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REVIEW ARTICLE

Wastewater Treatment and Concomitant Bioelectricity Production Using Microbial Fuel Cell: Present Aspects, Up-Scaling and Future Inventiveness

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Abstract
The requirement for a low-cost option for wastewater treatment and simultaneous bioenergy and resource recovery from the wastewater to make treatment sustainable has prompted the researchers to seek innovative technologies. Microbial fuel cell (MFC) is one of the bio-based novel technologies that converts the chemical energy of substrate into electrical energy using electrochemically active bacteria as biocatalyst. With the forefront energy crisis, the MFC has gained widespread popularity due to its capability to harvest direct electricity, while simultaneously treating wastewater. To make this technology scalable, significant efforts and modifications have been attempted by the researchers, including improved design, hybrid concepts, use of low-cost materials for the basic components (electrodes, membrane), establishing innovative low-cost catalysts, identifying several microorganisms as exoelectrogens and methods of pre-treatment of mixed anaerobic sludge to enrich electrogens, etc. This review summarises some of these recent advances pertaining to the MFC and few upscaling applications of MFC. Furthermore, a concise future scope is elaborated in the view of common challenges in the field of MFC for wastewater treatment.

Keywords Bioelectricity · Cathode catalyst · Ceramic separator · Microbial fuel cell · Wastewater treatment

Introduction

The bio-electrochemical systems (BES) are a group of engineered systems that have been in the limelight for wastewater treatment and resource recovery. While several variants of BES exists today, the first-generation systems, namely the microbial fuel cells (MFCs) have been profoundly explored for recovery of bioelectricity as well as other valuables, while facilitating treatment of wastewater. The concept of recovering electricity by utilising microbial colonies that are abundantly found in nature, and have the ability to consume waste-based or other sources of oxidisable organic matters, was first demonstrated by M. C. Potter in 1911 (Potter 1911). The investigation documented the production of electrical energy using selected pure culture strains of bacteria and fungi (*Escherichia coli* and *Saccharomyces*). This thought was promulgated further, when almost 25 years later, Cohen stacked up 35 cells to derive 2 mA of current generation (Cohen 1931). In the year 1976, Suzuki et al., demonstrated a stable hydrogen generation with a suitable design for MFC (Karube et al. 1976).

Further to this, the application of synthetic mediators for shuttling electrons between microbes and electrode led to the design of MFC, which has undergone minimal architectural changes till the date (Allen and Bennetto 1993). However, a paradigm shift in the operational procedure occurred when Kim and Al discovered electroactive bacteria that did not require any mediators to shuttle electrons (Kim and Al 1999). This drastically reduced the economic demand of BES technology by eliminating the need or expensive external mediators. Subsequent to this, the last two decades have witnessed a sizeable amount of research on BES design, optimization of physical, chemical and biological operating conditions, optimization of microbial metabolism, appropriate selection of exoelectrogens and construction materials to enhance the electron transport vis-á-vis enhanced efficacy of the different BES variants (Logan et al. 2006; Ghangrekar and Shinde 2008). Presently, there are five major variants

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of BES that have been developed over the last two decades. Among these, MFC and microbial electrolysis cell (MEC) are the two variants of first-generation BES, while the other types, namely microbial carbon-capture cell (MCC), microbial desalination cell (MDC), and the microbial electrosynthesis cell (MES) can be thought as the derived variants of the two fundamental types of BES.

It is estimated that domestic wastewater contains higher energy than the energy required for its treatment. This states that theoretically, wastewater treatment can be a self-sustained process. One of the most recent approaches of energy generation from wastewater is via the use of MFC, which has the capability of bioelectricity generation through oxidation of organic matter (Li et al. 2014). Unlike other processes such as methane and hydrogen production via anaerobic digestion and biofermentation, respectively, that require two stages for electricity generation, MFC offers an advantage of onestep electricity production. Apart from electricity production, MFCs are energy saving technology that does not require aeration (for air–cathode MFC), thus contributing to reduced energy input. Compared to the conventional activated sludge process, MFC contributes to far less sludge production (He 2013 Li et al. 2014). Moreover, the anode in MFC acts as an electron sink and makes the process of organic matter degradation independent of other terminal electron acceptors, which are essential in the conventional anaerobic digestion (Logan 2009).

Although, the BES technology has a niche over the conventional treatments and has opened up an entirely new field of transdisciplinary research augmenting biotechnology, energy science, materials chemistry, surface chemistry, chemical engineering, and electrochemistry; however, the majority of investigations are still imited to lab-scale. Similar to the conventional fuel cells and electrolysis cells, which are used for electricity generation and other industrial applications, respectively, the MFC and MEC also have similar bottlenecks associated with the usage of electrodes, catalysts, and membranes. In addition to these, in the majority of cases biological reactions drive the waste treatment processes and the electricity generation, hence the direct energy that can be harvested is very low for grid-based utilisation.

Moreover, the different problems related to scaling-up, such as high cost of electrodes, high diffusion losses for a larger sized reactor, inadequate electrode surface area to volume ratio, higher fabrication cost leading to smaller size of membrane panels, even while using low-cost ceramic membranes, etc., need to be addressed. These are the universal bottlenecks of BES variants as well as bottlenecks pertaining to the scaling-up of MFC, a first-generation BES. The present technological development and research findings are driven towards finding solutions to overcome or mitigate these constraints to move towards scaling-up of this state-of-the-art technology that enables wastewater treatment and consequential one-step valuables and/or energy recovery. The discussions in this review paper are primarily focused on the advancements in the field of MFC and the decadal developments as well as addressing future research requirements for the possible field-scale application of this technology.

Description of Microbial Fuel Cell and Other Bio-Electrochemical Systems

A MFC can have a dual chamber configuration having an aqueous cathode or a single chamber with an air exposed cathode, which directly use oxygen from air (Jadhav et al. 2017). The dual chamber MFC has a separator in between the anodic and the cathodic chambers, which is usually a cation/proton exchange membrane (CEM/PEM) (Fig. 1a). The anodic and the cathodic chambers have anode and cathode electrodes, respectively, which are connected through an external load using conductive wires. The materials popularly used for anode and the cathode are carbon felt,

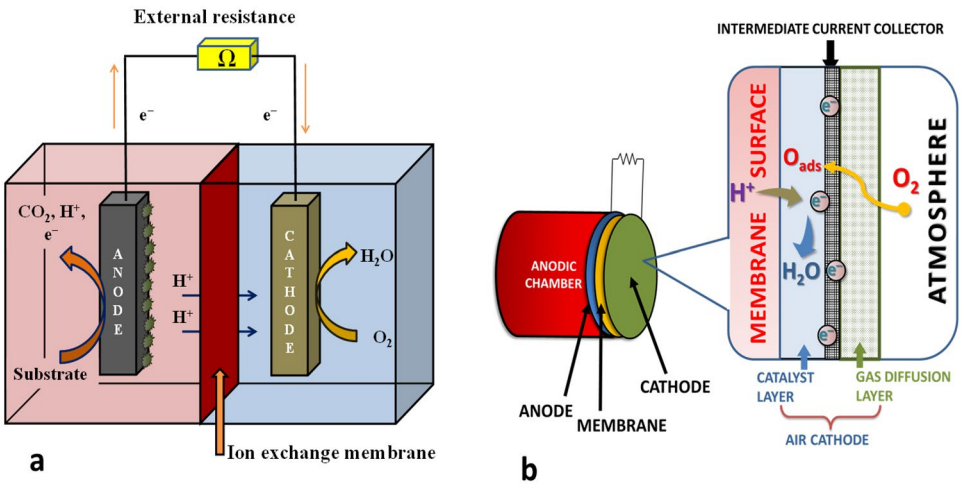

Fig. 1 Typical arrangements of microbial fuel cell with **a** dual chamber and **b** single chamber air cathode configuration

carbon fibre, carbon cloth, and stainless steel mesh modified suitably to sustain biofilm in case of anode, and facilitate gas diffusion in case of air cathode. Other suitable materials such as biochar (Huggins et al. 2014), activated carbon granules (Neethu et al. 2020b), graphite granules (Zhang et al. 2011), polymer-based electrodes (Yuan and Kim 2008) have also been developed to be used as electrodes in MFC. The anodic chamber houses the bacterial inoculum that utilises the organic substrate for metabolism and in the process releases electrons (Eq. 1) (Logan et al. 2006):

$$CH_3COO^- + 4\,H_2O \rightarrow 2HCO_3^- + 9\,H^+ + 8\,e^- \quad \left(E' = -0.296\ \text{V, vs. Standard hydrogen electrode, SHE at pH} = 7\right). \tag{1}$$

These electrons are transferred to the anode of the MFC via electrically conductive nanowires and mediators. The electrons thus passed on to the anode travel through an external circuit to reach the cathode. On the cathode surface any suitable chemical species, generally O_2, act as a terminal electron acceptor. When O_2 is used as an electron acceptor, then the cathodic reaction is termed as oxygen reduction reaction (ORR) owing to the reduction of oxygen to H_2O_2 (Eq. 2) or H_2O (Eq. 3) by accepting two or four electrons, respectively, from the cathode and utilising the H^+ that migrates through the CEM/PEM from the anodic to cathodic side (Rabaey and Verstraete 2005) (Fig. 1a):

$$O_2 + 2\,H^+ + 2e^- \rightarrow H_2O_2 \quad \left(E' = 0.328\ \text{V, vs. SHE at pH} = 7\right), \tag{2}$$

$$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O \quad \left(E' = 0.805\ \text{V, vs. SHE at pH} = 7\right). \tag{3}$$

In case of single chamber MFC, the cathode has a gas diffusion layer that is exposed to the air and a catalyst layer that is exposed to the anolyte either directly or juxtaposed to an ion exchange membrane that faces the anolyte and anode (Fig. 1b). The oxygen diffuses through the gas diffusion layer and reaches the catalyst layer, where it reacts with the migrated proton to form H_2O or H_2O_2 (Noori et al. 2016; Dong et al. 2018). In the case of both dual chamber as well as single chamber MFC usual practice is to employ CEM/PEM. However, the use of PEM, such as Nafion, also allows transport of other cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) as well, apart from the proton (H^+). Typically in MFCs, the concentration of other cations is 10^5 times higher than protons. This cation transport to the cathodic chamber results in a drop of anolyte pH in the anodic chamber and an increase of catholyte pH, leading to reduced cathode potential (Rozendal et al. 2006). Hence, in certain cases, anion exchange membranes are also used for the operation of MFC and the OH^- generated during cathodic H_2O dissociation migrates to the anodic chamber, where it balances this pH imbalance created due to the generation of H^+ during the anaerobic respiration (Rozendal et al. 2007; Pandit et al. 2012).

Apart from the pH imbalance due to the application of PEM/CEM in MFC, there are several bottlenecks that have to be addressed prior to the commercialization of this technology. One major issue is the slower interaction of the bulk media and the anodic biofilm in case of larger reactors. The larger reactor size also limits the flow of ions 'from' and 'to' the surface of the anodic biofilm due to slow diffusion and mass transport rates of ions. The larger size of MFCs with higher bulk volume also increases the susceptibility of substrate and proton scavenging biochemical and chemical reactions. In addition to this, scale-up also necessitates the usage of low cost electrode materials while achieving high conductivity, chemical stability, biocompatibility (in case of anode and biocathode), having low charge transfer resistance, and favouring higher oxygen reduction reaction (ORR) catalytic activity (in case of cathode) (Wei et al. 2011; Yuan and He 2015).

Hence, in light of the above discussion, it is imperative that for scaling-up of MFC and to make it sustainable, research should be focussed on several of issues a few out of them being: development of low cost electrodes and membranes; novel reactor design to maintain electrode area to volume ratio; novel hydraulic design to reduce the diffusional and mass transport losses; minimise the unwanted scavenging reactions; and developing novel power management systems for boosting the power harvested from MFC. In the subsequent sections of this review, the research developments towards achieving these goals have been discussed. In addition to these, the performance of MFC in the field of contaminant removal has also been highlighted.

Recent Developments in Microbial Fuel Cells for Enhancing Performance

Suppression of Methanogenesis from Mixed Anaerobic Sludge Used as an Anodic Inoculum

In the anodic chamber of MFC, exoelectrogens transfer the electrons released during the oxidation of organic matter to the anode. However, the use of mixed anaerobic sludge as inoculum in the anodic chamber leads to substrate and proton loss due to the presence of acetoclastic and hydrogenotrophic methanogens. Interestingly, the hydrogenotrophic methanogens exist in syntropy with the exoelectrogens in nature, wherein the electrons generated during the metabolic activity of exoelectrogens are transferred to the hydrogenotrophic methanogen by means of hydrogen ion (Kim et al. 2005; Schröder and Harnisch 2017). Instead of transfer of protons to the cathode via cation exchange membrane, the available hydrogenotrophic methanogens in the mixed sludge consume hydrogen and CO_2 and produce methane. Thus, the presence of methanogens leads to methanogenesis instead of electrogenesis reflecting in reduced current production in MFC. On the other hand, the acetoclastic methanogens compete with the exoelectrogens for the substrate in the form of acetate when both of the species co-exist in the anodic chamber of MFC (Kim et al. 2005). This points to the fact that the methanogens are unwanted species in the anodic chamber of MFC and the presence of methanogens reduces power production both by reducing substrate availability as well as by scavenging H^+ and e^- (Nath and Ghangrekar 2020). Hence to improve the performance of MFC by suppressing the methanogenesis several strategies have been devised by the researchers (Table 1).

The strategies applied for suppression of methanogenesis in the inoculum sludge in anodic chamber of MFC can be classified into two different categories, viz., physical or chemical techniques. The physical suppression techniques include the application of heat treatment, ultrasonication, and regulation of anode potential (Ghangrekar and Shinde 2008; More and Ghangrekar 2010; Grüning et al. 2015). Among chemical techniques, the application of 2-BES has been a popular choice due to the effective suppression of methanogenesis in the anodic chamber. Other compounds and chemical species that have been experimented for suppression of methanogens include antibiotics (Ray et al. 2017), algal fatty acids (Rajesh et al. 2015), and metal ions such as Al (Bagchi and Behera 2019). The suppression of methanogenesis has also been achieved by regulation of anode potential as well as external resistance. It has been observed in the past investigations that the population of methanogens get attenuated at positive anode potentials or potentials near to zero (Zhao et al. 2019; Nath et al. 2021). Regulation of external load also is an indirect manifestation of the anode potential regulation and has been demonstrated to be successful in enriching electrogens in the anodic chamber of MFC in past investigations (Rabaey et al. 2005).

In an investigation, marine algae *Chaetoceros* was employed to inhibit the methanogenesis in the mixed anaerobic sludge used as an anodic inoculum. This can be achieved by the impact of hexadecatrionic acid, which is present in this marine algae, on the cell membrane of the methanogens

Table 1 Different methanogenesis suppression measures tried on anodic sludge in MFCs

Method of methanogenesis suppression	Configuration of MFC	Sludge used in anodic chamber	Maximum power density (W m^{-3})	Coulombic efficiency (%)	Reference
Low-frequency ultrasound	Dual chamber MFC	Mixed anaerobic sewage sludge	65.34 mW m^{-2}	2.93	More and Ghangrekar (2010)
2-Bromoethanesulfonate	Single chamber air cathode MFC	Sewage sludge	115 mW m^{-2}	7.8	Zhuang et al. (2012)
Variation in external resistance	Dual chamber MFC	–	3.5	29	Rismani-Yazdi et al. (2013)
Lauric acid addition	Dual chamber MFC	Septic Tank sludge	4.8	11.6	Rajesh et al. (2014)
Extended starvation via lack of substrate	H-type MFC	Anaerobic sludge	–	59.2	Kaur et al. (2014)
Marine algae *Chaetoceros*	Dual chamber MFC	Mixed anaerobic sludge	21.43	45.18	Rajesh et al. (2015)
Neoatroviridin (A-D)	Dual chamber MFC	Mixed anaerobic sewage sludge	9.68	53.5	Ray et al. (2017)
Nitroethane	Dual chamber MFC	Mixed anaerobic sludge	20.5	39.85	Rajesh et al. (2018)
Aluminium	Dual chamber MFC	Anaerobic sludge	1.84	24.59	Bagchi and Behera (2019)
Air exposure	Dual chamber MFC	Anaerobic sludge from pond	656.10 mW m^{-3}	17.21	Raychaudhuri and Behera (2020)

(Rajesh et al. 2015). Application of biogenic compounds for suppression of methanogenesis was also demonstrated by employing extracted peptaibiotics from *Trichoderma* sp. for suppression of methanogenesis in the anodic chamber of MFC (Ray et al. 2017). The MFC inoculated with mixed anaerobic sludge pre-treated with the peptaibiotics exhibited a 2 times increase in power density as compared to the control MFC with similar anode and cathode catalyst configurations and inoculated with mixed anaerobic sludge without any pre-treatment. Extending this work, another research demonstrated that the plant extracts had a profound effect on the power density of MFC when applied in different concentrations (Neethu et al. 2020a). However, different follow-up investigations revealed that the effects of plant extract are manifold and not limited to the suppression of methanogenesis. The plant extracts, on one hand, cause changes in the cell morphology and stimulates gene expressions that trigger conductive nanowire growth in the methanogens, while on the other hand acts as an electron shuttle for the extracellularly projected electrons (Nath and Ghangrekar 2020).

These investigations indicate that the methanogenesis suppression and promotion of exoelectrogenesis can be achieved by low cost facile biogenic methods. Even certain wastewater characteristics can cause intrinsic suppression of methanogenesis as it is a well-established fact that methanogens are susceptible to high organic fluctuations, high ammonia concentration, and are vulnerable to acidic and alkaline pH. This was observed in a work done by Bhowmick et al., in which the high ammonia content of the fish processing wastewater caused inhibition of the methanogenesis and enhanced the power density of MFC, while treating fish processing wastewater (Bhowmick et al. 2020).

Cathode Catalysts for Microbial Fuel Cell

As elaborated in "Description of microbial fuel cell and other bio-electrochemical systems", the terminal electron acceptor is reduced at the cathode of MFC by incoming electron from the anode. The ORR kinetics on the cathode is directly dependent on the cathode material and unmodified carbon electrodes with lower content of active sites lead to sluggish ORR. This sluggish ORR causes overpotential losses, which directly affects the power generation of the MFC. This has prompted researchers to develop the electrocatalytic material for enhancing ORR at the cathode and harvest a higher amount of electricity from the MFC. Over the years the research in the BES domain has led to the development of a wide array of cathode catalysts (Table 2), which includes metal-based, carbon-based catalysts, and biocatalysts (Rismani-Yazdi et al. 2008; Khilari and Pradhan 2017).

Platinum is the popularly used benchmark cathode catalyst in MFC, which is giving excellent performance in terms of power generation due to enhanced ORR (Logan et al. 2005). When Pt was used as a cathode catalyst at a loading of 0.1 mg cm^{-2} the catalysed MFC was capable of generating the maximum power density of 340 mW cm^{-2} (Cheng et al. 2006), thus reflecting improved ORR of catalysed MFC even at very low Pt loading. However, high cost and catalyst poisoning limits the use of Pt for practical and scaled-up MFCs. In this regard, considerable efforts have been made to develop low-cost cathode catalysts using metals, metal oxides, combinations of various metal oxides, and metal-based composites to cut down the cost of the MFC fabrication and to make it more practicable (Yuan et al. 2016).

Over the years, for the replacement to Pt, metals such as Co (Lefebvre et al. 2009), Ni (Ghasemi et al. 2013), Pd (Das et al. 2020b), and Pt-based catalysts like Pt–Co (Huang et al. 2006), Pt–Ni (Yang et al. 2004), Pt–Pd (Quan et al.

Table 2 Representative metal-based and carbon-based cathode catalysts used in MFCs

Cathode catalyst	Catalyst loading (mg cm^{-2})	COD removal efficiency (%)	Maximum power density (mW m^{-2})	Coulombic efficiency (%)	Reference
Pt	0.1	–	340	4.5–7.5	Cheng et al. (2006)
Co	0.1	88	–	24	Lefebvre et al. (2009)
Ni/C	1	> 90	94.4	20.7	Ghasemi et al. (2013)
Pt–Pd	Pt @0.1 and Pd @0.05	–	1274	-	Quan et al. (2015)
V_2O_5 microflower	0.5	80	6.06	15.2	Noori et al. (2016)
WO_3	0.5	81	3.11 W m^{-3}	18.5	Das and Ghangrekar (2020)
Carbon nanotubes supported MnO_2	3	84.8	97.8	–	Lu et al. (2011)
Rh deposited over activated carbon	2	93	9.36 W m^{-3}	–	Bhowmick et al. (2019a)
Sewage sludge biochar	5	–	500	–	Yuan et al. (2013)
Watermelon rind biochar	0.5	–	0.262 W m^{-3}	–	Zhong et al. (2019)

2015), exhibited resilient ORR activity when used as cathode catalyst in MFC (Table 2). In one of the investigations, V_2O_5 micro-flowers were effectively used as cathode catalyst in an air cathode MFC (Noori et al. 2016). The electrochemical analysis demonstrated enhanced ORR that caused 6.06 W m^{-3} of maximum power density along with 80% of chemical oxygen demand (COD) removal from fish market wastewater. Improved electrochemical performance of MFC using V_2O_5 might be linked to a reduction in the charge transfer resistance in addition to the highly porous structure, which aided in superior oxygen penetration. Similarly, other metal oxides, viz. lead oxide (Morris et al. 2007), manganese oxide (Liu et al. 2010), cobalt oxide, iron oxide (Bhowmick et al. 2019b), tungsten oxide (Das and Ghangrekar 2020), etc., have been widely used as cathode catalyst in MFCs.

The use of carbon-supported metallic catalyst is another class of cathode catalyst that has gained popularity due to its superior electrochemical performance. Carbon-based materials, such as carbon nano tubes (CNT), activated carbon (AC), graphene, graphitic carbon, etc., have excellent electrocatalytic properties (Yang et al. 2013; Ben Liew et al. 2014). The graphene and CNT-based catalysts are capable of forming a 3D structure with an improved surface area. Moreover, catalyst modification using the hydrothermal technique caused improved conductivity and electron transfer efficiency due to 3D aerogel and hydrogel microstructures formation in N and S doped graphene (Verma et al. 2020). Hence, these materials are becoming a choice for the development of novel high performance cathode catalysts in MFC (Wang et al. 2011a; Ma et al. 2015). In an investigation by Yuan et al., the application of amino-functionalized multi-walled CNT as a support matrix for iron phthalocyanine has demonstrated four-electron pathway for oxygen reduction, thus reflecting high oxygen reduction potential. The corresponding maximum power density of 601 mW m^{-2} obtained by MFC was even better than the MFC having Pt/C cathode (Yuan et al. 2011). Similarly, other carbon-based metal catalysts used are: (1) carbon-supported Cu-Sn (Noori et al. 2018a), nickel-phthalocyanine/MnO_x (Tiwari et al. 2017); (2) CNT supported MnO_2 (Lu et al. 2011), Co and Fe (Türk et al. 2018); (3) graphene supported MnO_2 (Khilari et al. 2013), Co–Ni (Hou et al. 2016), Pt–Co (Yan et al. 2013); (4) graphitic carbon-supported Ag–Fe_2O_4 (Ma et al. 2015); (5) AC supported silver (Pu et al. 2014), Cu_2O (Zhang et al. 2015), MnO_2 (Singh and Chandra 2013), Rh (Bhowmick et al. 2019a).

Carbonaceous catalysts are much cheaper than metal-based electrocatalysts and are proven to be effective as cathode catalyst in MFC. One of the major benefits of carbon-based catalyst is low-cost, as these catalysts can be synthesised using pyrolysis of the waste products as well. The AC had also been used as cathode catalyst in MFC derived from various precursors, such as coal, coconut shell, peat, hardwood, etc. Coal-derived AC has resulted in a maximum power density of 1620 mW m^{-2}, additionally the n value of 3.6 indicated a nearly four-electron pathway of oxygen reduction (Watson et al. 2013). Yet, the catalytic activity towards ORR is still lower, due to which modifications are required in pure AC matrix (Zhang et al. 2014; Lv et al. 2018).

Doping of nitrogen in carbon matrix is one of the effective ways of improving the ORR catalysis in AC catalyst. Over the years, researchers have explored pre-treatment methods for effective nitrogen doping in the carbon matrix. The combination of acidic and alkaline pre-treatment using H_2SO_4 and KOH, respectively, has resulted in an increase in nitrogen content to 8.65% in the AC catalyst. The H_2SO_4 pre-treatment with $KMnO_4$ produced oxygen-rich group in AC and successive KOH treatment caused activation of AC. When the pre-treated AC was pyrolyzed with external N in the form of cyanamide, the amines group in cyanamide reacted with oxygen-rich group of pre-treated AC. This caused the formation of C_3N_4 deposition over AC that facilitated the increase in N content. The successive acid–alkali pre-treatment aided in development of oxygen-rich groups, which directly assisted in increased N content due to C_3N_4 deposition. The improved ORR activity might be due to the occurrence of pyridinic-N (5.56%), which is capable of reducing the energy barrier to ORR (Zhang et al. 2014). In another case, nitrogen doped rice straw-derived carbon in three step process (hydrothermal carbonization, freezing followed by heat treatment in NH_3) was used as a cathode catalyst in air–cathode MFC. Three step process successfully synthesised nitrogen-doped carbon with 5.57% of nitrogen and when used in MFC, a maximum power density of 2300 mW m^{-2} was harvested from the system (Liu et al. 2015). Similarly, Fe–N doped AC proved to be an excellent cathode catalyst compared to AC with nearly twice the maximum power density (2437 mW m^{-2}) than plain AC (Pan et al. 2016).

Biochar, which is derived from waste-based precursors, such as sewage sludge, *alfalfa leaf*, corncob, watermelon rind, etc., has proved to be a cheaper option of cathode catalyst in comparison with metal-based electrocatalysts. In addition, to the properties such as high surface area, presence of pyrrolic, graphitic, and pyridinic nitrogen, and presence of phosphorus make it an attractive contender for low-cost cathode catalyst (Chakraborty et al. 2020c). Microalgae used for the tertiary treatment of wastewater have an inherent higher content of nitrogen and phosphorus in its cells. In one of the recent investigations, the biochar synthesised from the microalgae using heat treatment revealed the uniform presence of nitrogen and phosphorous. The MFC having cathode modified with microalgae derived biochar catalyst successfully achieved a maximum power density of 12.86 W m^{-3}, while simultaneously achieving the maximum

COD removal efficiency of 79.5% in the anodic chamber (Chakraborty et al. 2020a).

Low-Cost Ceramic-Based Proton Exchange Membranes for Microbial Fuel Cell

The PEM/CEM is one of the most essential components in a dual chamber MFC as it separates catholyte and anolyte, thus maintaining aerobic and anaerobic conditions in respective chambers. It is estimated that the use of membrane is associated with about 38% of the total capital cost in BES (Rozendal et al. 2008). Earlier, Nafion was by far the most widely used PEM in BES for the lab-based investigations owing to its excellent proton conductivity. However, in the later stages, it was revealed that oxygen leakage from cathode to anode, substrate crossover, and biofouling were a few of the major drawbacks associated with the use of Nafion as a PEM (Chae et al. 2008). From the view of upscaling, low mechanical stability and high cost of Nafion further reduces its acceptance for commercial application in scaled-up MFCs.

Ceramic is one of the low-cost membrane materials, made by using naturally available clay soil, which has considerably better mechanical and structural properties than polymeric membranes. Ceramic materials, such as terracotta, red soil, black soil, mullite, pyrophyllite, etc., have been used successfully as ion exchange membranes in MFC (Winfield et al. 2016). The first application in this regard was reported by Park and Zeikus with porcelain septum as PEM in MFC. The single chamber air cathode MFC with porcelain septum as PEM was capable of generating a maximum power density of 788 mW m^{-2} with Mn^{4+} and Fe^{3+} coated graphite as anode and cathode, respectively (Park and Zeikus 2003). The implemented single chamber MFC configuration is superior to dual chamber configuration in terms of scalability, due to non-requirement of the external aeration. In another investigation earthen pot (wall of 4 mm thick) manufactured from locally available soil with kaolinite, illite, and smectite was used as a medium for proton exchange. The earthen pot MFC achieved the coulombic efficiency (CE) of 64.5%, using stainless steel mesh cathode and $KMnO_4$ as cathodic electrolyte (Behera et al. 2010a). The same research group revealed better organic matter removal in MFC using clayware separator compared to the Nafion as a separator. The MFC with clayware ceramic separator was capable of generating a power density of 14.59 W m^{-3}, which ascertains the efficacy of clayware ceramic separator in electricity generation as well as wastewater treatment (Jana et al. 2010). The advantage of the ceramic material is that the same can act as a separator as well as the chamber made from it acts as the anodic chamber (Fig. 2). The configuration can be used as a single chamber MFC by exposing the cathode to air or as a dual chamber MFC by immersing the cylinder in a bigger container having catholyte.

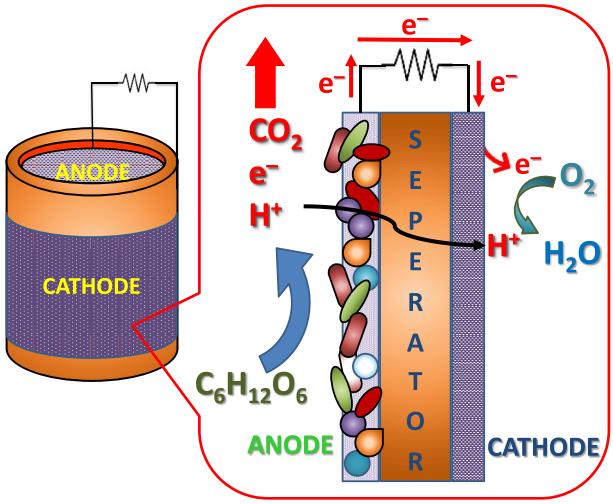

Fig. 2 Schematic of a typical ceramic-based microbial fuel cell

Though ceramic membranes are successfully employed as a separator in MFC, naturally available clay has limited proton exchange capability. However, some minerals such as vermiculite, montmorillonite, illite, kaolinite, and halloysite possess high availability of cation exchangeable sites (Carroll 1959). One of the early investigations of blending montmorillonite and kaolinite in different ratios in natural clay for the development of scalable cation exchange membrane was undertaken by Ghadge and Ghangrekar (Fig. 3a). Blending of 20% montmorillonite in natural clay and using these membranes in MFC not only exhibited a maximum power density of 7.5 W m^{-3} but also these membranes demonstrated better cation exchange and reduced oxygen diffusion and substrate crossover compared to other ratios of montmorillonite and kaolinite (Ghadge and Ghangrekar 2015). Establishment of ceramic separator having cation exchange capacity comparable with Nafion and suitable for application in MFC as a separator, has actually worked as a breakthrough to see few pilot-scale MFC demonstration plants.

In another case, four types of ceramic membranes, namely mullite, earthenware, pyrophyllite, and alumina, were used as cation exchange membrane in MFC with human urine as anolyte. All the modifications resulted in faster start-up, whereas the highest power density was observed using pyrophyllite (6.93 W m^{-3}). Though ceramic is a cheaper option, long term operation revealed increased internal resistance, biofouling of the porous membrane, and deposition of uric salts, which might affect the power output in long term operation (Pasternak et al. 2016).

Fig. 3 Low-cost ceramic-based cation exchange membranes typically used in pilot-scale microbial fuel cells, **a** montmorillonite blended clayware ceramic tile, and **b** ceramic tile made from coconut shell derived activated carbon and natural clay composite

Table 3 Performance of microbial fuel cells with ceramic-based cation exchange membranes

Material of CEM	MFC configuration	Anolyte	COD removal (%)	Maximum power density (mW m^{-2})	Reference
Porcelain septum made from kaolin	Single chamber air cathode MFC	Sewage sludge	–	788	Park and Zeikus (2003)
Earthen pot	Dual chamber MFC	Rice mill wastewater	96.5	48.64	Behera et al. (2010b)
Terracotta pot	Single chamber air cathode MFC	Acetate	–	33.13	Ajayi and Weigele (2012)
Red soil with Montmorillonite	Dual chamber MFC	Synthetic wastewater	85.4	7.55 W m^{-3}	Ghadge and Ghangrekar (2015)
Terracotta	Dual chamber MFC	Sodium acetate	92	–	Gajda et al. (2015)
Mfensi clay	Dual chamber MFC	Real wastewater	88.1	78	Tamakloe et al. (2015)
Pyrophyllite	Single chamber air cathode MFC	Human urine	50.2	6.93 W m^{-3}	Pasternak et al. (2016)
Coconut shell activated carbon and clay	Dual chamber MFC	Synthetic wastewater	81.05	3.7 W m^{-3}	Neethu et al. (2019)
Natural clay and geothite	Dual chamber MFC	Synthetic wastewater	87.7	112.81	Das et al. (2020c)

Biochar produced from pyrolysis of organic fraction can be another option for PEM as biochar has a high surface area and more surface functional groups in addition to cation exchange property (Chakraborty et al. 2020b). In this regard, Neethu et al., fabricated a composite PEM using coconut shell derived carbon and natural clay (Fig. 3b), which unveiled high ion exchange capability and lower charge transfer resistance and oxygen crossover. Moreover, the capital cost of the composite membrane (45 \$ m^{-2}) was 38-folds lower than Nafion, thus giving it an edge over the polymeric membranes for practical use (Neethu et al. 2019). Owing to the low-cost and comparable performance to the polymeric membranes, ceramic-based membranes are becoming a popular choice amongst the researchers for its application as PEM in MFC (Table 3). Moreover, ceramic-based membranes provide superior mechanical and chemical stability and make ceramic-based PEMs an economical and viable choice for upscaling of MFCs in pilot and field trials.

Complex Wastewater Treatment Using Microbial Fuel Cell

Apart from the domestic wastewater, MFCs have been successfully implemented for the treatment of complex industrial wastewaters as well as wastewaters laden with emerging contaminants (ECs). The degradation process in the anodic chamber of MFC using exoelectrogenic bacteria is of anaerobic nature, which does not require external energy, thus it can offer a low-cost solution for the treatment of industrial wastewaters. The anode in MFC acts as a continual electron sink for generated electrons (Logan 2009), thus making the process independent of dissolved terminal electron acceptors in anodic chamber. This makes MFCs capable of treating complex organics from wastewater, which cannot be easily accomplished by means of conventional anaerobic processes (Table 4).

Over the past decade treatment of industrial wastewaters ranging from high strength alcohol distillery wastewater to toxic recalcitrant pharmaceutical wastewater had been accomplished in MFC (Pandey et al. 2016). The treatment of carbohydrate rich and high organic contained cassava

Table 4 Performance of MFCs treating complex industrial wastewater in the anodic chamber

MFC configuration	Wastewater type	COD removal efficiency (%)	Maximum power density (mW m^{-2})	Reference
Single chamber air cathode MFC	Paper recycling wastewater	76	501	Huang and Logan (2008)
Single chamber air cathode MFC	Starch processing wastewater	98	239.4	Lu et al. (2009)
Dual-chamber MFC	Mustard tuber wastewater	85	46	Guo et al. (2013)
Dual-chamber MFC	Palm oil mill effluent	45	45	Baranitharan et al. (2013)
Single chamber air cathode MFC	Brewery wastewater	87	205	Feng et al. (2008)
Dual-chamber MFC	Distillery Wastewater	54.4	4.3 W m^{-3}	Tiwari and Ghangrekar (2018)
Single chamber air cathode MFC	Textile wastewater	82.14 (74.8% colour removal)	38.6	Sonu et al. (2020)
Dual-chamber MFC	Pharmaceutical wastewater	83	204.9	Ismail and Habeeb (2017)
Single chamber air cathode MFC	Landfill leachate	37	344 mW m^{-3}	Puig et al. (2011)

wastewater with initial COD and cyanide concentrations of 16,000 and 86 mg L^{-1}, respectively, was attained in MFC demonstrating COD removal of 88% after 120 h. The presence of cyanide had no detrimental impact on the performance of MFC, which achieved a maximum power density of 1771 mW m^{-2} (Kaewkannetra et al. 2011). Rice milling wastewater is another agro processing wastewater, which was successfully treated with 96.5% of COD removal in MFC. The novelty of the research lies in the application of clayware as a membrane, thus providing a cheaper solution to Nafion (Behera et al. 2010b). Easily biodegradable wastewater emerging from dairy, food processing, and slaughterhouse have been treated with COD removal efficiency in excess of 80% using MFC (Katuri et al. 2012; Mahdi Mardanpour et al. 2012; Jayashree et al. 2016).

Paper recycling wastewater, which typically contains high values of cellulose, was treated in MFC to attain 76% of COD removal, while simultaneously generating a maximum power density of 501 mW m^{-2}. In addition, cellulose removal (96%) in the same setup, indicated the capability of MFC to degrade complex substrate, such as cellulose, in addition to organic matter (Huang and Logan 2008). In another case, biodegradation of diesel with n-alkane markers from C-8 to C-25 in MFC (81%) was 2.6 times higher than control setup (without electrical circuit). The sulphate concentrations in MFC was higher than the control setup, which suggested that in MFC, anode was preferred over sulphate as terminal electron acceptor (Morris et al. 2009). Though 21 days of retention time was required to achieve the aforementioned removal, it suggests that MFC can be used for in-situ bioremediation of contaminated sites. Although, electricity production is an attractive proposition when using MFC, enhanced pollutant removal and capability of eliminating complex organics present in industrial wastewaters gives this technology an edge over the conventional systems.

Industrial wastewater often contains a high concentration of sulphide. During the anaerobic treatment of wastewater, sulphate is reduced to sulphide by the sulphate reducing bacteria. The conversion of sulphate to sulphide can be inhibitory to the methanogens, which causes a reduction in the methane yield (McCartney and Oleszkiewicz 1991). The anaerobic treatment in the anodic chamber of MFC can be considered as a potential technology for treating sulphate laden wastewater. In the anodic chamber of MFC, to remove the sulphate, sulphate reducing bacteria should work along with electrogens. In one of the investigations, the MFC coupled with upflow anaerobic sludge blanket (UASB) reactor demonstrated 98% of sulphide removal, while simultaneously generating 101 mW L^{-1} of maximum power density (Rabaey et al. 2006). Various other researchers have also successfully applied MFCs for treating sulphate laden wastewater with simultaneous electricity production (Zhao et al. 2009; Ghangrekar et al. 2010; Lee et al. 2015; Chatterjee et al. 2017). In addition, it has also been reported that sulphate reducing bacteria are capable of direct electron transfer to the anode, which is beneficial for the performance of MFC (Kang et al. 2014).

Removal of phosphorus is one of the key parameters in controlling the eutrophication of surface water. Chemical precipitation is one of the most widely used forms for phosphate removal along with biological processes. The use of MFC gives a unique option of phosphate recovery, unlike other biological processes. Phosphate removal in the MFC is via precipitation at the cathode in the form of struvite. High localised alkalinity near the cathode leads to deposition of struvite at the cathode from where it can be scrapped and recovered. In one of the early investigations, iron phosphate from the dried sludge was reduced to orthophosphate at the cathode of MFC. Later, following the addition of ammonium hydroxide and manganese dichloride, the struvite precipitates were obtained at pH of 10 (Fischer et al. 2011). In

another case, it was observed that simultaneous wastewater treatment and struvite recovery was possible on the aqueous face of the air cathode in a single chamber MFC. The precipitation of struvite predominantly on the cathode suggested that localised alkaline pH contributed to the chemical precipitation. The MFC contributed to 70–82% of phosphorus removal of which, 4.6–27% phosphorus was recovered as struvite (Ichihashi and Hirooka 2012). However, it was later revealed that electricity generation is reduced with an increase in struvite precipitation on the cathode, which might be due to the reduced approachability of the reacting species to the cathode surface owing to mass transfer limitation (Hirooka and Ichihashi 2013). Hence to prevent the reduced electricity generation in MFC, a two-stage system comprising of separate chamber for struvite precipitation can be an attractive option for the successful long term stable operation of MFC.

Improved lifestyle and recent developments triggered the higher occurrence of ECs in domestic wastewater apart from the organic matter and nutrients. Commonly used biological secondary processes for wastewater treatment are not effective for the removal of EC. However, MFC offers a unique advantage of simultaneous organic matter and EC removal, which cannot be achieved in conventional biological secondary treatment processes. Over the years the use of MFC has been explored for the removal of ECs, such as dyes, pharmaceuticals, pesticides, polyaromatic hydrocarbons, surfactants, etc., apart from the removal of organic matter and nutrients while simultaneously harvesting the bioelectricity (Solanki et al. 2013; Kronenberg et al. 2017; Zhang et al. 2018; Sathe et al. 2020). Current generated from MFC is a direct function of a suitable environment and substrate availability for exoelectrogenic microorganisms in the anodic chamber of MFC. Thus, the current response from MFC can also be a reliable and timely indication of possible toxicity induced by ECs, based on which suitable dilution can be considered.

Azo dyes are generally unaffected in aerobic conditions; however, undergo reductive biotransformation to aromatic amines under anaerobic conditions. Hence the anodic treatment in the MFC can successfully transform the azo dyes into aromatic amines. A single chamber MFC accomplished > 90% of the acid orange transformation into aromatic amines at a loading rate of 70–210 g m^{-3} d^{-1}. A second stage aerobic bioreactor ensured degradation of aromatic amines into simpler non-toxic metabolites (Fernando et al. 2014). Several investigators have also reported the successful application of BES-based two-stage treatment processes for the degradation of dyes (Sultana et al. 2015; Yuan et al. 2017).

Staking of MFC is considered as a solution for upscaling of MFC in field-scale application. It has been observed that stacking not only has a positive impact on the reduction of overpotential losses but also has beneficial effect on the decolourisation of azo dyes. A stacked MFC with three modules demonstrated 80.3% decolourization of azo dye, which was 1.7 times higher than decolourization in a single module of MFC (Kong et al. 2018). Similarly, a dual chamber configuration of MFC can also be used for simultaneous treatment of organic matter in the anodic chamber and dye degradation in the cathodic chamber. Wherein, the in situ synthesised •OH at the cathode via bio-electro-Fenton oxidation contributed to 95% of Rhodamine B decolourization using Fe_2O_3 and non-catalysed carbon felt cathode (Zhuang et al. 2010). This proves the capability of simultaneous wastewater treatment and dye degradation using MFC.

Heavy metals are generally not affected in the secondary treatment processes and demand tertiary treatment for their removal from the wastewater. In MFC, during the anaerobic degradation of organic matter, the released electrons are transferred to the cathode via an external circuit, which can be used for the reduction of heavy metals at the cathode. Heavy metals such as Cr(VI), As(III), Cu(II), Fe(III), etc. have redox potential higher than the anode potential of MFC and hence can be directly reduced at the cathode from where the deposited metals can be recovered. It was witnessed that Cr(VI) was completely removed from the catholyte with an initial concentration of 100 mg L^{-1} in 150 h of contact time. The MFC simultaneously generated a maximum power density of 133 mW m^{-2} (Wang et al. 2008). In another investigation, it was revealed that cuprous oxide and metal copper deposits were detected on the cathode of MFC used for removing copper from catholyte. At an acidic pH (4.7) more than 99% of copper was removed with an initial concentration of 200 mg L^{-1} (Tao et al. 2011). Other heavy metals that have been reduced at the cathode of MFC include As(III) (Wang et al. 2014), Hg(II) (Wang et al. 2011b), V(V) (Zhang et al. 2009). Apart from these, noble metals (gold and silver) have also been successfully reduced at the cathode of MFC in the past investigations (Choi and Hu 2013; Ali et al. 2019). However, other metals with negative redox potentials cannot be reduced by the incoming electrons. In such cases, the reduction can be accomplished via supplementing external power as in the case of MEC.

Though MFC is still in the lab-scale stage in terms of the treatment of complex industrial wastewater and EC removal, successful implementation of MFC for sewage treatment has been reported in recent investigations as elaborated in "Up-scaling of microbial fuel cell". The addition of a few antibiotics such as penicillin caused improved electricity generation; whereas tobramycin addition had resulted in a negative impact on power generation (Wen et al. 2011; Wu et al. 2014). This indicated that the optimum concentration and loading rate for each EC will be different and there is a need to optimise the operating parameters for given conditions. Also, there is a need of identifying the by-products

emerging from the degradation of target pollutants based on which follow-up treatment can be decided.

Modelling of Microbial Fuel Cell

Similar to other biochemical and electrochemical reactors, modelling of biochemical and electrochemical reactions of MFC has been undertaken in the past research. In an investigation done by Zeng et al. (2010), the cathodic reaction was found to be the limiting factor for the performance of MFC. In a different approach, it was stated that by modelling the MFC as a potentiostat and accounting for the different losses by incorporating appropriate factors, one could model the power supply pattern of a bigger-sized MFC with a steady state electrical model (Serra et al. 2020). In a different work, the direct effect of extrinsic parameters such as change in substrate concentration, effect of resistance on biofilm growth, and effect of anode surface area on the biofilm growth and in turn the power of MFC was modelled (Karamzadeh et al. 2020). It was observed that higher resistance induced growth of biofilm that has low conductivity. The investigation also emphasised that utilising low strength substrate increased the mass transport limitation of the reactant species (Karamzadeh et al. 2020). In addition to controllable extrinsic factors, effect of environmental factors also has been modelled for MFC. For example, by integrating a machine learning approach with statistical and mechanistic models, the developed algorithm could predict the qualitative trend of power production with temperature changes (Yewale et al. 2020).

In a more fundamental work, the correlation of substrate and mediator concentration with current output was established. The current response in regards to the varying substrate strength is delayed in comparison to the reducing intermediates; whereas, a pronounced effect of varying mediator concentration was observed on current output (Zhang and Halme 1995). While it is imperative to understand the effect of the different substrates and other operational parameters, it is also important to understand the flow dynamics and the mass transfer modelling in MFC. This would be beneficial towards identifying the mass transport and the diffusion limitations that can be further translated to effective hydraulic designs and reduction of dead pocketing inside the individual MFC. A simulation study using computational fluid dynamics approach emphasised the negative correlation of the boundary layer thickness around anode fibres on power density (Alvarez et al. 2020). The same investigation also indicated the existence of an optimum boundary layer thickness for three-dimensional graphite fibre brush anode for deriving maximum power density.

Coupling computational fluid dynamics models with other relevant modelling approaches have also been explored in past. The research conducted by Zhao et al. (2016) coupled computational fluid dynamics with the Butler–Volmer equation to simulate heterogeneous species distribution and the convective flow conditions. The model could well predict the current generation trend. The investigation further emphasised the scope of further improvement of the model performance by incorporating factors such as dynamic cathodic potential conditions, biomass decay, consideration of more diverse bacterial speciation, and complex hydrodynamic conditions (Zhao et al. 2016). In another investigation coupling Anaerobic Digestion Model 1 with complex computational model of MFC achieved a holistic model for predicting power and substrate utilisation pattern with considerable accuracy (Picioreanu et al. 2008).

As mentioned previously, Alvarez et al. (2020) demonstrated the effect of boundary layer thickness and in turn, the anode geometry is a limiting factor for the electrical performance of MFC. The effect of anodic processes, anode configuration, and geometry has been extensively investigated in the past. For example, modelling the anodic oxidation rate of a substrate (electron donor) by deriving a combined Nernst–Monod equation demonstrated a limiting value of anodic biofilm that can support an optimum value of current density (Marcus et al. 2007). The investigation further emphasised that if the biofilm is considered to be a conductive solid matrix, then the electron donor oxidation and consequently the current flux achievable is greater for higher values of biofilm conductivity. Higher values of this biofilm conductivity ($> 10^{-3}$ mS cm^{-1}) can enhance the development of an active biomass layer to more than tens of micrometre away from the anode surface (Marcus et al. 2007). In a different investigation, the one-dimensional model proposed by Marcus et al. (2007) was further implemented to multi-dimensional geometry and it was concluded that the current flux was directly proportional to the availability of nutrients in the biofilm matrix (Merkey and Chopp 2012). The current flux reduced due to enhancement of microbial array in a three-dimensional direction that led to the development of nutrient decreasing concentration gradient in the inner layers of the biofilm.

Several other approaches towards modelling of MFCs, such as the implementation of artificial intelligence methods (Garg et al. 2014), equivalent circuit modelling (Sindhuja et al. 2016), neural network modelling (Ma et al. 2019), etc. have been implemented. Further detailed discussion on the same can be found in past review work focussing in detail on this subject (Jadhav et al. 2020). The modelling of bio-electrochemical processes occurring in MFC can aid in designing further experiments without actually executing them and also in simulating scaling up situations before actual construction. This would save considerable time and resources and would be a sustainable approach towards understanding the performance of MFC. However, further investigations are required for coming up with a more robust model that

can be implemented to different configurations and has provisions of user defined input for different operating, extrinsic and process parameters pertaining to the MFC operation.

Up-Scaling of Microbial Fuel Cell

From the above discussion, it can be witnessed that MFC is a promising technology for wastewater treatment and has the potential of upscaling. Of the various operating parameters, temperature affects the performance of MFC. Similar to that of conventional anaerobic digestion the mesophilic temperature range is found to be optimum for MFCs as well (Behera et al. 2011). Past investigations have demonstrated that there is only a 1.1 times increase in the maximum power density in MFC operated at mesophilic temperature of (30 °C) compared to an ambient temperature of 23 °C (Ahn and Logan 2010). Although at a lower temperature the electrical performance of MFC deteriorates, for the practical implementations, and for maintaining the low cost of treatment, it might not be economically viable to employ a temperature control mechanism for anolyte. Moreover, a temperature control mechanism at a pilot or field-scale setup would increase the capital as well as operating costs.

The advent of low-cost ceramic-based PEMs and Pt-free catalysts aided in minimising the capital cost of MFCs. Though successful lab-based applications have been demonstrated, very few investigations have been reported on possible scaled-up or pilot scale operations of MFC. In an early investigation, Feng et al. tried a 250-L horizontal plug flow typed MFC for domestic wastewater treatment. Despite of high COD removal efficiency (79%), the system could harvest only 0.47 W m^{-3} of maximum power density possibly due to higher internal resistance than typical lab-scaled setups (Feng et al. 2014). A 90-L MFC, consisting of 5 modules operated for more than 6 months, was used for the treatment of brewery wastewater. Based on the results of electricity generation, it was estimated that the net electrical energy harvested was 0.021 to 0.034 kWh m^{-3} (Dong et al. 2015).

With an effort to reduce the fabrication cost of MFC, ceramic separator was used as PEM in a 45-L pilot scale MFC. Following the optimization, it was observed that MFC achieved a maximum current of 42 mA at an organic loading rate of 4.5 g COD L^{-1} d^{-1}, with an internal resistance of 12.4 Ω (Ghadge et al. 2016b). The main advantage of a ceramic separator is the capability to handle more hydraulic pressure than polymeric membrane, which can offer an advantage for its application for field-scale MFCs. The ceramic membranes have been widely used for field-scale applications of MFC by Ieropoulos and group for the PEE-power urinals. The first trial of 330-L MFC was conducted at Glastonbury Music Festival in England which consisted of 12 MFC modules (total 432 MFCs in stack). The assembly generated an average power of 300 mW, which was stored in supercapacitors for powering LEDs (Ieropoulos et al. 2016). In the subsequent trial, efforts were made to increase the capacity of urine treatment using cascade type MFC modules, which produced an average power of 424 mW. In the field-scale trial, the COD removal of 48% was achieved at the hydraulic retention time of 700 min (Walter et al. 2018). In the recent investigation, 6-chambered stacked MFC with a working volume of 720-L was used for the treatment of sewage (Fig. 4). The cathode was coated with $Co_{0.5}Zn_{0.5}Fe_2O_4$ and Sn_5Cu_{84} as cathode catalyst; whereas, goethite was used as anode catalyst in the MFC. The electrical energy harvested (maximum power generation of 61 mW) was stored in supercapacitors for illumination at night. The overall hydraulic retention time of 18 h resulted in a COD removal efficiency of 78.4%, which improved to 87.3% following a doubling of hydraulic retention time (Das et al. 2020a).

In order to prove that MFC can be a scalable technology for wastewater treatment, initial pilot and field-scale investigations act as a benchmark based on which future course of action in this direction can be finalised. Based on the available literature on scale-up MFCs, current issues that still need to be addressed include high capital cost,

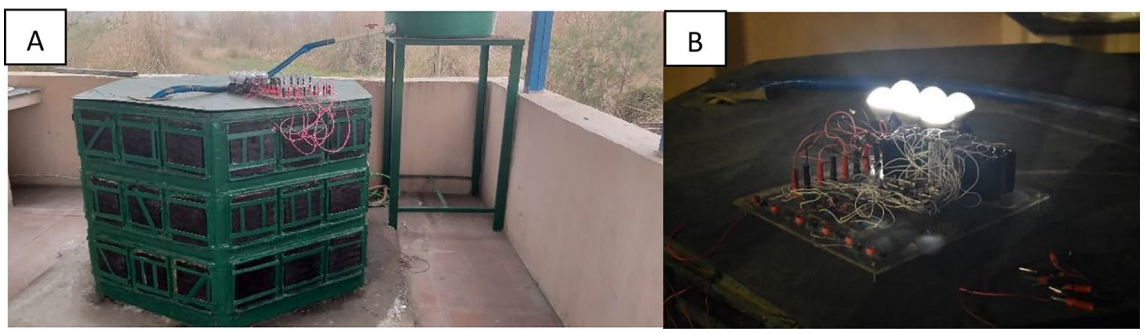

Fig. 4 **a** Field-scale application of 6-chambered MFC installed at the National Thermal Power Corporation, Netra, Greater Noida, India for treating sewage generated from guest house, **b** Illumination at night using the electricity harvested while treating sewage

overpotential losses, high internal resistance, and operational issues related to long-term operation, such as stability of cathode catalyst and membrane fouling. Thus, continual development pertaining to these issues is essential to make this technology a commercial treatment system for wastewater treatment.

Future Scope

The MFC has been a widely researched technology in the last two decades owing to its ability to treat wastewater, while simultaneously generating renewable energy in the form of bioelectricity. The majority of the past investigations have been in the lab-scale setup (up to few litres). Based on this it can be concluded that, although successfully operated in the lab-scale, MFC is still not fully matured to be used for the field-scale operations. Although MFC has the capability of bioelectricity generation, the harvested electricity is far less than that required for direct applications. Presently, MFC research is associated with a variety of limitations, such as activation losses, mass transport and diffusional losses, ohmic losses, and other concerns pertaining to scavenging reactions, which limits electricity production. The high value of internal resistance in MFC causes a potential drop, thus drastically deteriorating the power output of the MFC. Oxygen is the most practical terminal electron acceptor in MFC; conversely, the fugitive diffusion of oxygen into the anodic chamber can affect the performance of anaerobic microorganisms, thus affecting the rate of electricity generation (Pham et al. 2006). High capital cost is another drawback associated with the use of MFC for field-scale applications. To reduce the capital cost, ceramic-based CEM and carbon-based cathode catalysts can be a suitable option as elaborated in "Low-cost ceramic-based proton exchange membranes for microbial fuel cell" and "Cathode catalysts for microbial fuel cell", respectively. In addition to this, diffusion barriers considerably reduce the power generation of large MFCs; hence to enhance the power generation, stacking arrangement of multiple small size MFCs can be practiced (Ieropoulos et al. 2016).

Also, the anode and cathode surface area provided with specific electrochemical properties of the material selected plays a very important role. The ratio of area of the electrode and volume of the anodic chamber provided for desired organic loading rate is crucial. It has been reported that Butler–Volmer kinetics dominates the anode surface area required than the area required for polarisation and biofilm formation because the activation loss is the predominant factor that affects the rate of electrochemical transformation and power output from fuel cell (Ghadge et al. 2016a). Therefore, anode surface area is governed by Butler–Volmer kinetics and based on this necessary anode surface area should be provided to harvest more electricity from the MFC to optimise the benefit from this system.

The air–cathode configuration of MFC is practicable for field-sale applications, the design is still associated with practical difficulties, such as salt depositions and biofouling of cathode (An et al. 2017). The fouling problem can be mitigated by incorporating the catalytic material which also has the biocidal properties, such as silver nano particles (Noori et al. 2018b), to have long term stable performance of the MFC. Further to the task of maintaining long term stable performance, reducing cost of the electrodes, PEM/CEM, and catalysts, without compromising desired electrochemical properties, is still a challenging task associated with this technology, which make the system comparably expensive and unpredictable than conventional systems. Future research in the aforementioned issues needs to be performed to make MFC a promising technology for wastewater treatment in the upcoming years.

Conclusion

The application of MFC for onsite wastewater treatment and concomitant power recovery is a state-of-the-art technology that has the potential to become the central theme of future waste treatment and valorisation facilities. The present scaled-up studies of MFC exhibit immense potential in terms of onsite electricity usage for small devices, area illumination as well as for holistic treatment of wastewater. Moreover, the ability to remove aromatic and other complex organic pollutants both by anodic biodegradation and cathode-based oxidation and low sludge generation owing to anaerobic metabolism pathway are clear advantages over conventional biological processes. These findings point towards the fact that in near future, MFC-based treatment units could become a game changer in the domain of waste treatment.

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Data availability All data generated or analysed during this study are included in this article.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

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