieve a maximum of 22 % nitrate removal in 7 days (168 h) operation with a removal rate of (0.0436 mg NO₃/cm²) (Dima et al. 2005; Park et al. 2005). In addition, it was observed that nitrate removal percentage was increased by increasing the cell voltage from 0.5 to 0.7 V for all types of cathodes. In another study by Fang et al. (2011), nitrate ions were used as the oxidant in MFC to generate electricity from organic compounds with simultaneous nitrate removal. The MFC using nitrate as oxidant could generate a voltage of 111 mV (1000 Ω) with a plain carbon cathode. The maximum power density achieved was 7.2 mW/m² with a 470 Ω resistor. In the presence of Pt catalyst dispersed on cathode, the cell voltage was significantly increased up to 450 mV and the power density was 117.7 mW/m², which was 16 times higher than the value without Pt catalyst. In a different study, electricity generated from the MFC is applied to the bioelectrical reactor (BER) directly as electrical stimulation for enhancement of bacterial denitrification to remove nitrate effectively from groundwater.

The results showed that with nitrate removal a maximum power density of 502.5 mW/m² and voltage outputs ranging from 500 to 700 mV were observed (Zhang et al. 2014). In some studies, nitrate and sulfite have been removed simultaneously. In a study by Cai and Zheng (2013), a two-chamber MFCs was constructed to remove sulfide and nitrate using activated sludge. When the external resistance was 1000 Ω, the initial concentrations of sulfide and nitrate were about 60 and 10.5 mg/L, respectively; maximum current density of the MFC was 138.31 mA/m². The main end products were nitrogen and sulfate (Cai and Zheng 2013). In another study, Cucu et al. (2016) have studied denitrification in MFC. The anode consisted of cow manure and fruit waste and the cathode consisted of cow manure and soil. With initial COD/nitrate nitrogen ratio from 2 to 40 at the cathode while keeping the anode ratio fixed at 100. Maximum current density of 190 ± 9.1 mA/m² and power density of 31.92 ± 4 mW/m² of electrode surface area. A comparative analysis of current and power output of all the xenobiotics and wastes is depicted in Table 3.

Commercialization of MFC

Success of any technology depends upon its commercialization when it is marketed in huge amounts and used by a large number of people. Since MFC deals with production of electricity by employing waste materials, its commercialization will offer several advantages such as:

1. Production of low-cost electricity from waste materials.
2. The electricity will be produced all round the year since waste and xenobiotics are readily available.
3. People would be able to produce electricity in their homes.
4. This technology will be helpful for the people living in poor countries such as Africa where huge infrastructure required for set of energy production plants is not available.
5. MFC will lead to clean up of wastes and xenobiotics. So, it can be used as an alternate method for bioremediation.

The output of MFC depends upon a number of parameters such as its configuration, type of substrate, its concentration, microorganism used, catalyst, materials used in cathode and anode, suitable membrane, which play an important role in its performance (Logan and Regan 2006a, b). Many reports are available of scaling up of MFC from few ml to several thousand liters. The results of these studies have demonstrated that a major drawback in commercialization of MFC is that scaling up causes decreased power output. These studies have

Table 3 A comparative analysis of Power and current output obtained with wastes and Xenobiotics

S. No.	Xenobiotics/Wastes	Concentration	Current/Power output	Reference
1	Hexavalent chromium	80 mg/L	123.4 mA/m ² and 55.5 mW/m ²	Tandukar et al. (2009)
2		39.2 mg/L	2.4 W/ m ³	Wang et al. (2008)
3		10 mg/L	21.4 mW/ m ²	Gangadharan and Nambi (2015)
4		100 mg/L	767.01 mW/m ²	Xafenias et al. (2015)
	Agrowaste			
5	Cassava waste water	16000mg- COD/L	1771 mW/ m ²	Kaewkannetra et al. (2009)
6		1, 086 mg - COD/L	22.19 W/m ³	Prasertsung et al. (2012)
7	Cellulose	1g/L CMC	143 mW/ m ²	Ren et al. (2008)
8		4 g/L	4.9 mW/ m ²	Rezaei et al. (2009)
9		1 g/L	188 mW/ m ²	Sedky et al. (2012)
10	Vegetable waste	0.5 g COD/L clover sap	70 mW/m ³	Clauwaert et al. (2008)
11	<i>Dioscorea zingiberensis</i> tubers	3000 mg- COD /L	175 mW/m ²	Li and Ni (2011)
12	Brewery waste water	600 mg-COD/L	830 mW/m ³	Wen et al. (2010)
13	Chocolate industry wastewater	1459 mg/L COD	0.302 mA/cm ²	Patil et al. (2009)
14	Domestic wastewater	600 mg/L	0.06 mA/cm ²	Wang et al. (2009)
15	Protein-rich wastewater	1.75 g/L COD	0.008 mA/cm ²	Liu et al. (2009b)
16	Starch processing wastewater	4852 mg/L COD	0.09 mA/cm ²	Lu et al. (2009)
17	Slaughter house waste water	900 mg-COD/L	578 mW/m ²	Katuri et al. (2012)
18	Chicken feathers	10g/L	1206.78 mW/m ²	Chaturvedi et al. (2013)
19	Rice straw hydrolysate	400 mg- COD/L	137.6 mW/m ²	Wang et al. (2014)
	Azo dyes			
20	Acid orange 7 (AO7)	35mg/l	39.2 mW/m ²	Fernando et al. (2012)
21	Azo dye with glucose	300mg/l	0.09 mA/cm ²	Sun et al. (2009)
22	Methyl orange	0.05 mM	0.0154 mA/cm ²	Liu et al. (2009a)
23	Congo red and glucose	Congo red (300 mg/L) and glucose (500 mg COD/L)	0.0897 mA/cm ²	Sun et al. (2009)
24	Reactive blue 221 (RB221)	112.5 mg/L	27.5 mW/m ²	Bakhshian et al. (2011)
25	Acid navy blue r (ANB) dye	200 ppm	2,236 mW/m ²	Khan et al. (2015)
26	Reactive brilliant red X-3B (ABRX3)	300 mg-COD/L	0.852 W/m ³	Fang et al. (2015)
27	Selenium	25 mg/ L	2,900 mW/ m ²	Catal et al. (2009)
28	Nitrate		117.7 mW/m ²	Fang et al. (2011)
29			502.5 mW/ m ²	Zhang et al. (2014)
30		10.5 mg/L	138.31 mA/m ²	Cai and Zheng (2013)
31		40 mg-COD/L	31.92 mW/m ²	Cucu et al. (2016)

shown that the factor which affects power output in MFC during scaling up is the distance between electrodes. As the size of electrodes is increased during scaling up, the distance between electrodes is not increased to same extent because it will make MFC more bulkier. This is the reason why power output is decreased. Another factor which hinders its scaling up is the cost of electrodes. It should be sufficiently low. However, in reality, the electrodes are very costly because these are not produced industrially and also the material with which they are made is very costly. The membranes used in MFC are usually made up of nylon which is costly. Another important factor is the substrate; in laboratory conditions,

when MFC is run on pure substrates the power output is very high but when it is run on waste materials its power output is diminished dramatically. This is due to the fact that microorganisms are not able to metabolize waste materials as efficiently as pure carbon sources. These are the major factors which hinder commercialization of this technology.

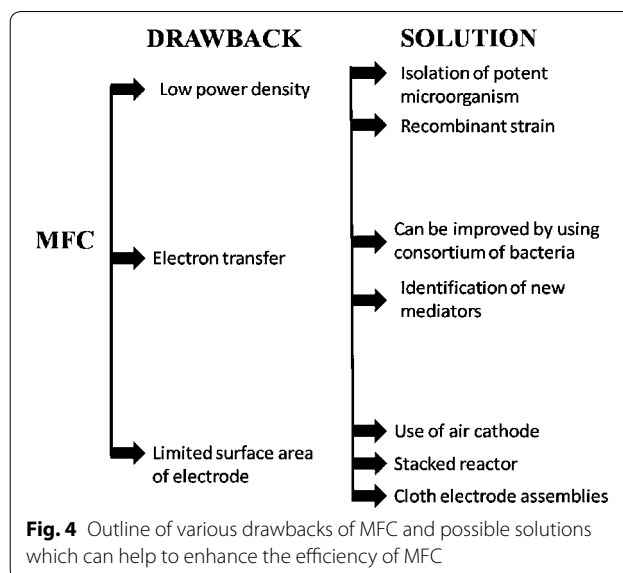
Major pit holes of the technology

MFC being a promising technology for power generation by employing waste material suffers from many challenges which hinder its commercialization. Some of the important pit holes of this technology are as follows:

1. The power density obtained with xenobiotics and wastes is very low as compared to pure carbon sources such as glucose. This hinders its applicability in waste management and generation of electricity for day to day purposes.
2. Pure carbon sources cannot be routinely employed for electricity generation because they are costly as compared to wastes.
3. The material used in cathode/anode and membrane during scaling up of MFC is costly, which hinders its commercialization.

Future prospects

MFC is a promising technology for generation of electricity from organic substances, especially from organic waste of different origin. However, there are certain drawbacks, which has hindered to make it more applicable when practical applications are concerned. The major drawback of MFC technology is the low power density; this can be rectified by either isolation of potent microorganisms that can efficiently transfer electrons to anode or by generating engineered strains through recombinant DNA technology that show greater electron transfer rates. Many reports have confirmed that rather than pure cultures, consortium of many bacteria show improved electron transfer rates to the anode. Many bacterial strains have been shown to produce mediators which efficiently transfer electrons to the anode. Identification of new mediators can also increase the performance of MFC technology. Another drawback of MFC is the limited surface area of the electrodes where microorganisms adhere. Extensive studies have been performed to identify methods that enhance the performance of MFC reactors and have resulted in the designing of more efficient laboratory-scale MFCs. These technologies include the use of air cathodes (Liu and Logan 2004), stacked reactors (Aelterman et al. 2006) and cloth electrode assemblies (Fan et al. 2007). Among these, the use of air cathodes (Liu and Logan 2004) is very effective since it helps in efficient use of oxygen from air and avoids the need for aerating the water or using chemical catholytes such as ferricyanide that must be regenerated. Air cathodes have been optimized for the use in MFCs (Cheng et al. 2006a, b), and the effects of shape and position on MFC performances have been evaluated using different reactor designs (Zuo et al. 2007; Fan et al. 2007). These efforts have resulted in highly efficient small-volume laboratory MFCs (~20 ml in anode volume) that produced electrical outputs of over 1000 W m³ (Fan et al. 2007). However, it is still a challenge for MFC researchers to construct large-scale MFCs that have both high power production and stable performance (Zuo et al. 2007). Liu



et al. (2008) have recently reported the construction of a 500-ml MFC reactor with the maximum power density of 20 W m³ (Fig. 4).

Another drawback of this technology is in treatment of wastewaters and scaling up of MFC. Scaling up of MFCs for large-scale applications and for improving the overall performance of MFC technology will help in treatment of wastewater, which is present in large quantities.

Conclusions

MFC is a state-of-the-art technology for production of electricity from metabolism of microorganisms. In this review, we have dealt with major wastes and xenobiotics, such as hexavalent chromium, agrowastes, nitrates and azo dyes. Some of them such as hexavalent chromium and azo dyes are very toxic to the ecosystem and cause death of organisms. In MFC, they are used for electricity production and also they are transformed into less toxic metabolites, which demonstrates its another potential use in waste management and pollution control. Till now, a large number of microbes and a waste variety of substrates (including waste and xenobiotics) have been used to produce electricity. However, a major drawback of this technology is that the power output is very low and scaling up leads to a decrease in power output. This is the main reason why this technology has yet not been commercialized. So, a lot more work is required so that this technology becomes efficient, applicable and widely accepted.

Authors' contributions

PV planned the review. VC carried out the literature survey. PV and VC prepared the MS. Both authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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