



Review

Bioremediation of wastewater through a quorum sensing triggered MFC: A sustainable measure for waste to energy concept



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ABSTRACT

A mission for fast advancement has constrained us to unpredictably tap various natural assets. The reckless utilisation of fossil fuels led unmanageable wastes which have greatly affected our health and environment. Endeavours to address these difficulties have conveyed to the frontal area certain creative natural solutions particularly the utilisation of microbial digestion systems. In the previous two decades, the microbial fuel cell (MFC) innovation has caught the consideration of the researchers. The MFCs is a kind of bio-electrochemical framework with novel highlights, for example, power production, wastewater treatment, and biosensor applications. Lately, dynamic patterns in MFC inquire about on its synthetic, electrochemical, and microbiological perspectives have brought about its observable applications. The MFCs have begun as a logical interest, and in numerous regards, these remaining parts to be the situation. This is especially a result of the multidimensional uses of this eco-accommodating innovation. The innovation relies upon the electroactive microorganisms, prominently known as exoelectrogens. In the first place, it is the main innovation that can create energy out of waste, without the contribution of outer/extra energy. Modification of electrodes with nanomaterials, for example, gold nanoparticles and iron oxide nanoparticles or pretreatment techniques, for example, sonication and autoclave disinfection have indicated promising outcomes in improving MFC execution for power generation and wastewater treatment. The MFC innovation has been likewise explored for the remediation of different heavy metals and hazardous components, and to recognize the poisonous components in wastewater. What's more, the MFCs can be adjusted into microbial electrolysis cells to produce hydrogen energy from different natural sources. This article gives a thorough and cutting-edge appraisal of the novel magnitudes of the MFC.

1. Introduction

The progressive world has a high demand for energy for satisfying our day-to-day life. As a result of which, energy sources have been overexploited leading to loss or depletion of non-renewable fossil fuels (Logan et al., 2015). Besides these over usage of non-renewable fuels masking 'Mother Earth' with the polluted environment through emission of noxious gases that affect the entire biosphere and a non-avoidable reason for global warming. Nowadays, seeking an alternative to fuel deficiency has become a trend. This led a way to find an eco-friendly, economically viable and sustainable technology to compensate for the energy crisis through a greener approach.

To solve the current existing problem - which is critical due to

unstoppable use and carelessness - communicating microorganisms would be the best solution to overcome future unseen man-made calamities. Quorum sensing (QS) through their various biotechnological applications could solve this problem before situation become more serious. This aids in developing the microbial fuel cells (MFCs) for power generation through a sustainable approach. The MFC is a highly reliable, renewable, highly configurable system and in future live reactors could be employed for treating a variety of wastes that are generated from domestic and industrial practices (Yong et al., 2014; Gajda et al., 2017; Hu et al., 2017). The MFCs are gadgets that produce electricity through degradation of organic wastes, domestic wastewater, and industrial wastewater by employing live microorganisms as a catalyst to transfer electrons from the wastes through waste-to-energy

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concept (Gude, 2016). The MFCs can be used as novel tools for bioelectricity production, biohydrogen production, wastewater treatment, biosensor development and bioremediation contaminants using solid or liquid waste as a potential feedstock (Butti et al., 2016).

The first report of the electrogenic bacteria (Kumar et al., 2017) contributes a lot to the design and development of MFCs for various applications. In general, the MFC consist of two electrodes in the chamber (Potter, 1911). While the microbe present in the anode chamber breaks the organic waste by means of enzyme activity and releases the electrons, which get transferred through membranes to the cathode chamber, where the electrical voltage is measured (Hassan et al., 2014; Song et al., 2014; Karthikeyan et al., 2016). Though the MFC is good in electricity production by waste degradation, the efficiency is quite low. Microbes play a key role in the degradation of substrates as well as electron transfer (Wang et al., 2016; Zhao et al., 2017). Hence, by enriching the biofilm formation on the anode, one could produce high-energy output with stable supply (Cheong et al., 2014; Turan et al., 2017; Yong et al., 2015). Crosstalk between the cells must be improved and enhanced to have a stable and potential energy generation (Glasser et al., 2017).

Nowadays, in microbial populations, cell-to-cell contact is highly acknowledged by scientists. Physical and chemical signalling process in the cell-to-cell contact of the microbes occurs through chemical signalling, exchange of chemicals via contacts etc (Cai et al., 2016; Kalia et al., 2017). In the QS, signalling molecules i.e. auto-inducers are secreted out of the cell and control a range of physical actions viz. virulence, conjugation, symbiosis, competence, production of antibiotics, and formation of biofilms etc. The intra-specific common language is through acylated homoserine lactones (AHLs), which encompasses the cell electrode electron transfer through the action of stimulated respiration (Koul et al., 2016; Koul and Kalia, 2017; Kumar et al., 2015; Pérez-Rodríguez et al., 2015; B. Rekadwad and Khobragade, 2017; Rekadwad et al., 2016; Shiva Krishna et al., 2015). The cell-to-cell contact through auto-inducers happen between and within the bacterial species and that has been possible through recent developments in the field of QS. Using the electrochemical bioreactors, the transfer of electrons for bioelectricity production can be enhanced through further research and developments in multi-purpose QS technology in the form of novel techniques with the help of new discoveries. QS system could aid in the transfer of electrons efficiently by producing signalling molecules (Liu et al., 2015; Sun et al., 2016). These molecules transfer the chemical signals between the cells and are responsible for bacteria to bacteria communication. It ultimately leads to good and stronger biofilm formation in the anode area (Kumar et al., 2016; Zhang et al., 2012). Degradation of wastes play an important role at the anode and thus aid in high-energy production and other associated applications (Kumar et al., 2017; Venkata Mohan et al., 2014). Having this in mind, this chapter surveys the quorum sensing of microbial fuel cells and their applications for the sustainable utilisation of wastewater.

The microbial QS was categorised into four types, based on the nature of autoinducers (Turan et al., 2017):

i. Gram-negative bacteria-Homoserine lactones

In gram-negative bacteria, QS is controlled by acyl-homoserine-lactone (AHL) molecules i.e. through the protein system LuxI/LuxR (Dang et al., 2017). The LuxI proteins build the QS circuit through the synthesis of AHL, while the protein LuxR activates all genes involved in when the sufficient quantity of the autoinducers are available (Ball et al., 2017). Similar studies were reported in later days in case *Vibrio* sp., which has LuxM/LuxN (Hmelo, 2017). The gram-negative bacterial genera viz. *Pseudomonas*, *Aeromonas*, and *Rhizobium* were found to own these sorts of mechanisms.

ii. Gram-positive Bacteria-Oligopeptides

Unlike Gram-negative bacteria, Gram-positive bacteria contains auto-inducing oligopeptides (AIPs) which act as a signalling molecule (Todd et al., 2017; Wolf et al., 2017).

iii. Interspecies communication-Autoinducer-2 (AI-2)

QS in the *Vibrio* sp. of bioluminescence marine bacteria was first described over 35 years ago to study gene expression in the cell-to-cell signalling (Nealson and Hastings, 1979). Contemporary developments in the field report that the bacteria secrete chemical inducers to communicate and coordinate their behaviour (Miller and Bassler, 2001). Utilising the monoculture or single organism for a targeted production through modification of genes is restricted. These constraints can bypass by developing the consortium of microbes via synthetic biology (Scott and Hasty, 2016). The large microbial communities have been used to find novel candidates, which can be eventually used for QS through ecosystem engineering. The AI-2 molecules are belonging to the type-II class of signalling molecules found in bacteria. LuxS protein is in charge of the generation of furanosyl borate di-ester and luminescence features of *Vibrio* and *Salmonella* (Hurley et al., 2017; Lentini et al., 2017; H. Park et al., 2017).

iv. Pseudomonas quinolone signal (PQS) and AI-3

Bacterial virulence becomes infectious with the presence of the virulence factor and when cross-talk between the pathogens happens (Borges et al., 2017; B. N. Rekadwad and Khobragade, 2017). The PQS (2-heptyl-3-hydroxy-4-quinolone), C4-HSL and 3-oxo-C12-HSL (N-(3-oxododecanoyl)) were the predominant autoinducers found in the *Pseudomonas aeruginosa*. The PQS regulates the virulence factors (elastase, LecA, and pyocyanin) which considerably influence the infection progress (Ball et al., 2017). The virulence and the regulation of the genes were greatly impacted by the PQS. Thus, PQS led a way to develop a strategy to control opportunistic pathogens (Bodelón et al., 2017; Pérez-Pérez et al., 2017).

2. Wastewater bioremediation – a sustainable approach through MFC

2.1. Augmentation of microbial fuel cells through quorum sensing

Microbial fuel cells are routinely used for electricity production. Various extracellular electron transfer pathways were involved in transferring the electrons to the solid extracellular electrodes. The exoelectrogens uses two different pathways for the electron transfer include self-secreted electron shuttle and direct extracellular electron transfer through c-type cytochromes or nanowires (conductive pili) of the bacteria (Yong et al., 2014). The exoelectrogenic signals from the *Geobacter*, *Shewanella* and *Pseudomonas* forms the electroactive biofilm and facilitates the rapid electron transfer to enhance the anodic potential of the MFC/MECs (Fig. 1). The *Geobacter* and *Shewanella* sp. are the well-studied model organisms. *Geobacter sulfurreducens* have role conductive pili direct electron transfer. *Shewanella oneidensis* (release flavins) and *Pseudomonas aeruginosa* (release phenazines) were employed as the models for self-synthesized redox-mediated indirect electron transfer (Chen et al., 2017; Koch and Harnisch, 2016). The production of flavin and phenazines were regulated through QS. The higher biofilm development rate was achieved by the intercession of short chain AHL (3OC6) signalling molecule.

Few extracellular signalling compounds such as short chain AHL (3OC6) was allowed growth of biofilm. This process was remarkably enhanced the hydrogen production by 5.57% at 0.8 V, 38.68% at 0.6 V and 81.82% at 0.4 V of the external power supply. The addition of AHL in the cathode altered the microbial community structure. It has resulted in increased growth of *Gamma-proteobacteria*. Furthermore, the AHL was found to increase the diversity, abundance and EPS

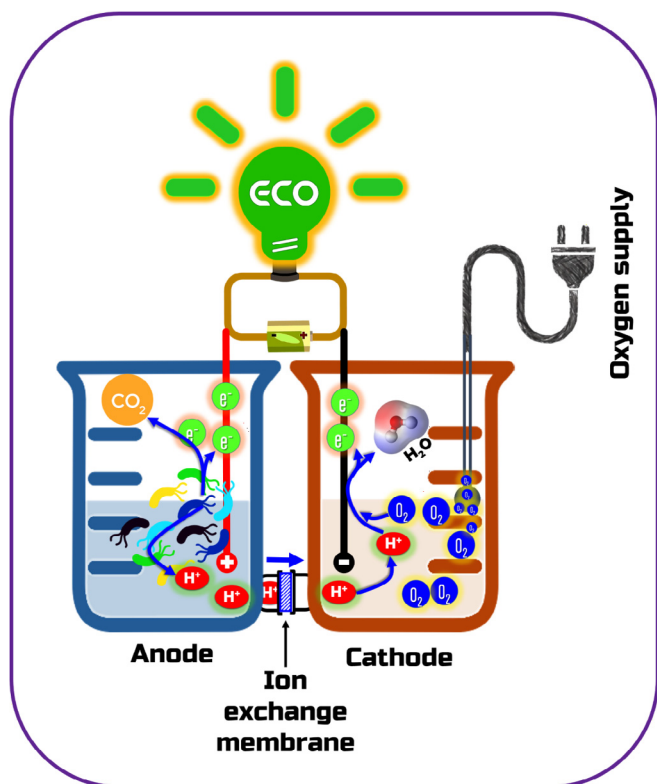


Fig. 1. Quorum sensing mediated microbial fuel cell system.

composition and thereby increase the redox activity (Q.-Y. Chen et al., 2017). The industrial discharges, oil and gas pools discharging a large amount of wastewater, which is of higher strength and higher salinity. A 30% improvement in the current density was observed along with up to 95% increase in biofilm mass due to the addition of quinolone. The study concludes that the addition of quinolone at trace level in the MF could greatly enhance the bioelectricity production by efficient treatment of the high strength wastewater (Monzon et al., 2016; Shehab et al., 2017). Improved extra-cellular electron transfer in the exoelectrogens could lead a way to develop a novel MFC for efficient energy recovery. Concerning this, a facile resolution-contrast mixed bacterial MFC (m-MFC) to substantiate the redox-mediated output current was developed. In addition, the phenazine-1-carboxylic acid, 2, 4-diacetyl phloroglucinol, 10-dione, trimipramine and 1-hydroxyanthracene-9 were found to be the promising redox mediators (G. Wang et al., 2017).

2.2. Uses of microbial fuel cells on wastewater treatment

The MFCs contain wide applications such as bioelectricity production, bio-hydrogen production, wastewater treatment, biosensor development and bioremediation of contaminants using solid or liquid waste as a sole source for MFC operation (Fig. 2 and Table 1).

2.3. Electricity generation from waste

Pseudomonas aeruginosa was used bioelectricity using solid-organic wastes. The overexpression of the NAD synthase gene (*nadE*), the intracellular cofactor NAD (H/+) would rise and supply three times higher electricity from $10.86 \mu\text{W}/\text{cm}^2$ to $40.13 \mu\text{W}/\text{cm}^2$. The increased electrochemical activity and reduction in charge transfer resistance were the important reasons for higher electricity generation (Yong et al., 2014). A dual chamber MFC was designed with a novel sulfonated polyethersulfone (SPES) membrane by chlorosulfonic acid sulfonation for efficient wastewater treatment. The Nafion 117 membranes were used to test the efficiency of the newly fabricated SPES membrane.

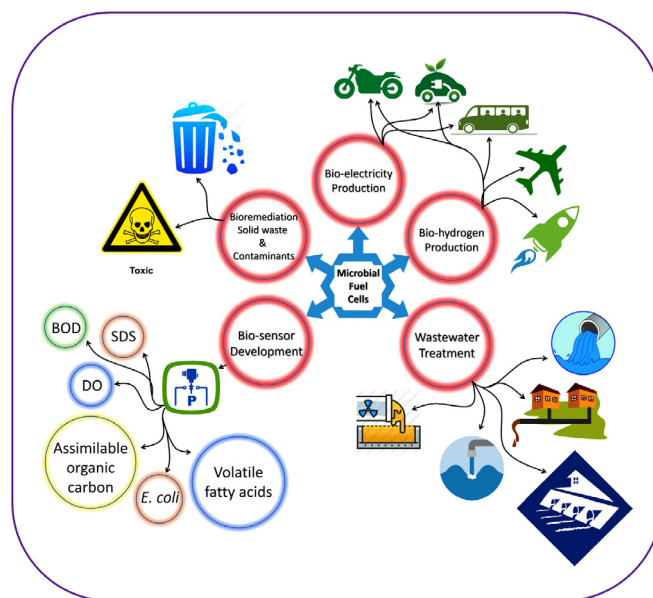


Fig. 2. Potential of microbial fuel cells (MFCs).

The SPES membrane yielded higher electricity of 58.7 mWm^{-2} at 317.1 mA m^{-2} of current density. The Nafion proton membrane yielded 45.5 mWm^{-2} at 228.6 mA m^{-2} . SPES membrane is highly suitable to the substantial yield of current in MFCs (Zinadini et al., 2017). The bioelectricity production reported in the photosynthetic alga microbial fuel cell (PAMFC) using *Chlorella vulgaris* as a catalyst (Gouveia et al., 2014). Maximum current produced was $62.7 \text{ mW}/\text{m}^2$ at $96 \mu\text{E}/(\text{m}^2\text{s})$ light intensity. The light intensity proportional to the carotenogenesis, which was responsible for the higher yield. Considering the beneficial aspects of *Shewanella*, *Scenedesmus* and *Chlorella*, they can be readily utilised for the efficient and economically feasible wastewater treatment system. The co-culturing of *Saccharomyces* and *Shewanella* yielded maximum electricity up to $123.4 \text{ mW}/\text{m}^2$ (Cui et al., 2014; Liu et al., 2017).

Furthermore, electricity was produced using an acetate single chamber microbial fuel cell and studied the dominant phyla of adherent microorganisms (Khater et al., 2017). It was observed that the anode terminal adhered with dense microbial forms. The dominant phyla were observed in the 16S rRNA sequencing were Firmicutes, Gammaproteobacteria, Alphaproteobacteria, Actinobacteria, with ten dominant strains viz. *Bacillus firmus*, *Shewanella profunda*, *Bacillus isronensis*, *Brevundimonas bullata*, *Pseudomonas putida*, *Planococcus citreus*, *Micrococcus endophyticus*, *Acinetobacter tandoii*, *Bacillus safensis* and *Shewanella xiamenensis*. This system yielded the maximum current of 791 mV at 86.1 mW m^{-2} of power density with 354 mA m^{-2} of the stable current density of and 65% of high Faraday efficiency. Moreover, an artificially fabricated MFC with three-dimensional (3D) nitrogen-enriched graphite carbon (NGC) is useful for enhanced bioelectricity production (Doyle et al., 2017; Santoro et al., 2017; You et al., 2017). The electrodes were heavily augmented with *Geobacter metallireducens* in the lactate fed system as revealed in the metagenomic and metatranscriptomic studies. During the enrichment of the *G. metallireducens*, 400 mV of applied potential was found to produce an unsustainable high current, observed due to the thick film, low pH and oxidative stress. Moreover, identified two novel strains of *Enterobacter* and *Aeromonas* sp., which are found to be capable of extracellular electron transfer in the carbon electrodes by using the electron donors of lactate and acetate (Faria et al., 2017). At the advancement of the MFC technology, an extremophilic halotolerant bacterium was used for electricity generation using wastewater as a source (Grattieri et al., 2017). A fabricated single chamber MFC production media with the natural sea condition (35 g/L of salinity) was used for the production of electricity. Higher production of electricity

Table 1

Sl. No.	Type	Substrate	Application	Yield	Source
1	MEC	Cane sugar effluent	Biohydrogen production	1.59 mmol/L/D	Jayabalan et al. (2018)
2	MEC	Acetate solution	Biohydrogen production	2.72 m ³ H ₂ m ³ d ⁻¹	Jeon et al. (2018)
3	MEC	Wastewater	Biohydrogen production	1.434.268 mmol m ⁻³ h ⁻¹	Kim et al. (2018)
4	MEC	Wastewater	Biohydrogen production	0.45 m ³ H ₂ /Cm ³ .d	Jafary et al. (2018)
5	MEC	Wastewater	Biohydrogen production	0.48 m ³ H ₂ m ⁻³ d ⁻¹	Gude (2018)
6	MFC	PRW	Bioelectricity	28.27 W/m ²	Mohanakrishna et al. (2018b)
7	sMFC	PRW	Bioelectricity	132 mW/m ²	Mohanakrishna et al. (2018b)
8	MFC	PRW	Bioelectricity	250 mV	Guo et al. (2016)
9	MFC	PBS	Bioelectricity	26.6 A/m ³	Naga Samrat et al. (2018)
10	sMFC	Methylene blue	Bioelectricity	670.97 mW m ⁻²	Lee et al. (2018)
11	MFC	Wastewater	Wastewater treatment	72.76% degradation efficiency	Mohanakrishna et al. (2018a)
12	tMFC	Industrial wastewater	Wastewater treatment	Nitrogen removal rate 10.0 ± 1.3 g Nm ⁻³ d ⁻¹	Zhang et al. (2018)
13	tMFC	Industrial wastewater	Wastewater treatment	Sulfide removal rate 206.5 ± 1.9 g S m ⁻³ d ⁻¹	Zhang et al. (2018)
14	UtMFC	n-alkanes	Bioremediation	79% removal efficiency	Wang et al. (2012)
15	MDC	Wastewater	Bioremediation	0.71 kg COD/m ³ /day	Sevda et al. (2017)
16	MFC	PRW	Bioremediation	24% aliphatic hydrocarbon removal	Guo et al. (2016)
17	sMFC	Wastewater	Bioremediation	TOC removal rate 85.7 ± 7.4%	Zhang et al. (2013)
18	sMFC	Wastewater	Bioremediation	TN removal rate 91.5 ± 7.2%	Zhang et al. (2013)

MEC: microbial electrochemical cells, MFC: microbial fuel cells, sMFC: single chamber MFC, tMFC: triple chamber MFC, UtMFC: U-tube soil MFC, MDC: microbial desalination cells, PRW: petroleum refinery wastewater, PBS: phosphate buffered saline, COD: chemical oxygen demand, TOC: total organic carbon, TN: total nitrogen.

(36 mW m⁻²) recorded was 820 mA m⁻² of current density. This technology offers a proof for highly efficient, low cost, eco-friendly MFC system for bioelectricity production.

2.4. Bio-hydrogen production from wastewater

Hydrogen is a renewable clean and high-density energy fuel, which could be used as a better alternative for fossil fuel. The hydrogen can be generated from various domestic wastes through microbial electro-hydrogenesis cells (MECs) (Q.-Y. Chen et al., 2017). A single chamber MEC was fabricated with a stainless steel cathode to produce hydrogen-using acetate as substrate (Rivera et al., 2017). The yield of hydrogen production would greatly depend on the surface area of the cathode and the spacing of the electrode in the single chamber MEC. It was observed that the cathode size (142 cm²) 9% higher yield of 0.24 L H₂/L^{-d} than the 71 cm² cathode. On the contrary, 78% boost of hydrogen production rates to the cathode area was observed in the smallest cathode (71 cm²) than the cathode with the largest surface area (142 cm²). This negative effect could be due to the greater catalytic interaction of the large surface area. It results in elevation of the electric conflict while the production rate was reduced. Thus, the MEC performance was highly facilitated by electrode gaps. The higher production of hydrogen would also be impacted by the recovery method. In general, platinum (Pt) coated carbon cloth (Pt/CC) was used as a catalyst for the efficient production of hydrogen. Though it is efficient, the practical application of carbon cloth is restricted because of its high cost and weakness. To overcome this issue, cheaper and novel Pt-coated nickel foam (Pt/NF) was developed for the enhanced hydrogen production in the MEC system (L. Wang et al., 2017). Maximum hydrogen evolution reaction was observed in the Pt/NF than the Pt/CC. At 0.8 V, the maximum yield of hydrogen was attained as 0.71 ± 0.03 m³/m³ using the Pt/NF. Electrical energy efficiency was also reported to be higher than that of the Pt/CC. It is observed that the methane formation was reduced to 56% as the hydrogen evolution activity increased during the longtime experiment. The higher hydrogen production achieved due to the porous structure of the nickel foam, which is a feasible and cost-effective catalyst. Similarly, another single chamber MEC was fabricated with nickel foam, Ni-P coated nickel foam and stainless steel (SS) cathode for enhanced hydrogen production. This SS cathode is highly cost-effective than the Pt cathode. The Ni-P was found to have considerably greater hydrogen evolution performance than the SS and nickel foam cathodes. The Ni-P attained the 2.29 ± 0.11 L H₂ L d at 0.9 V, which was 7.5% higher than the nickel foam and 110% higher

than the SS cathode. This could be due to the higher power density, which suppresses methane production and led ample generation rate and recovery of hydrogen (X. Li et al., 2017).

Biofilms are greatly impacts on bio-hydrogen production. Chloroethane sulphonate enriched microbial consortia were used as bioanode in the MECs for hydrogen production (Catal et al., 2017). A single chamber MEC was fabricated without the membrane and by the addition of furfural and hydroxyl-methyl-furfural (HMF). HMF yielded an effective hydrogen production, whereas the furfural was failed to produce hydrogen. However, the power density of the MECs was similar in the furfural (5.9 mA/cm²) and HMF (6 mA/cm²). This study showed that the single chamber MECs have enriched biofilm, which significantly influenced the hydrogen production. Among other factors, anode acclimation might significantly improve the production of hydrogen in the MECs. This was supported by development in strategy for anode acclimation. The acetate, butyrate and corn stalk fermentation effluent (CSFE) were used for the initial acclimation of the anode in the MFCs. Later on, the acclimated anodes were used in the MECs for hydrogen production along with the CSFE substrate. Among the three types of acclimation, the butyrate showed up with the higher hydrogen production (5.21 ± 0.24 L of Hydrogen per L of CSFE) and high current density (480 ± 11 A/m³). Whereas, the acetate and CSFE showed comparatively low hydrogen yield (4.22 ± 0.19 L of Hydrogen per L of CSFE and 4.55 ± 0.14 L of Hydrogen per L of CSFE respectively). This could be a significant strategy for biohydrogen production through effluent treatment (F. Li et al., 2017). Over the period, the fabrication and improvement of MECs towards biohydrogen production is well addressed. Troubleshooting the recovery and purity would cause significant development in the biohydrogen production. In this context, light-assisted microbial photoelectrochemical cells (MPEC) were made-up with CaFe₂ to use as photoelectrode for real-time hydrogen production (S. Chen et al., 2017). The MPEC was found to produce higher hydrogen evolution rate (6.7 μL/h⁻¹/cm⁻²) than the Cu₂O photocathode. Furthermore, the MPEC yield was highly stable and efficient than the other cathode (TiO₂). This revealed that the MPEC is far better than the existing photocatalytic water splitting technology and other techniques.

Yet again binders were used as a cathode catalyst in the MECs for hydrogen recovery. In common, Nafion binders were used for the hydrogen production. It is essential to develop a novel, efficient and cost-effective binders like Pt/NF for the enhanced yield. Different kinds of binders had been used for the hydrogen evolution reaction in MEC such as anionic binders-Nafion, BPSH20, BPSH40 and S-Radel cationic

binder-Q-Radel) and neutral binder-Radel, BAEH. Among these, the anionic binder BPSH40 was found to be the best performer in steady-state polarisation due to their higher water content (56%) compared to others. The design of a cathode for an effective MEC should contain highly hydrophilic binders. The MECs can effectively be used for hydrogen production through sustainable utilisation of wastewater. It was estimated that around 1.17 billion m³ of domestic and 0.38 billion m³ of industrial wastewater were discharged per year. Hence, the government was seeking for a sustainable wastewater treatment system in the waste-to-energy theme. Initially, total electricity production was expected to be 434 MWe in 2015 when the MECs were utilised for wastewater treatment. By advancing the MEC technology, the total electricity production could be increased as 612 MWe for 2025 and 767 MWe for 2035 upon the sustainable utilisation of domestic and industrial wastewater. This can be achieved by standardising the saturation kinetics, ohmic, loss of concentration and other challenging factors involves the reduction of hydrogen production.

However, scaling up the industrial use is still lagging due to many challenging factors. To rectify these issues, an anaerobic digestion system was established to utilise the wastewater for hydrogen production as a potential alternative (Khan et al., 2017). The anaerobic MEC digestion system is said to be better because of its cost-effectiveness and eco-friendliness. It was recommended that the combination of MEC and MFC could lead a sustainable wastewater treatment system to generate higher energy by producing high-density hydrogen as well as electricity through the waste-to-energy process. This can be achieved by process optimisation for hydrogen production regardless of their substrates, challenging parameters, COD removal etc. An anaerobic sludge digestion system equipped with energy efficient flat-plate dual chambered microbial peroxide producing cell (MPPC) as an anode for converting the primary sludge into hydrogen peroxide would be a solution (Ki et al., 2017). A ~230 mg/L of hydrogen peroxide was produced during the batch cathode process (6 h). In addition, it was reported that a ~0.87 kWh/kg H₂O₂ of energy was utilised than the previous studies. Comparison of MEC and MPPC showed that they have attained the Faraday efficiency with ~30% recovery. The MPPC showed with a 12% increase of Faraday efficiency than the MEC due to the inhibition of methanogenic microbial forms. Though other factors are highly influencing the hydrogen production, inoculum also plays a key role in determining the hydrogen yield. The requirement of inoculum, enrichment and other operational conditions to start-up a successive MEC will greatly influence the hydrogen production. Performing MECs with monoculture is viable in the laboratory experiments. When practical scale-up concern, microbial consortia impact significantly on the treatment of feedstock and high-density hydrogen production. This can be achieved by enriching the bio-electrochemical consortia to subdue the activity non-bio-electrochemical forms. Later on, the enriched consortia can be used to develop an active biofilm layer on the anode to perform the hydrogen production. With the enriched anodic fabrication, their potential, operational temperature, and feedstock concentrations would be considered for the successive start-up of the MECs. Along with these factors, the membranes, type of electrode used and their external and internal resistance were also being considered for successful fabrication of the cells, which led the great start-up and constant process (Kumar et al., 2017).

2.5. Wastewater treatment for sustainable utilisation

Today, the natural water resources are depleting due to increased demand and parallel consumption. The generation of wastewater is huge in terms of the output of those smoke breathing buildings. This becomes a severe problem in disposal and remediation of the wastewater. A two-in-one cleaner technology is required for the remediation as well as sustainable utilisation of the wastewater. The inventions of microbial fuel cells are greatly impacted by wastewater treatment, which helps to achieve the waste-to-energy goal. They can be

configured to utilise and treat any type of wastewater (municipal and industrial waste) for bioelectricity generation. The positioning of the anode is much important in MFCs to stabilise the electricity production. Cathode oxygen crossover greatly affects the current generation in the close-spaced out anode. To stop the oxygen crossover can be controlled by a composite anode consisting mesh and brush self-possessed to stabilise and improve the mesh potential and performance (Wu et al., 2017). The composite brush and mesh anode stand with $524 \pm 20 \text{ mW m}^{-2}$ of higher power density over the normal anodes used. This yielded a 20% increase in current density over normal graphite brush ($436 \pm 17 \text{ mW m}^{-2}$) and 150% increase over anodes with carbon mesh ($206 \pm 22 \text{ mW m}^{-2}$). The composite anode showed a stable output compared to the normal anode brush. Biofilm formation on the cathode was also reduced when using the composite anode, led the increase of Faraday efficiencies. This could be due to the reduction of resistance in charge transfer, which led stable and higher current density with high anodic potential in the MFC. The composite anode fabricated MFC can be effectively used for domestic wastewater treatment. Bio-anodes are typically used for organic compound degradation and power production using efficient MFC cells (Cheng et al., 2017).

An MFC was fabricated with aerobic granular sludge (AGS) as bio-anode for the remediation of epoxy reactive diluent wastewater. The results yielded a higher current density ($491 \pm 8 \text{ mW m}^{-2}$) with maximum COD removal ($82 \pm 5\%$). The higher degradation of epoxy reactive diluent wastewater was achieved due to the higher toxicity tolerance of AGS. Another effective wastewater treatment is MFC combined with flocculation which aid for the residual COD removal. This would yield higher power generation with the maximum removal of nitrogen and COD. After the experiment, the MFC attained a maximum of 37.5 W m^{-3} with a Faraday efficiency of 21.6% (40:60 ratio) along with the efficient removal of ammonia ($269 \pm 0.5 \text{ g m}^{-3} \text{ d}^{-1}$). Moreover, the maximum of 82.5% COD was removed during the MFC operation and in addition, flocculation has reduced the COD to 96.6%. A net benefit was about $\$0.026 \text{ m}^{-3}$ was achieved from the combined treatment process (Ding et al., 2017).

Besides, an MFC was designed and operated with multimode flow directions and electrode combinations along with varied COD conditions to treat the wastewater (He et al., 2016). Parallel or series feeding was followed for domestic wastewater with the altered flow direction. This showed up with uniform electricity generation and the current densities of parallel and series flow were 4.8 W m^{-3} and 4.2 W m^{-3} , respectively. A 1.9% high yield of power was recorded with the anode with twin cathode over the anode with the single cathode. These altered flow conditions did not affect the COD concentration. In addition, it was recommended to perform additional optimisation studies to scale-up the power generation. In this context, the MFCs were combined with membrane bioreactors (OMBRs) for the superior energy generation through wastewater treatment. The MFC-OMBR is capable of producing higher electricity (11.5 W m^{-3}) and aid the active removal of phosphorous and organics at the mesophilic conditions (Hou et al., 2016). The OMBR favoured an MFC by accumulating the buffer capacity and solution conductivity. At the outset, low sludge production and sludge load ($0.076 \text{ g TSS/g COD}$ and $< 350 \text{ mg/L TSS}$) was formed due to the lower membrane fouling. This would be an effective and feasible technology for wastewater treatment.

On the other hand, organic-rich solid municipal waste was treated with dual-chamber MFC for promising bioelectricity production. Substrates, inoculum, and mesophilic anaerobic sludge was considered as key factors and is optimised using the design of experiments (DOE) for the enhanced production of bioelectricity (Koók et al., 2016). It was identified that the inoculum of mesophilic anaerobic sludge showed a negative impact on electricity generation. This study showed that the lowest COD level yielded maximum energy of $8\text{--}9 \text{ J g}^{-1}$. The MFC was found to be efficient in the degradation of solid municipal waste with a maximum of 94% of COD removal ($1.9 \text{ kg COD m}^{-3} \text{ d}^{-1}$). The substrate concentration significantly favoured the MFC performance for

higher energy production. In general, the wastewater treatment system needs energy for the supplementation of air to handle the leftover slurry, would cost around 50% of the operating cost. MFCs with air-cathode have been developed to cut-down the aeration cost of wastewater treatment. The treatment of high-strength wastewaters would need long hydraulic retention time than the low-strength wastewater. MFC was fabricated with twin air cathode used for the continuous treatment of swine wastewater consisting of 8 g/L of COD. After 12 days, a higher current density was recorded ($750 \pm 70 \text{ mW/m}^2$) in the swine wastewater. Conversely, severe fouling on the cathode reduced the electricity production to 85%, after 185 days. Moreover, the usage of external resistance at a lower level could increase the COD removal rate, which was higher than the low strength wastewater. Result obtained suggest that high-strength wastewater was best suited than the low-strength wastewater for energy production through wastewater treatment (Kim et al., 2016).

In recent days an MFC unit equipped with flat-panel air-cathode (FA-MFC) was designed to treat the domestic wastewater, which efficiently removes the nitrogen, and organics using short HRT (2.5 h). The removal of total nitrogen ($1.7 \pm 0.1 \text{ mg/L}$) and COD ($20.7 \pm 2.5 \text{ mg/L}$) were considerably increased from 85% to 94% upon 8 months of the experiment. The first and second MFC unit were observed with the highest COD and total nitrogen removal ($0.62 \text{ Kg-N/m}^3/\text{d}$). On the contrary, though the FA-MFC produced very low electricity (6.3 W m^{-3}); the COD and total nitrogen were simultaneously removed from the domestic wastewater. The cathode was studied for their microbial community composition. Result obtained revealed that the presence of *Nitrosomonas*, *Nitrareductor* and *Acidovorax* in the cathodic chamber could be responsible for the nitrification, de-nitrification and thereby the removal of nitrogen and organics from the wastewater. Thus, the MFCs can effectively be used for the sustainable utilisation of domestic and industrial wastewater towards energy production (Y. Park et al., 2017).

2.6. Biosensor development to monitor the wastewater treatment

Microbial fuel cells are bio-electrochemical system uses electrochemically active microorganisms to catalyse the organic substrates and releases electrons. Those electrons can be measured by output voltage and used for environmental monitoring through bio-sensing. The MFC is best suited for biosensor development because of their stable performance, higher reproducibility, quick response and easy recovery (Schröder et al., 2015). A model organism of *Geobacter* involves an accumulation of electrons on the surface of the electrodes by which the environmental signals are translated into electrical impulse (Koch and Harnisch, 2016). The transformation of bioanodes into biosensors involves many key factors such as electrochemical activity, which is essential in the microbial electrochemical system. A study suggests that the encapsulation of the microbial catalyst could be highly recommended in developing pre-colonized electrodes because of its higher reproducibility and quick reactive nature. The microbial electrochemical systems can be used as biosensors for the detection of DO, BOD and assimilable organic carbon etc. In the same way, an MFC biosensor would have application in real-time monitoring of an MFC integrated up-flow anaerobic sludge bed reactor (UASB). It was found that the process was constant and steady. In a relationship with voltage and the time required for a change in concentration of COD were assessed which examined the signal feedback. The experiment showed that the pH was less sensitive parameter than the electrical signal feedback. The threshold sensitivity varied in concentrations were $S = 3 \times 10^{-5} \text{ V/mg/L}$ and $S = 8 \times 10^{-5} \text{ V/mg/L}$. This integrated MFC was translated the 0.94% of the COD into an electrical signal for bio-sensing (Jia et al., 2016).

Monitoring chemical contaminants in the industrial effluents is a mandate to avoid environmental pollution as well as their impact on the natural biosphere. For these, a novel biosensor has been developed

for the real-time monitoring of *p*-nitrophenol (PNP), a common pollutant found in industrial wastewater (Z. Chen et al., 2016). Anode bio-sensor was used for the *in situ* real-time PNP monitoring in dual chamber MFC. This can be done using the *Pseudomonas monteilii* LZU-3 as a biological hint for the detection of PNP. Because the *P. monteilii* LZU-3 have an ability to use PNP as a prime source for the formation of biofilm on the anode. MFCs key parameters were optimised (pH-7.8, temperature - 30°C , external resistance 1000Ω and the concentration of PNP 50 mg/L^{-1} max.) for the enhanced bioactivity of the MFC. Linear association was found between the higher electricity and the concentration of PNP (15 ± 5 to $44 \pm 4.5 \text{ mg/L}^{-1}$). Based on these results, a novel real-time device was developed to monitor the PNP under *in situ* condition. The result of this experiment also confirms that the PNP concentrations and the electricity production were significantly correlated along with the improved biosensor performance from 9 ± 4 to $36 \pm 5 \text{ mg/L}^{-1}$. Finally, the cost-effective and rapid MFC biosensor can be effectively used in real-time monitoring of environmental samples for recalcitrant and toxic pollutants. In addition, the MFC biosensor can also be used in real-time monitoring of biological oxygen demand (BOD) in the wastewater system. A single chamber MFC was fabricated for the bio-sensing of the BOD in the synthetic rice washed wastewater-SMFC (Logroño et al., 2016). For the monitoring of the BOD concentration of the SMFCs were prepared at different concentrations such as 10 mg/L for SMFC1, 100 mg/L for SMFC2 and 200 mg/L for SMFC3. The observed results showed that the SMFCs have transitory, stable and rising phases. As per the BOD concentrations, the transitory phase showed up with the open circuit voltage (OCV) at the maximum. During the rising phase, a linear correlation was observed between the time and the OCV. The SMFC2 needed a long time than the SMFC1, whereas the SMFC3 failed. The SMFC1 was found to have higher OCV ($40.6\text{--}58.8 \text{ mV}$) than the SMFC2 ($18.2\text{--}32.9 \text{ mV}$). Thus, the SMFCs is highly recommended to use it as a bio-sensing device for monitoring the environmental hazards.

With reference to this, a single chamber MFC was fabricated with a novel MnO_2 as a cathodic catalyst for monitoring the oxygen reduction rate (Kharkwal et al., 2017). The novel MFC was used for bio-sensing of BOD along with domestic wastewater and sodium acetate for comprehensive study. The result of these experiments showed that significant R^2 value of the domestic wastewater (0.98) and sodium acetate (0.99) were produced by the optimum performance of the $\beta\text{-MnO}_2$ sensor. As per the standards, the BOD_5 value was highly correlating with the BOD values of the $\beta\text{-MnO}_2$ sensor in the domestic wastewater treatment. The long-term study of the MnO_2 /BOD bio-sensing showed up with higher stability and reliability in real-time monitoring of BOD, proves the domestic wastewater treatment through MFC have a vast scope of the application of BOD monitoring and biosensor development. The need and practice for the wastewater treatment system led people to develop novel, sustainable, cost-effective and eco-friendly technology that acts as an environmental monitor through bio-sensing. In this context, a paper-based disposable self-support multi-anode MFC (PMMFC) with an integrated power management system (PMS) is used for the real-time shock bio-sensing in wastewater treatment. Batch mode chamber was used for testing of three types of shocks viz. chromium, hypochlorite, and acetate. The result showed that the PMMFCs yielded four times higher current output than the conventional carbon cloth MFCs. This was because of the higher bacterial adhesion in the paper-based anode. The above result points out that the data transmission was more frequent in the PMMFC over the carbon cloth MFCs and single anode MFCs. Therefore, the disposable self-support shock sensor can eventually be used in the *in situ* real-time monitoring of the wastewater due to its tight paper packed structure with short acclimation period, high sensitivity towards shocks, and high power output (Xu et al., 2016).

Although dual electrode MFCs is used for, the development of biosensors, the stability and the reliability is still in the improving stage. To have more reliable and stable bio-sensing, three electrode cells have been developed (Li et al., 2016). This study had developed microfluidic

M3C over bench scale M3C. The reference electrode was separated by the laminar flow from the counter and working electrode of the microfluidic M3C. In the microfluidic M3C, the potential of the silver electrode was retained in a constant state of the integration of laminar airflow. Precise control over the potential of the working electrode was achieved which offer a definite electrochemical environment to the *Geobacter* sp. Quick response to formaldehyde and ferric citrate with short HRT was observed in the microfluidic M3C, reproducibility is an added advantage. As discussed earlier, the substrate concentration and the output voltage have an undeviating connection. This led a way to develop another microlitre (μ l) scale MFC development for bio-sensing of toxic materials in water. The μ l-MFC has fabricated with three electrodes, which offer improved sensitivity and reliability (Yang et al., 2016). The μ l-MFC also equipped with an air-bubble trap to avoid excess bubbles and increase microbial growth for consequent transfer of electrons. The system response was highly sensitive and immediate when it was exposed to different concentrations of the toxic compound formaldehyde (0.001%–0.1%) a 0.2 V current response was observed on the silver anode. Results of this study prove the sensitivity and reliability of the μ l-MFC on the bio-sensing. Therefore, further research is needed to scaling up the system to analyse the water toxic contents.

Moreover, disposal of wastewater containing toxic substances in the aquatic and terrestrial environment will have an adverse effect on the biota and habitat. Hence, it is mandatory to monitor the wastewater treatment system for toxic substances. MFCs can effectively be used for the real-time monitoring of the toxic substances in the wastewater treatment system. Having this in mind, a self-powered MF Chas developed for bio-sensing the toxicity level of the heavy metal ions in the wastewater (Yu et al., 2017). A total of six heavy metals were taken such as a copper (Cu^{+2}) as a reference compound, mercury (Hg^{+2}), zinc (Zn^{+2}), cadmium (Cd^{+2}), lead (Pb^{+2}) and chromium (Cr^{+2}) at the 2 mg/L concentration. After the experiment, the I-values were recorded as 12.56% for copper ion, 13.99% for mercury ion, 8.81% for zinc ion, 9.29% for cadmium ion, 5.59% for lead ion and 1.95% for chromium ion. Along with this, laboratory wastewater was also tested and it was showed up with 28.13% I-value. The detection sensitivity of the heavy metals occurred due to the inhibition of electrochemical bacterial respiration by the heavy metals. This result showed that the self-powered MFC biosensors are highly sensitive, ease of use and cost-effective and has proven toxicity detection in the wastewater system.

2.7. Remediation of contaminants

Persistent chemicals and highly toxic contaminants are the major cause of pollution and a major threat to the ecosystem as well as to human health. Anthropogenic activities such as domestic waste, agricultural practices, industrial and vehicle emissions contaminate the environment with heavy metal like pollutants. Hence, remediation of the contaminants through MFCs can be used as an efficient technology for the bioremediation of toxic contaminants in the environmental benefit.

Discharge of industrial effluents in the aquatic or terrestrial environment could lead the sedimentation and bioaccumulation of toxic substances. In the agricultural field, the use of excess pesticides and herbicides can accumulate those substances in the soil particles and lead persistent for years. These cause the degradation of soil or benthic forms and degrade the soil quality. Novel sediment MFCs have developed for the treatment of contaminated sediments. Novel microbial electroremediating cells (MERCs) consist of soil buried electrodes to accept the electrons through bio-electro venting was developed for biodegradation of a herbicide (atrazine). This novel technology showed a fivefold increase in biodegradation of atrazine than the natural degradation process. The post-biodegradation toxicity level of the degraded herbicide was assessed through different tests carried out using the bioindicators such as green algae-*Pseudokirchneriella* sp., bacterium-*Salmonella* sp.) and plant seeds-*Sorghum* sp. The result confirms that the

efficient removal of atrazine from the contaminated soil in a short span of time was achieved through the MERCs (Domínguez-Garay et al., 2016).

Naphthenic acids (NAs) are one of the toxic components contaminates the water body from the oil extraction sites. The NA concentration was increased to 250 mg/L from 100 mg/L, which would enhance the rate of biodegradation. The NA biodegradation supports the bacterial growth in diauxic condition. The degradation of cyclic NA was greatly impacted by the occurrence of linear NA. The substantial improvement of the degradation could be due to the added electron transfer through broad biofilm formation on the granular graphite electrode. This continuous flow MFCs showed their proven efficiency in the biodegradation rate of naphthenic acids (Valdes Labrada and Nemati, 2017).

Most of the terrestrial and aquatic ecosystems are found to possess toxic heavy metal such as chromium, which causes damage to human health and the ecosystem. Over again, the removal of chromium from the contaminated site is a tedious task. This can be achieved using plants by bioaccumulation followed by removal of the toxic compound. To have a more sensitive and effective treatment system for the remediation of chromium, MFC was developed by integrating live plants (Habibul et al., 2016). The novel system is the so-called plant-microbial fuel cell (PMFC) bio-electrochemical system. The heavy metal Cr (VI) was used for the PMFC evaluation. The results showed that the initial concentration of Cr(VI) plays a key role in the rate and removal efficiency of Cr (VI) up to 99%. This sustainable PFMC system found to be very stable even in the long-term experiment and provided with the proven efficacy towards the removal of Cr (VI). Similarly, a continuous flow MFC for the *in-situ* and *ex-situ* degradation of phenanthrene and benzene, which are carcinogenic and mutagenic, pose risk in human life. For biodegradation of these hydrocarbons, aqueous tubular MFCs were designed for *in situ* and *ex-situ* and operated for 155 days. The results of the *in-situ* experiment showed that the catholyte of petroleum hydrocarbons and bromate were observed with a higher degradation rate of > 90% and 79% respectively. On another hand, 10 days of HRT yielded with a high current density of 6.75 mWm^{-2} as a simultaneous output. The *ex-situ* experiment showed up with better HRT (30 h) with the current density of 6.75 mWm^{-2} , which was similar to the *in situ* output, and 77% of the COD removal was observed. The better MFC performance could be due to the ability to sustain the shock loadings and it suggests that the MFC can effectively be used in refinery effluent treatment and hydrocarbon polluted groundwater treatment at regardless of the concentration of the contaminants (Adelaja et al., 2017).

Similarly, textile dyes play a major role in water pollution. The textile effluent makes the soil infertile and affects the growth of the plants/crops that led the low yield. However, there are many ways to treat the dye effluent, over again the MFC acts as an apt technology for remediating the dye effluent with the co-production of electricity as a dual-purpose system. Hence, the fabricated single chamber MFC was used for the remediation of textile dyes (RBu 160 and RG19) and decolourised metabolites (DMs). *Shewanella* sp. WLP72 was used as a microbial catalyst for remediation purpose. A 43% of the MFC performance was observed during the decolourization of 600 mg/L of RG19 and 36% in 200 mg/L of RBu160. Hence, the dye decolourization and electricity generation were significantly increased due to the use of DMs incorporated MFCs (B.-Y. Chen et al., 2016). On another hand, Phenolic compounds are the major compounds, which contaminate the groundwater system through various industrial discharge and coal gasification etc. Hence, MFC was used to treat the phenolic compound contaminated groundwater containing phenolic compounds and their metabolite. Sulphate, nitrate, oxygen and iron electrode can be used as an electron acceptor in biodegradation study. The anode containing the electroactive bacteria consume the electron donor of the acetate and produces $\sim 1.8 \text{ mW/m}^2$ electricity. The anode enhanced acetate removal by 40%. On contrary, a short time was taken for the effective degradation of phenol. This was reported that the electricity production

and degradation of contaminants were mainly affected by microbial synergistic dealings (Hedbavna et al., 2016).

3. Conclusion and future perspectives

This chapter delivers information about the role of MFCs in electricity generation. In addition, a detailed investigation was made to summarize the MFC application in wastewater treatment through a sustainable approach for electricity creation, hydrogen production, remediation of contaminants/pollutants and biosensor development. Studies concluded that waste can be efficiently utilised, degraded or treated through the MFC novel system and thus can be a well optimised and configured for our need in the near future. Moreover, enhancing the MFC function is quite difficult by means of chemical approach. The quorum sensing was adopted to enhance the MFC action for sustainable energy production by coordinating the bacteria through auto-inducers to enrich the bio-anode. Since the future depends on the renewable energy sources for compensating the fuel need; the MFCs would pave a way for the renewable and eco-friendly energy production.

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