



The race between classical microbial fuel cells, sediment-microbial fuel cells, plant-microbial fuel cells, and constructed wetlands-microbial fuel cells: Applications and technology readiness level



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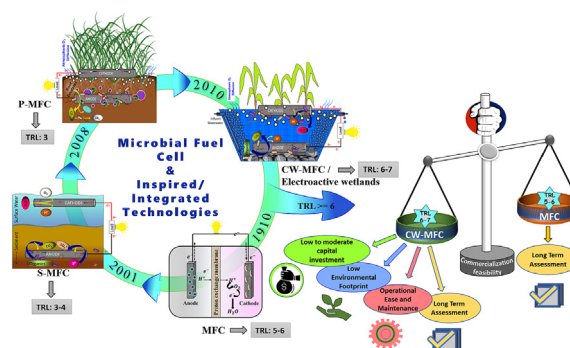
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HIGHLIGHTS

- MFC and its variant technologies S-MFC, P-MFC and CW-MFC are the promising self-sustaining bio-electrochemical systems
- S-MFC, P-MFC and CW-MFC are hosted in natural environments and give larger areal dimensions to existing MFC technology
- The TRL for MFC, S-MFC, P-MFC and CW-MFC achieved so far fall in the range of 5-6, 3-4, 3 and 6-7, respectively.
- The cost to benefit ratio for CW-MFCs is much lower compared to MFCs under both experimental and practical conditions
- CW-MFC remains leading technology compared to MFC and its inspired variants

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cell (MFC) is an interesting technology capable of converting the chemical energy stored in organics to electricity. It has raised high hopes among researchers and end users as the world continues to face climate change, water, energy, and land crisis. This review aims to discuss the journey of continuously progressing MFC technology from the lab to the field so far. It evaluates the historical development of MFC, and the emergence of different variants of MFC or MFC-associated other technologies such as sediment-microbial fuel cell (S-MFC), plant-microbial fuel cell (P-MFC), and integrated constructed wetlands-microbial fuel cell (CW-MFC). This review has assessed primary applications and challenges to overcome existing limitations for commercialization of these technologies. In addition, it further illustrates the design and potential applications of S-MFC, P-MFC, and CW-MFC. Lastly, the maturity and readiness of MFC, S-MFC, P-MFC, and CW-MFC for real-world implementation were assessed by multicriteria-based assessment. Wastewater treatment efficiency, bioelectricity generation efficiency, energy demand, cost investment, and scale-up potential were mainly considered as key criteria. Other sustainability criteria, such as life cycle and environmental impact assessments were also evaluated.

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1. Classical microbial fuel cell technology and its historical development

A classical microbial fuel cell (MFC), a variant of the biological fuel cell, is a bio-electrochemical device that converts the chemical energy stored in chemicals such as sugars and alcohols, directly into bioelectric energy with the use of microbes as biocatalysts (Shukla et al., 2004). A typical MFC setup is an assemblage of an anaerobic and an aerobic chamber, separated

by a proton exchange membrane, and equipped with anode and cathode electrodes, respectively. However, the anode and cathode electrodes are connected by an electric wire across an external load for harvesting the energy (Fig. 1). The anodic biofilm in an MFC acts as the engine of the process and catabolizes the substrates such as carbohydrates (low redox potential, $-E_h$) in the absence of oxygen while the generated electrons are taken up by an enzyme-active site, which acts as a reduced intermediate. In the presence of an electrode as a suitable electron acceptor, the electrons are

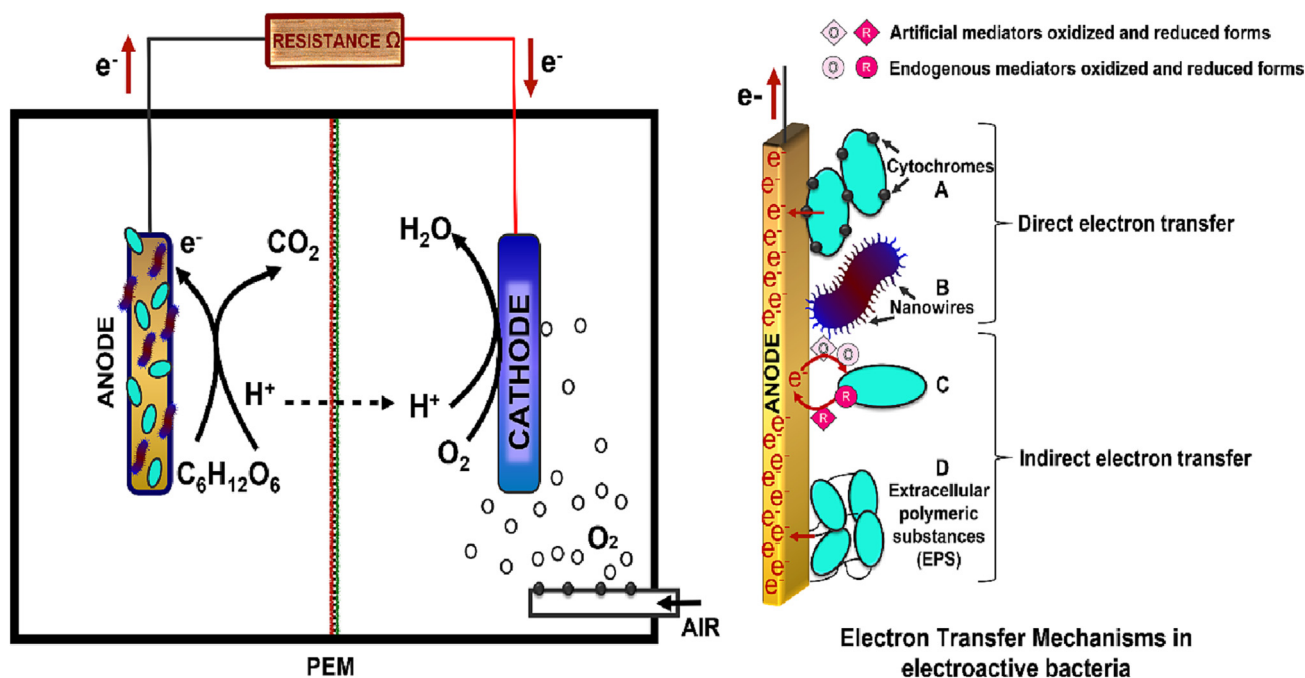
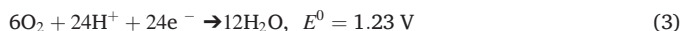
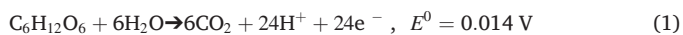


Fig. 1. Schematic representation of a typical MFC setup and the microbial processes assisting in electron transference and electricity generation.

then diverted to the external circuit, and ultimately, these electrons reduce molecular oxygen (electron sink, high redox potential, $+E_h$) at the cathode surface (Gupta et al., 2020a, 2020b; Li et al., 2018) as follows, resulting in the generation of electric current:



The history of MFC dates to the year 1790 when the twitching of an isolated frog leg upon a brief electrical discharge passed through it was first observed by Professor Luigi Galvani. The term bioelectricity was then coined based on this bioelectric phenomenon. Later in 1910, Professor Michael Cresse Potter observed the current flow between the platinum electrodes when dipped in the suspension of yeast and *Escherichia coli*; and revealed that bacteria could generate electricity. This discovery was the advent of research interest in MFC technology; however, it was very slow due to skepticism, and uncertainties. Cohen revived the idea in 1931 by demonstrating the production of $>35 \text{ V}$ in a biological fuel cell which was the combination of multiple small cells (10 cc of culture) connected in series with the unit cell yielding approximately 0.2 mA at a potential of 0.5 V (Choi and Ahn, 2013). However, it took another three to four decades when the National Aeronautics and Space Administration (NASA) in 1960 took an interest in generating current from waste in its long-haul space flights. The oil crisis in the 70s and 80s also renewed interest in biological fuel cells (Abbassi and Yadav, 2020; Li et al., 2018; Santoro et al., 2017; Shukla et al., 2004). The alarming concerns over the diminishing rate of fossil fuels and the increasing rate of greenhouse gas emission compelled researchers to look for clean energy-generating technologies, and MFC emerged as the best fit. Several researchers continuously contributed to MFC advancement by working on electrodes (Karube et al., 1986), mediators (Allen and Bennetto, 1993), biocatalysts (Chaudhuri and Lovley, 2003) etc. However, the interest in MFCs dwindled soon because of a lack of efficiency and long-term stability (Lovley, 2006).

Nonetheless, the progressive journey of MFC began in the 1990s when mediator-less MFC achieved success (Fadzli et al., 2021). Subsequent improvement in MFC targeted selection of new microbes, mediators, substrates, and modifications in the MFC design and configurations. The MFCs have complex structure involving several functional components and processes of diverse nature; thus, an interdisciplinary approach/understanding is required to realize the involved mechanisms. Therefore, modelling was utilized as an effective tool for better understanding the complex phenomenon occurring in MFCs including many biological, physio-

chemical, and electrochemical processes; and optimizing the operational conditions governing the MFC performance (Jadhav et al., 2021a; Ortiz-Martínez et al., 2015). For modelling of electricity generation in MFCs, researchers developed simple empirical equations to complex 3 dimensional (3-D) models based on electrochemical redox reactions. Also, simple analytical techniques such as black box models, fuzzy logic, and advanced computational tools (computational fluid dynamics, simulations, artificial neural networks), have been used in the MFC system. Broadly, these models are categorized as global models, which study the overall behaviour of MFCs; and specific models, which study the key components, processes, and variables in MFCs. These models describe MFC performance based on certain principles and equations, as stated in Table 1. Most of the early-stage models considered the single-phase approach based on the anodic biofilm while considering cathodic parameters constant. However, this created erroneous measurement during validation of modelling results. Hence, recently several research studies have focused on multi-species and multi-phase models based on interaction between anodic and cathodic dependent variables. Nevertheless, repeatability and replicability of the MFC performance remains challenging even in similar operating conditions (Jadhav et al., 2021a).

The MFC research domain is expeditious though the technology still lacks far behind any practical applications. Fig. 2 demonstrates the advancements in MFC research by plotting the publications investigating the different design, operational, and functional aspects, and modelling of MFC performance for electricity generation in the last two decades (2000–2021).

1.1. Primary function of MFC: as an electricity-generating device

The bioelectricity production with the oxidation of organic matter is the key highlighting feature of MFC technology (Mathuriya and Yakhmi, 2016); and a range of organic matter sources, both pure compounds to complex mixtures in wastewaters, have been used, which includes acetate, glucose, ethanol, lactate, mannitol, microalgae, phenol, sodium formate, starch, sucrose, brewery wastewater, protein-rich wastewater, synthetic wastewater, etc. (Pant et al., 2010; Saba et al., 2017; Y. Zhang et al., 2011). Recent reviews on MFCs have shown that acetate and glucose are used most frequently for electricity generation (Obileke et al., 2021). Acetate is a simple carbon source and prompts the electroactive microbes. The power density generated using acetate (506 mW m^{-2} , 800 mg L^{-1}) in a single chamber MFC was 66 % higher than that produced with butyrate (305 mW m^{-2} , 1000 mg L^{-1}) (Liu et al., 2005). Similarly, when compared to protein-rich wastewater, more than two folds increase in power and a decrease in external resistance were achieved in acetate-fed MFC (Liu et al., 2009). The energy recovery efficiency of glucose was, however, decreased

Table 1
Most used empirical equations in mathematical modelling in MFC systems.

Empirical equations	MFC variables considered	Formulae	Applications in MFC models
Monod kinetics	Microbial growth metabolism, Substrate degradation rate	$\mu = \mu_{\text{max}} \frac{C_s}{K_s + C_s}$	<ul style="list-style-type: none"> Describe substrate oxidation and microorganism growth (anode). Adapted to oxygen reduction reaction (cathode). Combined with Nernst equation to describe bacterial metabolism in response to electron release or electrical potential.
Tafel plot	Overpotential, current density	$E = E_{\text{eq}} + \frac{RT}{(1-a)nF} \cdot \ln \frac{i}{i_0}$	<ul style="list-style-type: none"> Combined with Monod equations to describe anode reaction kinetics. Describe cathode kinetics
Butler-Volmer equation	Current density, voltage difference	$i = i_0 \exp \left[\frac{(1-a)nF}{RT} (E - E_{\text{eq}}) \right] - i_0 \exp \left[-\frac{anF}{RT} (E - E_{\text{eq}}) \right]$	<ul style="list-style-type: none"> Calculate current density from oxidation reactions (anode). Combined with Monod equation to describe electrochemical anode and/or cathode reactions.
Nernst equation	Electron transfer, substrate species concentration	$E = E_0 - \frac{RT}{(1-a)nF} \cdot \ln Q$	<ul style="list-style-type: none"> Description of electrochemical behaviour. Combined with Monod equation to describe electrochemical anode and/or cathode reactions.
Nernst Plank equation	Species and mass transport	$F = -\frac{zF}{RT} D_i \frac{dc}{dx}$	<ul style="list-style-type: none"> Focus on extra-cellular activity. Describe mass, momentum and charge balances for ion fluxes.
Faraday's law	Mass transport, species concentration	$J = zF\theta$	<ul style="list-style-type: none"> Describe ion transport across the MFC separator (membrane). Describe mass transport losses and resistance
Ohm's law	Voltage, current profile	$V = I.R$	<ul style="list-style-type: none"> Calculate cell output voltage and current

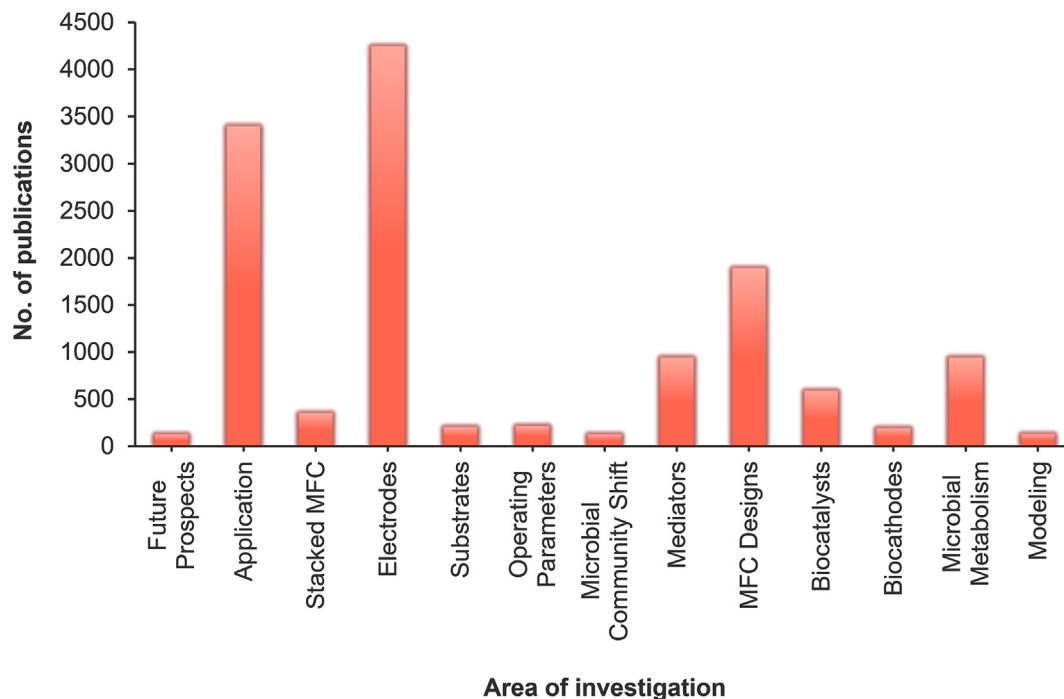


Fig. 2. Advancements in various aspects of MFC research over a period of two decades (2000-2021).

compared to acetate in MFC, which is because of carbon competition between fermentative and electroactive bacteria (Lee et al., 2008). Nevertheless, like acetate, high power density was generated by glucose (161 mW m^{-2}) compared to anaerobic sludge (0.3 mW m^{-2}) (Hu, 2008). Unfortunately, the concentration of glucose beyond a certain value was found to have an inhibitory effect on electricity generation. Igboamalu et al. (2019) demonstrated that increased power densities of 4.98 mW m^{-2} and 10.43 mW m^{-2} were obtained with 2.78 mM and 5.56 mM glucose concentrations which decreased to 4.26 mW m^{-2} and 3.02 mW m^{-2} when the glucose substrate concentration was increased to 13.89 mM and 27.78 mM , respectively. Similarly, Rahimnejad et al. (2010) revealed that the operation of glucose-fed MFC at concentrations of 2.0 , 5.0 and 7.0 mg L^{-1} achieved optimum values of 905 mV , 39.33 mW m^{-2} and 85.059 mA m^{-2} for voltage, power density and current density, respectively at 5.0 mg L^{-1} concentration.

Single chamber air cathode MFC fuelled by the mixture of domestic wastewater and olive mill wastewater produced a power density of 124.6 mW m^{-2} (Pepé Sciarria et al., 2013). Min et al. (2005) compared the electrical performance of a two-chambered aqueous cathode MFC with a single-chambered air cathode MFC fed with swine wastewater containing $8320 \pm 190 \text{ mg L}^{-1}$ of soluble chemical oxygen demand and obtained maximum power densities of 45 mW m^{-2} and 261 mW m^{-2} , respectively. The same single-chambered air cathode MFC fed with domestic wastewater produced higher power density of $146 \pm 8 \text{ mW m}^{-2}$ due to the higher concentration of organic matter in the swine wastewater (Min et al., 2005). Thus, the type and concentration of substrates oxidized in MFC largely influenced electricity generation. The adhesion of anodic biofilm over the electrode surface and the efficient transfer of electrons between them is another major aspect for electricity generation. Thus, several electrode materials for anode and cathode have been explored in MFC for enhanced power output. Carbon paper, graphite plates or sheets, and carbon cloth are the most common materials for plain electrodes (Obileke et al., 2021; Santoro et al., 2017). Two-chamber air cathode MFC with graphite plate electrodes (155 cm^2) produced a maximum power density (MPD) of 0.141 mW cm^{-2} (Dewan et al., 2008). A carbon mesh electrode (7.0 cm^2 projected surface area) employed in a single-chamber air cathode MFC inoculated with enriched bacteria from an active MFC produced a power density of 893 mW m^{-2} (Wang et al., 2009). Zhang

et al. (2009) reported the MPD of 46 W m^{-3} (with respect to anodic volume) obtained in a single-chambered air cathode MFC with carbon cloth electrode (7.0 cm^2 projected surface area) inoculated with enriched bacteria from an active MFC. However, the low specific area and high cost of plain electrodes refrained their use in large-scale MFCs. The packed and brush-structured electrode material was also investigated to identify their impact on power output. Granular activated carbon (GAC) packed single-chambered air cathode MFC produced a power density of 5.0 W m^{-3} (with respect to anodic volume 250 mL) while treating domestic wastewater (Jiang and Li, 2009a). Graphite brush (length, 4.0 cm and diameter, 3.0 cm) equipped with air cathode MFC produced a power density of 2.4 W m^{-2} (with respect to cathode area) or 73 W m^{-3} (with respect to liquid volume) (Logan et al., 2007). The volume of treating wastewater gets reduced by $50\text{--}60\%$ in packed electrode MFC; however, the treatment and electron capturing efficiency increase significantly.

The optimization of MFC performance has been done by several researchers by evaluating the different components through the modelling approach and using different equations (Table 1). Ghadge et al. (2016a, 2016b) optimized the anodic volume of MFC based on the Butler-Volmer approach, charge transfer limitations and limiting current density from Tafel analysis. It was stated in their study that 2 L anodic volume can generate a current of 750 mA , however, any further increase may promote the activity of methanogens over electrigenes. Further, a two-dimensional (2-D) model was proposed by Gadkari et al. (2019) which optimized electrode spacing, electrode area and substrate concentration to evaluate the performance of air-cathode MFC. It revealed that reducing the electrode spacing and increasing the initial substrate concentration enhance the energy recovery, whereas, decrease in anode size does not affect the MFC performance. The electron transfer between the bacteria, occurring as biofilm or suspended biomass, and electrode is crucial in electricity generation which is quantified by the bacterial metabolism rate and substrate concentration. Therefore, Monod Kinetics equation-based biofilm models were developed (Jayasinghe and Mahadevan, 2010). Franzetti et al. (2017) revealed that Monod kinetics fits well at low substrate concentrations ranging $0\text{--}100 \text{ mg L}^{-1}$ when acetate is used as an organic substrate in air cathode MFC. Further, considering the cathode as a non-limiting factor, a mathematical model was developed for anodic biofilm metabolism and the effect of substrate concentration; and current generation were

calculated using the charge transfer equation and Ohm's law (Gadkari et al., 2019). Based on the electron transfer activity in electroactive *Geobacter sulfurreducens* microorganism, the dynamic conduction based one-dimensional (1-D) model was developed which evidenced that the direct electron transfer in biofilm is limited by biofilm conductivity (Marcus et al., 2007). Gatti and Milocco (2017) developed the model to determine the Faradaic and capacitive current in the anodic biofilm. Picioreanu et al. (2007) developed a computational 3-D biofilm based model which disclosed that local current density was more intense for uniform thickness of electrogenic anodic biofilm. Considering cathode as limiting factor, cathode-based models also appeared in literature. Different high redox potential catalysts and chemical catholytes are used in MFCs for controlling the cathodic potential. By utilizing the Butler-Volmer equation, a polarization model has been developed to determine the voltage losses occurring in MFCs depending on enzymatic and electrochemical kinetics (Zhao et al., 2014). Electrochemical model is an important consideration for estimating the voltage output of a MFC under given operating conditions based on various redox reactions and an empirical approach. Radeef and Ismail (2019) developed a polarization model for a MFC treating potato chips processing wastewater and showed a good coefficient of determination of 0.99, 0.92 and 0.92 for current density, power density, and voltage, respectively by considering various electrochemical overpotential losses. Similarly, membrane-based models were developed to quantify the intensity and rate of ionic species transfer between anode and cathode chambers. Harnisch et al. (2009) showed that the application of cation membrane increased membrane resistance by maintaining more pronounced pH gradient between anodic and cathodic chambers which adversely affected the current generation.

The hydrodynamics of MFC i.e., fluid flow, proper substrate distribution and fluid residence time, greatly influence MFC's performance. Thus, several simulation models and fluid flow equations were proposed. A computational fluid dynamics based model developed using multi-order Butler-Volmer equation revealed that the effective mixing of the fluids in granular activated carbon containing anode of MFC enhanced the current output by 17 % with minimized mass transport losses (Zhao et al., 2016). Massaglia et al. (2017) demonstrated the fluid dynamics modelling using Navier-Stokes law and presented that optimized drop-like SCMFC showed the better behaviour with an effective concentration of sodium acetate close to the nominal one and an improved sensitivity for high flow rates with the maximum value of current density of $14 \pm 4 \text{ mW m}^{-2}$.

1.2. Secondary functions

In addition to bio-electricity generation, MFC is also advantageous in wastewater treatment while using wastewater as an organic matter source for its oxidation. It can therefore be stated that MFC presents probably the most balanced and close-to-nature form of energy production by directly converting the anthropogenic waste to electric current. Its potential to remediate wastewater and get powered by it was first realized in 1990s (Do et al., 2018). Thereafter, different types of wastewaters have been fed to MFC for electricity production and their simultaneous treatment. Recently, several reviews dedicated to MFCs have reported wastewater treatment and coulombic efficiency. Single-chambered air cathode MFC was found to remediate brewery wastewater ($1501 \text{ mg COD L}^{-1}$) with 20.7 % COD removal efficiency (Wen et al., 2010). Similar COD-containing biodiesel wastewater ($1400 \text{ mg COD L}^{-1}$) showed higher removal efficiency of 90 % (Feng et al., 2011). 41 % COD was removed from bad wine containing 7.8 g COD L^{-1} in a two-chamber MFC equipped with carbon felt and graphite electrode (Rengasamy and Berchmans, 2012). Corn stover hydrolysate ($1000 \text{ mg COD L}^{-1}$) treated in a single chamber MFC with carbon cloth cathode (Zuo et al., 2006). Two-chamber MFC treating high-strength cassava mill wastewater reduced the COD concentration from $16,000 \text{ mg COD L}^{-1}$ to $4480 \text{ mg COD L}^{-1}$ using graphite plates electrodes (Kaewkannetra et al., 2011). Rahimnejad et al. (2015) reported that up to 90 % COD can be removed from wastewater using MFC in certain cases. Gupta et al. (2020b) reviewed the MFC performance for recalcitrant

pollutant degradation i.e., dye wastewater treatment and electricity generation. Unlike electricity generation, MFCs targeting wastewater treatment are often continuous flow, single-chambered and membrane-less to suffice the upscaling goals. MFC technologies can be considered as complementary technology, however, low energy conversion efficiency and high capital investment remain the limiting factor. Nevertheless, relatively better-quality effluent is reclaimed from MFCs compared to existing conventional technologies such as anaerobic digestion (Do et al., 2018; Du et al., 2007).

1.3. Lab to land transfer limitations

The ideal performance of MFC has been vastly explored. It is deemed to be a fantastic technology for powering small devices such as biosensors for pollutant monitoring (particularly BOD biosensor) and process monitoring (Rahimnejad et al., 2015; Srivastava et al., 2022a), lifesaving devices such as pacemakers (Goel, 2018), and other remote applications such as wireless temperature sensor, LED lightening, digital wristwatch, mobile phone charger etc. (Santoro et al., 2017). However, not any big success story has been reported on the pilot study of MFC focussing its power generation potential as clean energy replacement of fossil fuels (Zhou et al., 2013). Moreover, the cost investment in MFC fabrication, operation, and maintenance with respect to its application as the sensor is indefensible (Jadhav et al., 2021b).

The upscaled MFC volume is crucial for high power production which would suffice the real-world demand (Jadhav et al., 2021b). A large number of accessible reports have shown that MFC could be configured from sizes of a few millilitres to a few thousand litres; however, they concluded that the power generated is adversely affected by the upscaling of MFC (Oliveira et al., 2013). A small-scale MFC (25 mL volume of the anode) produced 490 mW m^{-3} power density compared to 210 mW m^{-3} which was produced by 500 mL volume MFC (Ieropoulos et al., 2008). Any upscaling of MFC declined the power density to $<2 \text{ W m}^{-2}$ (with respect to anode surface area) which was even insufficient to power the pumps feeding MFC (Lovley, 2006). With the increase in MFC's size and volume, the size of electrodes also increases but in order to enhance the power production minimal inter-electrode distance is maintained. As a result, the bulk volume in MFC remains non-interactive with electrode and biofilm, and active electrochemical reactions occurring at the junction of wastewater, electrode and biofilm are refrained from utilizing full wastewater volume for power generation (Oliveira et al., 2013). By utilizing the Butler-Volmer approach, Monod kinetics and electrochemical models, Ghadge et al. (2016a, 2016b) stated that increase in volume beyond 2 L results in increased methanogenic bacteria activity which outcompetes the electrigenes and deteriorates the current production. Stacked MFCs have shown up some potential for upscaling MFCs; nevertheless, adverse phenomenon such as voltage reversal and parasitic current loss limits their optimum power output (Jadhav et al., 2021b). Sugnaux et al. (2017) attempted to understand the role of biofilm formation in voltage reversal using electrochemical based models; and computational and validation results revealed that the variability of biofilm and the external resistance applied in circuit are responsible for voltage reversal. However, the reversal caused can be minimized by periodic changes in the substrate flow rate and monitored recirculation of anolyte. So far, no long-term study has been reported on stacked MFC for real wastewater treatment disclosing the associated operational difficulties and overall performance stability with the view of presenting it as a future solution to the energy and/or, wastewater treatment sector.

The electrochemical reactions occurring at the anode for organic matter oxidation and at the cathode for oxygen reduction, ultimately, determine the electric energy generating potential of MFC. Nevertheless, the achieved cell potential is always lower than the theoretical value (Obileke et al., 2021). The internal losses at several interfaces, i.e., activation, ohmic and concentration losses, determine this voltage gap. Despite several attempts by researchers to narrow the gap, the highest cell potential achieved so far is 0.8 V compared to the theoretical 1.1 V (Logan et al., 2006; Obileke et al., 2021). The other major bottleneck in the upscaling and marketing of MFCs is its high cost. The fabrication materials used in MFC, particularly electrodes and proton exchange membrane, are quite expensive. They are

crucial for high power output and thus cannot be compromised. The less expensive alternatives such as carbon electrodes and ceramic-based membranes are, however, are being extensively researched to tackle with high cost. Moreover, air cathodes are being employed instead of aqueous cathodes to avoid aerators and the use hazardous chemicals like potassium ferri-cyanide for cathodic reduction reactions.

The wastewater remediation by MFC while simultaneously generating electricity has several challenges (Fadzli et al., 2021). The power output of MFC while treating wastewater is much lower than pure carbon sources such as glucose, etc. Moreover, different substrates produce different power outputs. This makes it difficult to optimize the MFC performance for the treatment of wastewater, which is complex and variable in nature and flows with fluctuating pollutant loads. The lower availability of degradable organic substrate in wastewater may impact remediation efficiency and energy generation because the low amount of organic substrate did not provide enough food and carbon to the bacterial population build-up and energy for their metabolic reactions, resulting in poor MFC output. The concentration of organic matter present beyond a certain limit also obstructs the removal efficiency and power output (Fadzli et al., 2021). Since much of the MFCs studies have been demonstrated at lab scales, it is necessary to upscale them while fuelling them with wastewater and using low cost materials and study their long-term performance. Scaling up of MFCs is also expected to achieve the levels of power needed to power real-world electrical devices. Simultaneously, to make MFCs suitable for real applications, such as wastewater treatment plants, it is critical to achieve high power densities at a large scale and low-cost of construction. The modelling approach, though claims to simplify the complex MFC system using different electrochemical and microbial kinetic approaches, most of the mathematical models have considered individual components or processes associated with MFC instead of integration of all the components and processes involved with such complex system. Also, several assumptions are made for validating the models which ignores the vital parameters such as system flow distribution, substrate homogeneity etc. For upscaling of MFCs it is crucial to consider all the components correlatively to derive an understanding.

2. From classical microbial fuel cell to inspired or integrated MFC technologies

As aforesaid in Section 1.3, the classical MFC technology is extensively recognized for its potential to generate sustainable bioelectricity from wastewater treatment, but it also struggles for neutral-energy operation, unable to generate sufficient electricity to run real world practical applications, non-suitable economic balance between investment and output. Moreover, a high capital investment, which largely includes the cost of fabrication materials such as expensive electrodes and separator/membrane, and other electrical devices such as dosing pumps, aerators, etc. for its operation, is the major bottleneck in its commercialization. To circumvent these limitations, the research community tried incorporating MFC within natural ecosystems as hosts such as plant system/waterlogged paddy fields, sediment-laden water bodies and wetland systems, which have inherently developed redox gradients (E_h); and termed these inspired systems such as plant-MFC (P-MFC), sediment-MFC (S-MFC) or integrated technology such as constructed wetland integrated microbial fuel cell (CW-MFC) or electroactive constructed, respectively (shown in Fig. 3). The inspired technologies are basically more or less like classical MFC, and majorly fuel substrates are changed; for instance, in P-MFC, plant roots work as a fuel substrate, while in the S-MFC, organic-containing sediment works as fuel substrate. However, in the case of integrated MFC technology, there is already an existing field scale technology mainly for wastewater treatment with some shortcomings; integration of MFC or MFC-like structure helps in overcoming the shortcomings of the main technology with the possible additional function such as electricity generation, but not necessarily. The CW-MFC is an example of integrated MFC technology where constructed wetlands are already employed at the field level for wastewater treatment application and suffer slow treatment kinetics. With the integration of

MFC components (electrically connected electrodes or conductive materials) in CWs, treatment kinetics is accelerated with the additional electricity generation feature (Srivastava et al., 2022b).

The inspired or integrated technologies benefited MFC by making its way out from the boundaries of the lab to a somewhat real field, and the natural system took advantage of the improved conductive material-microbe interactive environment for its better nourishment and functioning. Relying on the microbe-conductive material interaction for better and regulated electron flow, these inspired or integrated technologies are principally similar to MFC but their purpose, structure, and substrates are quite different. Often, these inspired or integrated systems are membrane-less, thus more techno-economic, and practical.

2.1. Sediment-microbial fuel cells

The water bodies such as lakes, ponds etc. represent a columnar system characterized by the uppermost zone saturated with oxygen, and the lower zone, which has the large deposit of organics-rich sediment but deficit in oxygen. These two zones are separated by the water column. So, the fundamental principle behind the design of S-MFC is the inherent anaerobic or anoxic microbial activity in anaerobic soil or sediments and uppers aerobic layer, such difference in the two zones creates a redox gradient (anaerobic/anoxic and aerobic) in the natural environment settings (Bose et al., 2018). The sediment offers a pure and limitless source of electron donors, and the oxygen gradient towards the surface of the water acts as the indefinite electron sink/acceptor, which is separated by a large water column. Thus, the implantation of a solid electron acceptor (anode electrode) within the sediment and electron donor (cathode electrode) overlying the water surface, connected through an electrical wire across an external load, facilitates harnessing the dead energy stored in benthic sediment as electric current. The S-MFC employment in isolated sediment deposits additionally benefits by accelerating the rate of organic matter oxidation as the rate of electron flow from sediment towards oxygen (electron acceptor) increases.

2.1.1. Designs and operational configurations

As discussed above, the engineering and design of S-MFCs are remarkably close to those of classical microbial fuel cells with fewer alterations. The most prevalent S-MFC configuration combines a suspended electrically conductive air-cathode in the surrounding water with a anode implanted in organic-rich sediment and represents the preliminary S-MFC design (Fig. 3a) (Reimers et al., 2006; Tender et al., 2002; Thomas et al., 2013). The further configuration advancements occurred by prioritizing enhanced energy production, both on a laboratory and pilot scale. Several configuration-related factors that impacted the S-MFC performance, such as electrode material (Song et al., 2012), distance between the electrodes (Sajana et al., 2013a), depth of water (Song et al., 2019), the height of anode embedded in sediment (An et al., 2013), cathode configuration (Bose et al., 2018), type of water (De Schampelaire et al., 2010) etc., were considered (Zabihallahpoor et al., 2015). Different S-MFC prototypes based on aerobic/anaerobic situations and the presence/absence of external stimulatory current, have been considered in prior years. Aerobically non-stimulated S-MFCs feature an air sparger in the cathode for improving the electrochemical reduction process leading to enhanced electricity generation. In contrast, aerobic stimulated S-MFCs are additionally assisted with external batteries along with air sparger for stimulating both anodic oxidation and cathodic reduction process, which enhances electrical energy generation, and the removal rate of contaminants present in the sediment, protecting the healthy state of water bodies. Furthermore, anaerobic stimulated and non-stimulated S-MFCs have also been explored with no air spargers in their cathode. However, stimulated S-MFCs have an external battery compared to non-stimulated S-MFCs (Abbas et al., 2017). Multiple anodes and cathodes were also installed at the sites. The innovation of S-MFCs with three-dimensional floating bio-cathodes was done to enhance the power output in an in-situ river water sediment with graphite as an anode. In recent years, similar research based on different electrode materials in S-MFC has been carried out to enhance power generation and

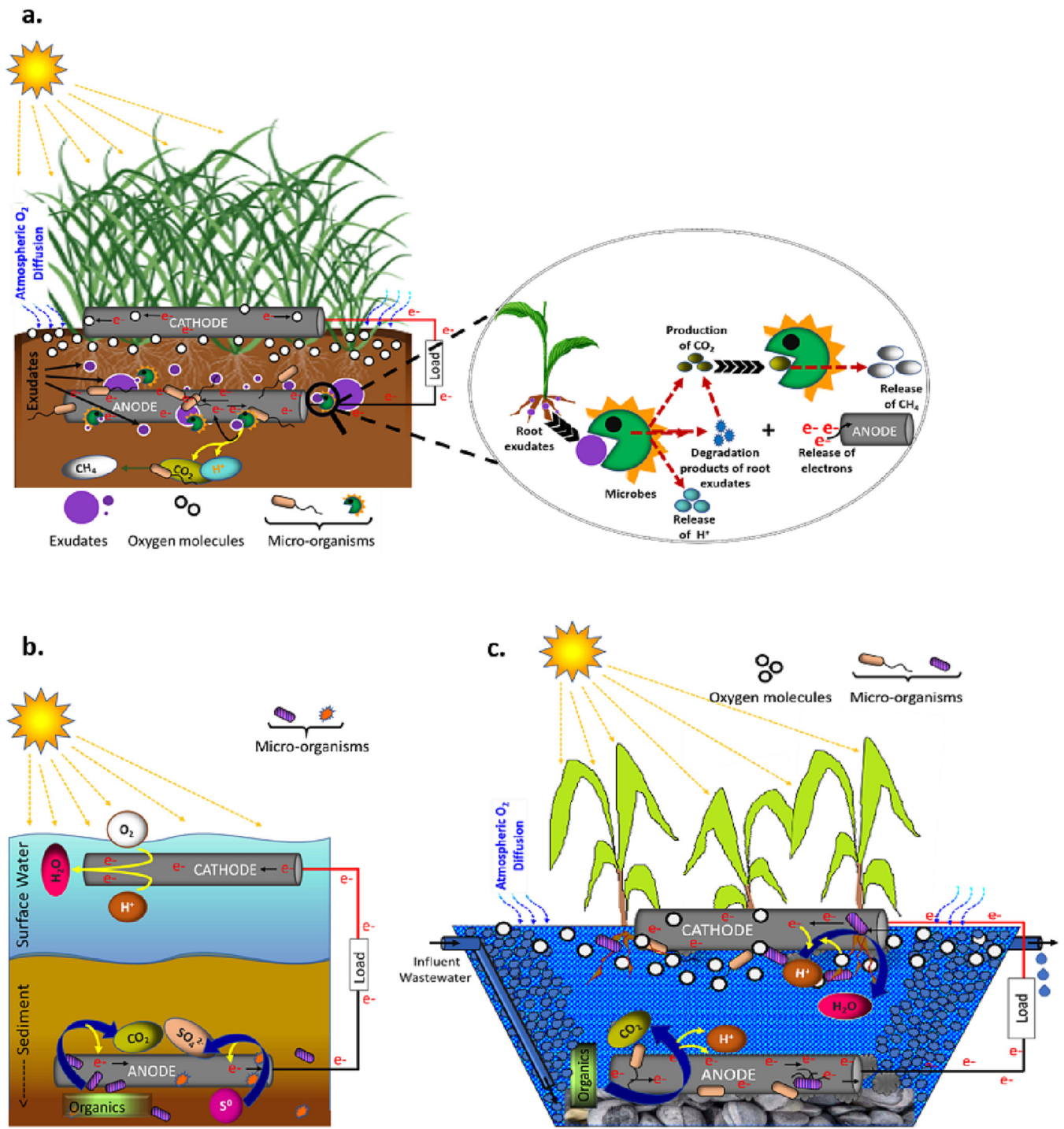


Fig. 3. Schematic representation of a basic prototype and associated functional processes of MFC inspired or MFC integrated variants: (a) Plant microbial fuel cell, (b) sediment microbial fuel cell, and (c) constructed wetland microbial fuel cell.

organics removal (Arends et al., 2012; Lawan et al., 2022; Prasad and Tripathi, 2018; Song et al., 2013; Song et al., 2011; Taşkan et al., 2020; Zhu et al., 2015). Additionally, research has also been conducted to investigate the number of S-MFCs and their arrangement for energy generation in open channels. The performance assessment of stacking three and then four S-MFCs connected in series and parallel modes were also done. The results concluded that the highest power generation was found with three S-MFCs connected in series, whereas in parallel mode four stacking S-MFCs received the highest power generation implying that using parallel connections can reduce the problem of losses caused by connections in series, resulting in high power production (Abazarian et al., 2016).

Furthermore, in a recent study, an S-MFC configuration including polyvinyl alcohol and polyvinyl elastomer separation membranes was also evaluated to test proton transfer and oxygen diffusion inhibition in anode part for better treatment and electricity generation performance (Liu et al., 2022). Similarly, several studies have also been done for the enhancement of oxygen diffusion in the cathode zone by using a rotating cathode (Suor et al., 2014), floating cathode (Morris and Jin, 2012), algae cathode (Wang et al., 2014), plant rhizosphere cathode (Moqsud et al., 2015), air cathode (Sheikhyousefi et al., 2017), comb-type cathode (C.-T. Wang et al., 2017). Moreover, studies on partitioned open channel S-MFCs were also carried out by connecting two S-MFCs in parallel and series and operating them

at different flow rates to acquire energy from a freshwater environment (Azari et al., 2017). The S-MFC operated in short circuit mode has shown greater COD and TN removal efficiency and power density compared to closed circuit S-MFC operated with external resistance of 700 Ω (Sajana et al., 2013b). In a recent study, Shi et al. introduced an S-MFC configuration with a cylindrical borehole immersed in the sediment layer to lower internal resistance and increase power density (Shi et al., 2021). S-MFCs have further been categorized according to the source of sediment in which these are installed i.e., marine S-MFCs and freshwater S-MFCs. The distinct feature of S-MFCs might be employed as a long-term maintenance-free and reliable power source for devices placed in aquatic and lake conditions (Donovan et al., 2013; Tender et al., 2008).

2.1.2. Primary function as a bioelectricity generation unit

The primary goal of developing S-MFCs was to generate energy for low-power applications by exploiting active microorganisms in sediment. These applications include powering wireless equipment used in environmental monitoring, oceanic investigations, and military tactical surveillance where real-time data capture from far-off areas are necessary (Gong et al., 2011; Sacco et al., 2012). S-MFCs are a viable alternative, particularly in deep water where batteries cannot be sustained for an extended period and there are no cable connections to the surface. This has also significantly lowered the cost (Donovan et al., 2008). Additionally, S-MFCs have been investigated for powering wireless sensors that monitor temperature, salt concentration, BOD, COD, tidal patterns, pH, humidity, pollution, and the presence of algae or any other species and marine fauna (Majumder et al., 2014; Scott et al., 2008). It has also been investigated to power wireless sensor nodes and radio data transfer. The results have affirmed its consistent performance over a long period with a high signal transmission rate (Thomas et al., 2013). The power management system (PMS) has been introduced to S-MFC for harvesting and storage of power for powering underwater ultrasonic sensors intermittently. The energy for this purpose was stored in capacitors which produced energy on an average between 3 and 10.4 mW (Donovan et al., 2013). Recently, a maximum voltage of 12 V was attained by Prasad and Tripathi (2021) while using stacked S-MFCs. They prevented voltage reversal while stacking by first charging a capacitor using each set of S-MFCs and then utilizing it to power the DC boost converter. An experiment has been performed using membrane-less S-MFC in an aerated and non-aerated cathode which resulted in 77.75 mW m⁻² and 45.04 mW m⁻² power density, respectively, implying the positive impact of aeration in membrane-less S-MFC (Abbas et al., 2019). Additionally, when a fabric barrier was used to separate a water layer so that the anode electrode could be maintained in a more anaerobic situation in sediment, the anode's kinetic activity was improved by the mass transfer of organics, which led to a 6.6-fold increase in the power output when compared to a typical S-MFC (Lee et al., 2015). Similarly, a modification was made to achieve high power density in S-MFC by utilizing algae to suffice the need for oxygen efficiently. The power of this sediment microbial carbon-capture cell was 22.19 mW m⁻², which was 3.65 times that of the normal S-MFC (Neethu and Ghangrekar, 2017). These strategies have benefited upscaling of S-MFCs by reducing the cost; thus, various studies have focused in recent years on the improved power generation in S-MFCs for its commercialization purposes (Donovan et al., 2013; Sacco et al., 2012; Gong et al., 2011).

The modelling approach of upscaling S-MFCs is however not much explored and only handful studies have reported it. Ma et al. (2019) demonstrated the start-up phase modelling of S-MFC for current generation using RBF neural network and ELM neural network, and presented that ELM neural network is better in forecast in the performance of S-MFC system. An electrochemical model was developed for a S-MFC performing anaerobic degradation of petroleum contaminated sediments and generating very low power density of ~ 4 mW m⁻². The model was used to determine the experimental parameters that contribute to the increased internal resistance and enabled the development of improved S-MFC with 20 times lower internal resistance and 47 folds enhanced power output (Alvarez-Benítez et al., 2022).

2.1.3. Secondary functions

As aforementioned, organic-rich sediments in aquatic environments have been recognized as a rich potential renewable energy source in S-MFCs. However, sewage from industrial and municipal sources has infiltrated into the surface layer of sediments, contaminating the water and causing methane emissions. These pollutants are hazardous to native organisms and plants (Yan et al., 2012). Although these pollutants have the potential to be used as fuel in S-MFCs. In addition to generating electricity, the S-MFC's anode is a perfect substitute electron acceptor that may accelerate the breakdown of organic materials in sediment via the biocatalytic activity of anodic biofilm. Furthermore, numerous oxides, including sulphate, nitrate, and Fe(III) oxides, can be employed as electron acceptors in anoxic natural environments so that microbes in contaminated aquatic sediments can anaerobically break down organic matter and assist in bioelectricity generation (Yan et al., 2012). Researchers have made several modifications to S-MFC technique for treating contaminants in sediment and sediment-water. Lab-scale S-MFCs were run under various circumstances for the in-situ treatment of rivers contaminated by organics and heavy metals. The results demonstrated that the S-MFCs working with normal cathodes showed reduction reactions with heavy metals in the surrounding water for 60 days and produced the highest removal efficiencies as 97.3 %, 87.7 % and 98.5 % for Hg(II), Cu(II) and Ag(I), respectively (M.S. Wu et al., 2017). Similarly, the impact of zero-valent iron on the degradation of polychlorinated biphenyl (PCB) and total organic carbon (TOC) removal in S-MFC was examined. The combined application (S-MFC and zero-valent iron) was shown to have a removal efficiency of 37.55 \pm 1.11 % for PCB and 49.72 \pm 1.54 % for TOC (Wu et al., 2019). Another research that used floating macrophytes to raise the dissolved oxygen at the cathode of a single chamber S-MFC in order to concurrently remove pollutants and produce electricity showed removal efficiency of total COD, nitrate, and sulphate as 57 %, 99 %, and 99 %, respectively. Bioelectrochemical oxidation at the anode, reduction reactions at cathode, and accumulation in macrophyte were among the pollutant removal processes observed in the study (Kabutey et al., 2019a). In recent research, an S-MFC was built, and starch was used to treat polycyclic aromatic hydrocarbon (PAH) in polluted aquaculture sediment. The findings revealed removal efficiency of 69.9 %, 55.6 % and 46.8 % for naphthalene, acenaphthene, and pyrene, respectively (Zhang et al., 2022). A planted sediment microbial fuel cell is an exciting prototype for harvesting energy and cleaning up a contaminated geo-environment using organic materials derived from the roots. Though, it requires certain considerations, such as the anode should be positioned appropriately under the roots to minimize the impacts of oxygen loss. When plant roots were placed on the anode surface, electricity generation did not improve because the high oxygen loss from the roots increased the anode's redox potential, caused aerobic bacteria to co-exist, and caused them to compete with electrochemically active bacteria for resources (Liu et al., 2018).

2.1.4. Challenges and implications

S-MFC is a potential substitute for renewable energy sources for specific applications, for example it can generate electricity to power sensors, devices, and storage while requiring little maintenance. Nonetheless, S-MFC has several manufacturing, installation, and performance optimization issues to become a reliable energy source. Microbial oxidation of substrates and transfer of generated electrons to anode significantly impact anode kinetics for electricity generation. However, the mass transfer limitations caused by low organics concentration decreased the current density of S-MFCs. Anode kinetics can be enhanced by applying microbial oxidants such as humic acid or other external mediators for charge transfer (An et al., 2013; Lowy et al., 2006). For the case of planted S-MFC, it is intriguing to note for future research about how the plant density, variety of plants, and installation position of plants affect the electrode performance. Plants can physically alter water flow and raise oxygen levels, which in turn affects the distribution of electron donors and acceptors in the water. To comprehend plant's function in catalyzing oxygen reduction at cathode,

further research should be done on the cathode community and rhizospheric bacteria in the presence of plants (Xu et al., 2015).

Advantageously S-MFCs are mostly membrane-less; however, it makes the cathode vulnerable to electron donors and the anode susceptible to electron acceptors that result in lower electrochemical reaction efficiencies. Potentially it could be overcome by decreasing the inter-electrode distance and placing a cation exchange membrane between them, but it eventually affects the cost. In that case, low-cost cathode catalysts like nitrogen-doped activated carbon (Zhang et al., 2014), and polyaniline-based graphene nanosheets (Ren et al., 2013) can be used to improve cathode reaction and simultaneously decrease the overall cost of S-MFC. Another way to accelerate the cathodic reaction is by increasing DO concentration in the cathode through aeration, however, it is also cost-intensive. Implementing photosynthetic organisms like algae in the cathode is an effective alternative (Xiao and He, 2014) and should be focussed on upscaled applications.

Future studies should concentrate on sediment bioremediation, in-situ bioremediation processes, and explore climatic, biological, and social aspects, as well as judicious use of stimulating external energy (from renewable sources) to enhance bioremediation. Most of the current S-MFC investigations have been conducted on simpler compounds in sediments. So, in the future, bioremediation of complex compounds in sediments should also be explored. Also, much of the research is confined to the lab scale. Therefore, the transfer of S-MFCs from the lab to open water environments like rivers or oceans will be challenged by passivating electrode components through electrochemical deposition, destruction of electrodes, and S-MFC setup being destroyed by current flow and fish grazing. The collaboration of several disciplines will help S-MFCs overcome some of the challenges.

Since the prototype S-MFC was produced in 2001 (Yang and Chen, 2021), much work has been done to make S-MFCs a long-term power source for subsea sensing devices. But the two major issues stand still for S-MFC upscaling. The first is the stability of S-MFC operation in the dynamic ocean environment, and the second is that most subsea sensors need a higher power. At the same time, S-MFCs have an intrinsic low voltage output due to energy loss and bacterial metabolic loss (de Miranda, 2018). Aquatic species and marine currents might leach oxygen into the soil through bioturbation, disrupting the anaerobic anode environment (Rabaey et al., 2010). Therefore, many anodes can be coupled to a single cathode to strengthen the stability of the anodic compartment and ensure that, if one anode fails, the others can still transmit electrons to the cathode (Karra et al., 2014). Power management systems and a charge pump/DC-DC converter are additional tools that may be used to store energy and enhance voltage, respectively. Consequently, multiple anodes/cathodes coupled with PMS can reduce the malfunction and enhance the robustness of the S-MFCs.

2.2. Plant-microbial fuel cells

Similar to S-MFC, P-MFC is a bio-electrochemical system that was introduced with the idea of generating electricity by implanting the anode electrode of MFC in the rhizospheric zone of living plants (Strik et al., 2008). The roots of the plants tend to liberate root exudates, the secondary metabolites produced in plants, which act as a source of substrate (electron donor) for anodic bacteria. The cathode electrode of MFC is exposed to the atmospheric oxygen (electron acceptor) at the air-water interface above the soil. Thus, by using the metabolic activities of the microbial population that lives in the rhizosphere region, P-MFCs convert the root exudates and rhizo-deposits into bioelectricity (Shaikh et al., 2021). P-MFCs have made solar energy conversion to bioelectricity production potentially feasible, which sparked the creation of varying combinations and hybrid P-MFC systems. Considering the above facts, P-MFC can be used indoors, on green roofs, and in gardens, P-MFCs have many promising future applications.

2.2.1. Designs and operational configurations

As aforesaid, P-MFC utilizes living plants, microbes and conductive electrodes for the direct conversion of photosynthetically fixed solar energy in

the form of biochemical compounds to bioelectricity (Strik et al., 2008). The basic prototype of P-MFC consists plants along with anode and cathode electrodes in its anaerobic rhizospheric zone and aerobic air-water interface, respectively (Chiranjeevi et al., 2018) as depicted in Fig. 3b. Primarily, two common designs of P-MFC have been reported to enhance the performance of the system: i) single chamber, with no separating membrane, and ii) dual chamber, divided by a separating membrane which prohibits the mixing of electrolytes and cathodic oxygen diffusion to anodic chamber (Helder et al., 2010; Strik et al., 2008). Nowadays, several other types of P-MFC configuration have also been designed to increase the system's efficiency. Chiranjeevi et al. (2018) reported use of two different designs of P-MFCs i.e., flat-plate model and tubular model. In flat-plate P-MFC, a vertical cation exchange membrane exists between the anode and cathode layer (Chiranjeevi et al., 2018). The vertical placement of the membrane in flat-plate P-MFC favours lower internal resistance, which simultaneously enhances the power and current output of the system (Helder et al., 2012a). On the other hand, several studies have reported use of tubular P-MFC consisting of a tubular anode having membrane at the bottom and the cathode is present below the anode (Strik et al., 2008; Sudirjo et al., 2019b). To enhance the bioelectricity generation capacity of such tubular P-MFCs, Wetser et al. (2015a) developed an integrated tubular P-MFC having a dual cathode and single anodic compartment. Moreover, it is observed that Flat-plate P-MFCs outperforms tubular P-MFCs as it has lower internal resistance (Helder et al., 2012a). Another design aspect of P-MFC includes floating planted MFC (floating P-MFC) which serves as a favourable energy recovery source from different water bodies such as rivers, seas, etc. (Schievano et al., 2017). In floating P-MFC, an electrically insulated medium exists between the anode and cathode compartment. The cathode was placed at the bottom to allow exposure to freshwater. In contrast, the anode was placed just above the cathode within a semi-enclosed system to maintain the anoxic/anaerobic environment (Apollon et al., 2021; Schievano et al., 2017). Various studies have also reported the use of another P-MFC configuration, i.e., rooftop P-MFCs where different types of P-MFCs are placed at natural rooftop conditions for bioelectricity generation (Tapia et al., 2017, 2018; Helder et al., 2013a). Srivastava et al. (2018a) also investigated a new type of techno-economic dual chamber P-MFC configuration with paddy plant as fuel substrate in anodic chamber and Pt coated carbon cloth as associated cathode in a blue-green algae chamber for passive aeration and enhanced current generation. Enhancement of bioelectricity generation not only depends on the type of P-MFCs used but also on the type of electrode material used for its development. P-MFCs generally incorporate two most common material for anode and cathode electrodes, i.e., carbon and graphite. Studies have reported the use of carbon fiber, carbon felt, glassy carbon, carbon mesh, granular activated carbon, carbon brush, carbon cloth, graphite rod, graphite granules, graphite sheet, graphite disk, graphite grain and graphite felt (Chicas et al., 2018). Guan et al. (2019) reported use of carbon felt in single-chambered P-MFC for remediating hexavalent chromium-contaminated soils. Use of similar electrode material, i.e., graphite felt interwoven with a carbon rod, was also used as anode and cathode material in single-chambered P-MFC (Arends et al., 2014). Gilani et al. (2016) reported use of nickel as cathode electrode material in single-chambered P-MFC. Arulmani et al. (2021) investigated the bioenergy generation capacity of dual-chambered P-MFC with graphite rod and carbon cloth as anode and cathode electrode material, respectively. Also, Helder et al. (2012a) investigated the power generation efficiency of flat-plate P-MFC using graphite felt as anode and cathode material. The use of granular activated carbon and carbon felt as anode and cathode material has also been reported for energy generation from roof-top P-MFC systems (Helder et al., 2013a). In addition, several studies have reported the use of P-MFC with modifications in design configuration, such as using anode material as carbon fiber brush (Sarma and Mohanty, 2018), manganese-based carbon air cathode (Md Khudzari et al., 2019), algae-based Pt coated carbon cloth cathode (Srivastava et al., 2018a) etc. Apart from the design of P-MFC and electrode material, plants used in P-MFCs also play a vital role in the enhancement of system efficiency. Helder et al. (2010) compared three flat-plate P-MFCs

planted with *Spartina anglica*, *Arundinella anomala* and *Arundo donax*, where, P-MFC planted with *Spartina anglica* outperformed the other two P-MFC in terms of power output capacity. Similarly, studies have also been reported for use of various types of plant species in different P-MFC configuration such as *Oriza sativa* L. (Sudirjo et al., 2019a), *Amaranthus viridis*, *Triticum aestivum* (Arulmani et al., 2021), *Rotala rotundifolia*, *Typha angustifolia*, *Pennisetum alopecuroides* (Guan and Yu, 2021), *Sporobolus arabicus* and *Cynodon dactylon* (Gilani et al., 2016), *Wachendorfia thyrsoflora* and *Cyperus papyrus nanus* (Gulamhussein and Randall, 2020), *Lolium perenne* (Habibul et al., 2016), *Pachira macrocarpa* and *Populus alba* (Lu et al., 2020), *Puccinellia distans* (Md Khudzari et al., 2018), *Dypsis lutescens* (Osorio-De-La-Rosa et al., 2021), *Sedum kamschaticum*, *Sedum rupestre*, *Sedum album*, *Sedum hybridum*, *Sedum spurium*, *Sedum sexangulare* and *Sedum reflexum* (Tapia et al., 2017), *Vetiveria zizanioides* (Regmi et al., 2018), *Brassica juncea*, *Trigonella foenumgraecum* and *Canna Stuttgart* (Sophia and Sreeja, 2017), *Epipremnum aureum* and *Dracaena braunii* (Sarma and Mohanty, 2018), *Aglaonema commutatum* (Zhao et al., 2019), *Glyceria maxima* (Timmers et al., 2013a). To maintain the growth and sustenance of those wide groups of plants used in P-MFC, different types of liquid medium were provided. Studies have reported use of rainwater in roof-top P-MFC (Helder et al., 2013a, 2013b), a combination of tap water and half-strength Hoagland solution (Arends et al., 2014), tap water (Goto et al., 2015; Guan et al., 2019), deionised water (Tongphanpharn et al., 2021), a combination of sodium acetate and phosphate buffer (Arulmani et al., 2021), a mixture of macro and micro nutrients (Gilani et al., 2016), ferric cyanide and phosphate buffer solution (Timmers et al., 2013a, 2013b), the combination of half-strength Hoagland's solution and phosphate buffer (Timmers et al., 2012b), nitrate-less ammonium rich plant growth medium (Wetser et al., 2015a), nitrate-less sulphate-less ammonium bicarbonate rich solution, nitrate-less ammonium bicarbonate solution (Helder et al., 2012b) and synthetic wastewater (Regmi et al., 2018).

2.2.2. Primary function as a bioelectricity generation unit

P-MFC has shown tremendous potential as green electricity-generating sustainable technology. Compared to S-MFC it could harvest 18 folds higher bioelectricity from its host environment (Kabutey et al., 2019b). The bioelectricity generation is guided by microbial oxidation in the rhizospheric region of P-MFC for effective production of electricity (De Schampheleire et al., 2008; Moqsud et al., 2015). The electrons produced in the rhizospheric zone are transferred to the anode and then to the cathode electrode. For enhanced power output, various types of anode and cathode materials with high electrical conductivity and low cost are used, facilitating efficient electron transfer and power production. Different electrode material used in P-MFC has different power production capacity. Timmers et al. (2013b) investigated the potential of two types of anode material: graphite felt and graphite granules, for electricity generation in P-MFC. The greater mass and surface area of graphite felt produced 15 times and 69 times higher mass and volume-based power densities than graphite granules, respectively. Whereas, Sudirjo et al. (2019a) compared the efficiency of four P-MFCs with four different types of substrates, i.e., 100 % marine sediments (MS 100), 33 % activated carbon + 67 % marine sediment (AC 33), 67 % activated carbon + 33 % marine sediment (AC 67) and 100 % activated carbon (AC 100). They observed AC 33 outperformed the other three P-MFCs in terms of power generation with an average highest power density of 1.04 mW m^{-2} followed by MS 100 (0.37 mW m^{-2}), AC 67 (0.12 mW m^{-2}) and lastly, AC 100 (0.00 mW m^{-2}). Studies have also reported enhanced power output in P-MFCs with similar substrate as anodic and cathodic material. For example, anode and cathode compartments made up of graphite felt and planted with *Spartina anglica* having dual (Wetser et al., 2015a) and single cathode (Wetser et al., 2015b) produces a power output of 679 mW m^{-2} and 0.34 W m^{-2} , respectively. Also, the difference in bioelectricity generation is observed with different plant species used in P-MFCs. Variation in the type and abundance of rhizodeposits from different plants causes fluctuations in anodic potential (Timmers et al., 2010). P-MFC planted with

Aglaonema commutatum having graphite felt as anode and cathode material produced voltage of 377 mV (Zhao et al., 2019). Whereas, a decrease in voltage generation is observed (-165 mV) when rice plant is used in P-MFC with graphite felt as electrode material (Takanezawa et al., 2010). Tongphanpharn et al. (2021) used interwoven circular carbon felt and titanium wire as electrode material where P-MFCs having *Typha orientalis* and *Oryza rufipogon* produced maximum voltage of 137.12 mV and 350 mV, respectively. Srivastava et al. (2018a) used rice paddy-planted microbial fuel cell assisted with a blue-green algal cathode, and produced the maximum power density and current density of 29.78 mW m^{-3} and 610 mA m^{-3} with a maximum voltage of 399 mV during light phase. Similar plants with similar anodic material produce differences in power output in different studies. P-MFC having graphite granules as anode material and planted with *Glyceria maxima* produces a power output of 12 mW m^{-2} in tubular P-MFC (Timmers et al., 2013b); instead, under a controlled potential similar setup produced a maximum power output of 0.12 W m^{-2} (Timmers et al., 2012b). Studies also report, *Glyceria maxima*, in addition to biocathode, produces an average power output of $0.0362 \pm 0.12 \text{ W m}^{-2}$ (Timmers et al., 2013a). Whereas, similar plants with different anode materials also cause significant changes in the power output of the systems. P-MFC with *Spartina anglica* and graphite felt as anode material produces a power output of 54 mW m^{-2} (Wetser et al., 2015a) and 100 mW m^{-2} (Timmers et al., 2010) respectively. P-MFCs, when used for bioelectricity production and pollutant removal, favour the enhancement of power output to about $242 \pm 10.5 \text{ mW m}^{-2}$ (Regmi et al., 2018). It is also observed that the synergistic interaction of plants and glucose helps in reducing the charge-transfer resistance which simultaneously enhances the voltage generation within the system (Zhao et al., 2019). Moreover, the power generated from P-MFCs is monitored and stored using several data acquisition and energy harvesting technologies. Some of the data acquisition technologies wired to P-MFCs for continuous monitoring are LoRa technology (Sudirjo et al., 2019b), FRAM technology (Rossi et al., 2017), LPWAN (Osorio-De-La-Rosa et al., 2021), Internet-of-Things (IoT)-wireless sensor networks (WSNs) (de La Rosa et al., 2019), wireless sensor node (Brunelli et al., 2016). The current generation in P-MFC is affected by the two opposing processes occurring in the rhizosphere i.e., stimulated by the release of root exudates and suppressed by the leakage of oxygen. A microscopic model was developed to characterize the two opposing processes within the rhizosphere-anode interface of the P-MFC, based on exudation, oxygen loss, biological oxidation, and biological current generation. The model was successfully validated by the experimental results which showed that the photosynthesis rate had no direct relation with current generation in P-MFC and to optimize its performance, the plant with high biomass production and low oxygen leakage should be selected (Timmers et al., 2012a). An analytic model was proposed to show the complete process of electricity production from the released organic compound in P-MFC with *Pandanus amaryllifolius* plant species. The electrical power output showed high similarity pattern with the bacterial growth curve model and the coulombic efficiency of 95.32 % was achieved (Cheng et al., 2020).

2.2.3. Secondary functions

Various studies have reported using P-MFCs not only for bioelectricity generation but also for remediation of broad categories of pollutants from different types of wastewaters (Regmi et al., 2018) and contamination sites (Guan et al., 2019). Regmi et al. (2018) reported removal of about 99 % COD in P-MFC planted with *Vetiveria zizanioides*. In addition to organic matter removal, plants also help in treating several inorganic pollutants, such as heavy metals, PAH, etc., with simultaneous electricity generation. Pamintuan et al. (2018) reported the use of P-MFC technology for phytoremediation of Ni^{2+} using *Eichhornia crassipes*. The use of P-MFC planted with *Lolium perenne* was extended for the removal of Cr(VI), where, plants majorly removed Cr(VI) through the release of root exudates in addition to bioelectrochemical reduction. Electrodes present in the system also effectively adsorbed the Cr(III) formed from the reduction of Cr(VI) (Habibul et al., 2016). P-MFCs planted with *Pennisetum alopecuroides* is able to remove Cr(VI) and total Cr as much as 99 % and 27 %, respectively.

respectively (Guan et al., 2019). Synergistic plant-surfactant interaction in P-MFC also helps in the effective treatment of petroleum present in the soil. P-MFC planted with *Aglaonema commutatum* could degrade PAH and crude oil to a minimum of 41 % present in soil (Zhao et al., 2019). These studies indicate that P-MFCs can not only be extended for heavy metal and COD removal from wastewater or soil, but can also be further applied for treating various other pollutants such as dye, pesticides, etc., from wastewater and soil. Till now very limited studies have been reported regarding the secondary application of P-MFC, i.e., treatment of contaminated soil and wastewater. Future research might help to get a deep insight into various applications of P-MFC in different fields.

2.2.4. Challenges and implications

The development of P-MFC started with the aim of green and sustainable electricity generation using living plants. For enhancing the power performance of the system, various design and configurations of P-MFC have been developed. Also, various electrode material, plant type, substrate material, and liquid medium modifications are examined to improve the potential of P-MFCs. Further, this idea of bioelectricity generation was combined with the remediation process, which helped in green energy production, along with the treatment of soil/water contaminated with heavy metals, PAHs and other pollutants. Thus, the multipurpose approach of P-MFC diversified its applications, including bioelectricity generation using different plants, remediating heavy metal-contaminated soil, treating wastewater, biosensing plant health, and power generation. However, while considering the consistent functioning of P-MFCs for large-scale operations, various challenges were observed relating to their performance stability. Sustenance of plants and deterioration of electrode material is a major challenge in the long term. Since plants' activity and metabolism regulate the microbial activity, enhancing power output and performance stability in P-MFCs. Therefore, long-lasting perennial plants with a developed root systems and requiring minimum maintenance are considered favourable for P-MFC. Selection of suitable plant and optimum operating conditions (physicochemical parameters and many more) is essential for the properly managing P-MFCs, as it helps in the development of proper microbial consortium. The microbes present in the rhizospheric zone helps in the effective transfer of an electron to electrode for the generation of bioelectricity. Subsequently, the maintenance of electrode and its material properties in P-MFC is also important. One among the challenges in P-MFCs is developing a technology having higher power output, requires the least maintenance, and has additional benefits. Besides, P-MFCs are developed focussing on bioelectricity generation with additional pollutant removal property from different types of soils; however, very few studies have been reported where P-MFCs helps in the removal of various pollutants in addition to efficient bioelectricity generation. There is large scope of several modifications in P-MFCs, such as use of efficient electrodes materials, search of robust plants, cost reduction in anode and cathode material, and use of advanced energy-harvesting systems, etc. which will not only effectively treat various types of pollutants from soil or other planting media but will also help in producing enhanced power output from the P-MFCs.

2.3. Constructed wetland integrated with microbial fuel cell

CW-MFC is the most recent variant of MFC-integrated technology and was first introduced in in 2010 (Yadav, 2010), followed by the first detailed study in 2012 (Yadav et al., 2012). Unlike P-MFC and S-MFC, where plant's root and degradable organic portion present in sediments are used as fuel substrates to generate bioelectricity, MFC is incorporated into CWs to improve the performance of the CWs which is a full-scale well-established proven wastewater treatment technology. In the CW-MFC, the incorporation of MFC into CWs is done to accelerate the treatment efficiency of CWs. Component wise, classical CWs are the assemblage of plants, microbes, packing matrices, and wastewater in a shallow basin. All its components interact with each other to carry out physio-chemical and biological processes and remediate the wastewater. It is a low-cost, energy and chemical neutral sustainable technology, however, slowness (it leads to large

land requirement) and sometimes dissatisfactory removal of organics and nutrients limits its application (Gupta et al., 2020c). The slowness in the CW performance is due to the insufficient availability of suitable electron acceptors, such as oxygen, in a large portion of the treatment bed of CWs which discourages the efficient oxidation of pollutants. This is due to the non-diffusion of atmospheric air deep into the CW bed, stratifying it into bottom anaerobic (electron acceptor deficit) and top aerobic (electron donor deficit) regions. With the continuous flow of wastewater through the treatment bed, the anaerobic situation dominates it largely, and only the near-surface region, which is exposed to the atmosphere and contains the rhizosphere of plants, remains aerobic. As a result, an increasing redox gradient ($-E_h$ to $+E_h$) is developed from its bottom to top. This allows the incorporation of MFC components in CW i.e., the anode in the anaerobic region and cathode in the aerobic region and unites the segregated situations (Fig. 3c) through conductive material. These conductive materials work as electron acceptor in anaerobic zone and donor in aerobic zone and catalyzes the microbial redox reactions for higher treatment kinetic. Thus, the synergy of the two technologies i.e., MFC and CWs, primarily aims at enhancing the treatment efficiency of the existing CW system with additional benefits such as resource recovery including bioelectricity generation.

The recent review on MFC merger technologies disclosed that several researchers considered P-MFC and CW-MFC analogous to each other due to the presence of plants (Guadarrama-Pérez et al., 2019). However, detailed studies have clearly stated that the said technologies are considerably different, in their structure and functioning and technology readiness level. As discussed earlier, the P-MFC technology primarily focusses on bioelectricity generation from the photosynthetically fixed carbon for which the anode of MFC is placed in the vicinity of the rhizosphere (to utilize photosynthetically fixed carbon or liberated root exudates) and the cathode is placed in the air soil interface away from roots, along with additional benefit of soil remediation. In P-MFC fuel substrate is plant's roots and the major goal to be achieved is bioelectricity generation. On the contrary, CW-MFC continues the legacy of wastewater treatment at enhanced rate for which the anode electrode is buried deep in the treatment bed where organics (abundantly present in wastewater) and inorganic such as ammonium are anaerobically oxidized and cathode is placed near the upper most zone for completing reduction reaction using rhizospheric oxygen and oxygen diffused from the atmosphere.

2.3.1. Designs and operational configurations

CW-MFC is the integration of MFC into CWs; thus, its basic architect depends on the type of CW utilized for MFC integration. Based on the broad classification of CWs, CW-MFCs are primarily designed as free water surface CW-MFC (FWS-CW-MFC) and subsurface flow CW-MFC (SSF-CW-MFC) (Srivastava et al., 2018b). Considering the socio-environmental benefits of SSF-CWs over FWS-CWs, SSF-CW-MFCs have been largely explored. The effective functioning of CW-MFC is greatly governed on biological, physico-chemical, electrical, and wastewater parameters such as chemical oxygen demand (COD) & dissolved oxygen (DO) concentration in the anode and cathode regimes, substrate conversion rate, anodic and cathodic overpotential, internal resistance, pH and temperature, electrode material type, electrode surface area, inter-electrode distance etc. (Gupta et al., 2021a). Thus, considering the influential factors responsible for enhancing the treatment and electrical performance of CW-MFC, several designs and configurations have been proposed and studied. Initial studies have investigated the effect of MFC integration into horizontal SSF CWs with the objective of enhanced organics degradation. In contrast, some others have studied MFC integration in vertical SSF CWs for enhanced nitrogen removal (Doherty et al., 2015a; Villaseñor et al., 2013). Further, with the understanding of processes and pollutant transformation mechanisms happening in CW-MFCs, upward vertical flow (UVF) (Teoh et al., 2020) and downward vertical flow (DVF) (J. Wang et al., 2017a), simultaneous up-down (Doherty et al., 2015a) and tidal flow (Saeed et al., 2022a; Saeed and Miah, 2021) configurations were researched targeting specific pollutants removal. The studies revealed that UVF CW-MFCs have been the most

popular among them. It is so because configurationally, the anode electrode is buried deep down at the bottom, and the cathode electrode is placed towards the upper surface; and operationally, wastewater is fed to the bottom i.e., anodic region where it is anaerobically oxidized ($-E_h$) and flows towards the cathodic region for accomplishing reduction reactions ($+E_h$). As a result, a maximum redox gradient is developed between the electrodes, achieving higher treatment performance and electrical efficiency (Gupta et al., 2021a). However, the large inter-electrode distance challenged the electrical performance. CW-MFCs are generally membrane-less which is why large inter-electrode distance is kept maintaining the redox gradient between two electrodes. To overcome this cheaper membrane alternatives are employed such as the non-conductive gravel layer (Srivastava et al., 2015), glass wool (L. Xu et al., 2018a), polyethylene liners (Tamta et al., 2020), ceramic/earthen membranes (Khuman et al., 2020; Saket et al., 2022) etc. Further, granular anode and cathodes were utilized along with charge collectors to enhance the treatment and electron capture efficiency and reduce the inter-electrode distancing (Fang et al., 2013; Oon et al., 2015). To increase electrical output, multiple anode assembly was investigated for harvesting the maximum possible electrons at the anode (Tang et al., 2019), and multiple cathode assembly was also used for enhancing the limiting cathodic reduction reactions (L. Xu et al., 2018b). This also helped in improving nitrogen removal by promoting simultaneous nitrification and denitrification (L. Xu et al., 2018b). Several other designs, such as stacked (Tamta et al., 2020), multistage (Gupta et al., 2021b), and hybrid (Srivastava et al., 2020a) CW-MFCs, were explored targeting enhanced nitrogen and organics removal. Stacked configuration was an upscaling approach where small CW-MFC units were hydraulically connected to represent a large system to enhance electrical output and treatment performance, and reduce land footprint. Similarly, short-circuited CW-MFC was designed as single electrode, with no electrical connection for electricity harvest, to maximize treatment efficiency with the idea of commercializing CW-MFC (named as METland) (Aguirre-Sierra et al., 2016). An interesting design also emerged where instead of harvesting electricity (CW-MFC) some additional low voltage was supplied (CW-MEC) to achieve even faster pollutant degradation (COD, ammonium, phosphate and trace metals) kinetics and reduced sludge generation. This configuration is a revolutionary solution to the substrate clogging problem as well as higher treatment rate and efficiency in CWs (Srivastava et al., 2021a).

The components of CW-MFC are very crucial in determining its performance. Therefore, plant species, substrate, and electrodes (type, material, and position) used in CW-MFCs have been rigorously investigated. Plant/macrophytes are primarily responsible for supplementing oxygen i.e., terminal electron acceptor, therefore, most of the studies have positioned it in cathodic region (Gupta et al., 2021a). Also, the roots exudates they liberated are utilized to flourish microbial consortia and heterotrophic denitrification or develop a biocathode. Different macrophytes explored include *Typha orientalis*, *Scirpus validus*, *Iris pseudacorus*, *Lythrum salicaria*, *Phragmites australis*, *Canna indica*, *Acorus calamus*, and *Ipomoea aquatica* etc. (Liu et al., 2020; J. Wang et al., 2017b; Yang et al., 2021). Recently, Saeed et al. (2022b) investigated the effect of saturation in filter media of microbial fuel cell integrated deep bed-partially saturated HF wetland and revealed it performed better for pollutant removal and power production than commonly employed shallow bed-partially saturated system. Further, the different substrates used in CW-MFCs have been explored for enhancing CW-MFC efficiency. The surface area, porosity, mechanical strength and biocompatibility are crucial factors for their selection as catalytic microbial biofilm develops and interacts with their surface during the course of operation. The commonly used substrates are biochar, graphite granules, zeolite, bio-ceramic, ceramsite, stone dust, concrete material, industrial waste etc. (Mittal et al., 2022; Mu et al., 2020, 2021; Sonu et al., 2021; Y. Wang et al., 2017; Zhao et al., 2013; Saeed et al., 2022c, 2022d). Similarly, different studies have investigated different electrode materials used in CW-MFCs depending on its biocompatibility, corrosion resistance, specific surface area, conductivity, electron transfer capacity, chemical stability, and biotoxicity in the system (Gupta et al., 2021a; Huang et al., 2021; Srivastava et al., 2017). However, carbon-based electrodes have been

preferred due to their good biocompatibility, electrical conductivity and low-cost (Gupta et al., 2021a), such as carbon fiber, graphite felt, carbon cloth, carbon brushes, activated carbon, graphite rod and modified carbons (like Pt. coated carbon cloth etc.) (Gupta et al., 2021a; Oon et al., 2015; Tang et al., 2019). These studies found that carbon cloth and carbon felt as electrodes material are more suitable for electroactive microorganisms, however, these are associated with problems like mechanical strength, high cost, etc. The high surface area of these electrode increases the power output, but in return internal resistance of CW-MFC also increases. Thus, parameter like reactor volume to effective area of electrode should be considered during CW-MFC design.

2.3.2. Primary function as enhanced wastewater treatment

As illustrated in previous sections, CWs technology hosts the functional components of MFC for the acceleration of slow wastewater treatment reactions such as anaerobic oxidation of organics and ammonium present in wastewater (Yadav et al., 2012). During the intensification of the treatment process, the implanted external electrical circuit allows the harvesting of the microbially generated electricity as an opportunistic additional benefit. So, the primary function of CW-MFC remains the intensification of the treatment process. Generally, wastewater contains degradable pollutants such as organic matter and nitrogenous pollutants, non-degradable such as heavy metals, phosphorus containing compounds, and recalcitrant pollutants with among others (Doherty et al., 2015b; Mu et al., 2020; F. Xu et al., 2018a). These pollutants are simple to complex in their structural form (Wen et al., 2021) and require different redox conditions (anaerobic/anoxic/oxic) for their transformation. The availability and efficiency of electron donors or acceptors greatly influence the rate and efficiency of the said redox reactions. Electron conductive electrodes of the CW-MFCs have direct positive influence on microbial redox reactions. Studies have shown that CW-MFC achieved 27-49 % higher COD removal than conventional CW (Srivastava et al., 2015). Similarly, higher nitrification and denitrification rates (Xu et al., 2016) and 12 % increased nitrogen removal was revealed with CW-MFC (Ebrahimi et al., 2021). Srivastava et al. (2020a) demonstrated a new process of electrode dependent anaerobic ammonium oxidation in CW-MFC and named it as electroanammox. Srivastava et al. (2021b) demonstrated the positive synergistic influence of sulphate and conductive material present in an electroactive wetlands for ammonium and organics removal. Other studies reported that the closed-circuit system where the role of such conductive material is demonstrated, continued to perform 37.7 % better than open circuit system (Srivastava et al., 2020b; Villaseñor et al., 2013). A similar increase in organic removal rate was observed with METlands which is one version of CW-MFCs (Aguirre-Sierra et al., 2016). METland is a specially designed CW-MFC system that maximizes wastewater treatment by utilizing all the generated metabolic electrons without any electron harvested for other applications. Also, the sequencing of different microenvironments in the form of multistage CW-MFCs or integration of different treatment proficiencies is beneficial. With these insights, a novel tiered CW-MFC was demonstrated to achieve improved COD removal from 83.2 % to 88.7 % compared single-stage CW-MFC (Xu et al., 2017a). Multiple anodes connected in parallel connection with a single cathode of CW-MFC across separate resistors showed the best wastewater treatment efficiency of 91.7 % of COD removal and 97.3 % of ammonia-N compared to other cathode working conditions of different connections, aeration, and local effluent recirculation (Tang et al., 2019). A study by L. Xu et al. (2018b) demonstrated the effect of multiple cathodes against a single anode and revealed that enhanced simultaneous nitrification & denitrification process was triggered in three bio-cathode systems compared to control CW-MFC due to the influence of the bioelectrical derived interaction between power production and systematic nitrification and denitrification rates. As a result, nitrification rate increased from $98.59 \pm 4.53 \text{ mg m}^{-2} \text{ day}^{-1}$ to $179.11 \pm 7.65 \text{ mg m}^{-2} \text{ day}^{-1}$ and denitrification rate increased from $89.64 \pm 4.57 \text{ mg m}^{-2} \text{ day}^{-1}$ to $163.55 \pm 11.88 \text{ mg m}^{-2} \text{ day}^{-1}$. Pyrrhotite is a promising electron donor for autotrophic denitrification in CW-MFC. It has been demonstrated that pyrrhotite as substrate in CW-MFC achieved

enhanced nitrogen removal in carbon deficit situation (Chu et al., 2022; Ge et al., 2020). The earthworm integration in CW-MFC could remove 96 % BOD, 99 % COD, 89 % N, 99 % P, 98 % solids and 97 % coliform from the drained wastewater (produced because of sludge stabilization) (Saeed et al., 2022e). A novel stacked CW-MFC with series connection treating municipal wastewater showed up to 98.5 %, 90.4 %, and 86.9 % COD, ammonium, and nitrate removal, respectively (Tamta et al., 2020). Considering the upscaling and efficient treatment of CW-MFC, low cost earthen and ceramic membranes were explored to treat hazardous wastewaters. The findings from the studies revealed 93 % COD along with 72.2 % Cr^{6+} removal (Mu et al., 2021), complete mineralization with 94.04 ± 2.87 % COD and 94.22 ± 1.33 % methyl orange removal (Mittal et al., 2022), and 95.80 ± 0.71 % COD removal along with 89.99 ± 0.04 % decolorization of high molecular weight diazo Congo red dye (Saket et al., 2022). A novel three-stage algal assisted CW-MFCs was explored with the advantages of earthen separator, algae as a passive aerator, and sand filter, and the findings revealed 96.37 ± 2.6 % COD, 85.14 ± 10.73 % NH_4^+ , 69.03 ± 10.14 % PO_4^{3-} and 68.41 ± 7.63 % NO_3^- removal (Gupta et al., 2021b). The other studies illustrated the impact of different substrates and electrodes on the performance of CW-MFC. Xu et al. (2016) presented that the modification of dewatered alum sludge with 10 % powdered activated carbon in the anode increased the COD and phosphate removal up to 80 % and 90 %, respectively. Also, ammonium and TN removal increased by 11.3 % and 12.2 %, respectively (Xu et al., 2016). Zhong et al. (2020) reported the removal of 93.8 % of NH_4^+ -N and 99.6 % of orthophosphate using ceramsite as substrate material. Recently, Mittal et al. (2023b) investigated the efficiency of two types of biochar processed by plasma (PB) and drum kiln (KB), and revealed COD removal of 72.32 ± 2.98 % and 59.91 ± 3.21 % in KB and PB-based CW-MFCs, respectively. Removal of COD and Cr^{6+} was reported by Mu et al. (2021) using different substrates and revealing 93 % COD removal by all systems but 99.0 %, 95.5 %, 89.7 %, and 72.2 % Cr^{6+} removal by volcanic rock, zeolite, calcite, and bio-ceramic, respectively. The presence of graphite in CW-MFC recorded almost complete removal of Cr^{6+} from synthetic wastewater, which was 42.9 % higher compared to the normal gravel-based system (Srivastava et al., 2020c). Recently, Ji et al. (2023) demonstrated the excellent removal efficiency of per- and polyfluoroalkyl substances (PFASs), a synthetic persistent pollutant (>96 %) in CW-MFC.

Several studies have reported on additional artificial aeration in cathode section (Oon et al., 2015; Srivastava et al., 2017; Tang et al., 2019; S. Wu et al., 2017) and effluent recirculation (Xu et al., 2017b) to achieve the desired higher oxidation. Another study explored the positioning of the charge dispenser of cathode in CW-MFC and concluded that a charge dispenser of cathode placed completely exposed to air than saturated with water could perform better (Yang et al., 2019). Recently, Mittal et al. (2023a) revealed high rate of evapotranspiration in tropical regions can also substantially increase oxygen saturation at cathode, ultimately resulting in considerable enhancement in treatment performance and high CE generation of 11.95% in upscaled CW-MFC planted with *Canna indica*. A study to understand the interrelation between macrophytes roots and cathode in CW-MFC is done, in this study, the macrophyte *Cyperus atrnifolius*, was positioned at three different locations with respect to the cathode. The study revealed that the placement of plant roots directly over the air cathode surface developed a “plant root-assisted bio- & air-cathode” which enhanced the CW-MFC performance (Ji et al., 2022). The *Typha angustifolia* vegetated CW-MFC removed 88 % COD, 97 % TP and ammonium (Saz et al., 2018). Wu et al. (2015) also reported >96 % TP removal using planted CW-MFC. The degradation and removal of sulphamethoxazole (SMX) were testified in CW and CW-MFC, which disclosed that the latter performed 11.05 % higher for SMX removal (Dai et al., 2021). Similarly, two polycyclic aromatic hydrocarbons namely phenanthrene and anthracene, that pose a great threat to the aquatic environment were treated in CW-MFC, results show that 88.5 % to 96.4 % concentration of initial PAHs was reduced; this study also showed a positive role of plants planted in the system for the removal of the studied pollutants (J. Wang et al., 2019). Di et al. (2020) studied the role of redial oxygen

release in CW-MFC for nitrobenzene degradation. They found the highest tolerance capacity with the plant *Scirpus validus* compared to the *Typha orientalis* and the *Iris pseudacorus* at an initial concentration of 20–200 mg L^{-1} nitrobenzene. Also, complete decolorization of acid orange 7 (AO7) was achieved with 10–150 mg L^{-1} of AO7 concentration in CW-MFC (Zhao et al., 2018). Considering the benefits of aeration and anaerobic electroactive process for ammonium removal, Srivastava et al. (2021c) demonstrated a self-powered CW-MFC assisted with PMS. It was used for the harvesting and storing of low power generated in CW-MFC that was further utilized for its artificial aeration resulting in enhanced ammonium removal by 10–12 %. Thus, CW-MFCs have progressed towards the practical level implementation in the field and are competitively performing much better than CWs.

2.3.3. Secondary functions

The emergence of CW-MFC is a timely and needful innovation in the field of constructed wetlands as well as microbial fuel cells. Since biological wastewater treatment can be correlated with the electron transfer/exchange in microbial oxidation and reduction reactions, in the CW-MFC, electrode captures the electrons generated during the pollutant oxidation and transfer through electric wire thus, it can generate the electricity. The first CW-MFC study reported a maximum power density of 15.73 mW m^{-2} and a maximum current density of 69.75 mA m^{-2} achieved during the treatment of dye containing wastewater (Yadav et al., 2012). Varying organic loading rates were demonstrated to enhance the power output. However, Liu et al. (2014) achieved higher power density (44.6 mW m^{-2}) with influent COD 250 mg L^{-1} compared to 500 mg L^{-1} (33.7 mW m^{-2}) and 1000 mg L^{-1} (21.33 mW m^{-2}). The different types of bio-cathodes investigated for power output efficiency i.e., granular activated carbon (GAC), stainless steel mesh (SSM) and carbon cloth (CC), performed differently, while GAC-SSM electrode produced the highest maximum power density of 55.05 mW m^{-2} (Liu et al., 2014). Configurationally, inter-electrode distance (5 cm, 10 cm, 15 cm) was analysed for improving electrical output and 10 cm was reported as optimum electrode spacing that produced highest power density of 441.4 mW m^{-3} compared to 422.7 mW m^{-3} (5 cm) and 272.8 mW m^{-3} (15 cm) (Mu et al., 2020). Similarly, multi-electrode assembly as anode/cathode was found beneficial for improving energy harvest. The power density of 7.99 mW m^{-2} was reported with multi-anode CW-MFC (Tang et al., 2019), whereas multiple-cathode CW-MFC achieved power density of 26.16 mW m^{-2} (L. Xu et al., 2018b). The intermixing of anolyte and catholyte, and oxygen diffusion into the anode, are detrimental, whereas a balanced ionic gradient between anodic and cathodic chambers is favourable for electricity generation. Therefore, researchers have reported using various types of membranes and separators. Application of often utilized PEM in MFC is not feasible in CW-MFC due to larger volumes. Therefore, Gupta et al. (2021b) utilized earthen membrane in algal cathode CW-MFC and achieved a maximum power density of 33.14 mW m^{-3} while treating initial COD of $1505.61 \pm 681.54 \text{ mg L}^{-1}$. Similarly, an earthen membrane was employed in an artificially aerated cathode, which produces maximum power density of 235.94 mW m^{-3} and 148.29 mW m^{-3} while treating recalcitrant azo dyes (Mittal et al., 2022; Saket et al., 2022). The findings reveal the effectiveness of an earthen structure or separator in place of a commercial membrane to inhibit electrolyte mixing and oxygen diffusion. Xie et al. (2018) compared the membrane less CW-MFC and MFC dedicated for nitrobenzene treatment and observed a higher maximum power density of 1.53 mW m^{-2} in CW-MFC compared to 0.59 mW m^{-2} in MFC. Realizing oxygen reduction reaction at the cathode as a limiting factor for power output, the techno-economic approach of planting macrophytes in the cathodic region was utilized in several studies. The CW-MFCs operated with intermittent aeration and planted with *Canna indica* were reported to produce maximum power densities of 31.04 mW m^{-3} and 19.6 mW m^{-3} (Srivastava et al., 2017). Another finding revealed that CW-MFC planted with *Ipomoea aquatica* produced a maximum power density of 12.42 mW m^{-2} which was 142 % higher than unplanted CW-MFC (Liu et al., 2013). However, the employment of plants follows the diurnal

pattern for voltage output. Also, different plants perform differently (Saz et al., 2018).

Another realistic application of CW-MFC is biosensing (Gupta et al., 2021a). Several studies have testified it as an organic pollutant biosensor for real-time biosensing of water quality (Corbella et al., 2019; Lu et al., 2022; Wei et al., 2015; L. Xu et al., 2021; Xu et al., 2017b). Use of metallic electrodes has produced a steadier response than carbon-based electrodes in CW-MFC. Similarly, continuous flow systems have also produced better responses (L. Xu et al., 2021). However, several fluctuations persist in bio-electrical output with various CW-MFC configurations.

2.3.4. Challenges and implications

The CW-MFC successfully intensified the treatment efficiency of CW along with reduction in land footprint and addition electricity generation that further reduced the operational cost of CW treatment facility. Interestingly, the MFC integration also helped to reduce the amount of greenhouse gas generated from CW. However, electricity generation from oxidizable pollutants in wastewater using CW-MFC is yet challenging. Also, the corrosive nature of wastewater adversely affects the electrodes stability and performance in long term. The number of CW-MFC studies reporting on a large scale and long-term applications are still low, and much more research is required to make it as popular as CWs among end users. The first pilot-scale study on CW-MFC, named as METland, has shown its full potential as an intensified treatment technology with a smaller land footprint and minimal operational cost. However, the study did not focus on electricity generation. Several other studies have shown its energy harvesting potential using electrically networked stacked systems or power management systems. However, these have not yet shown up to a large scale. Similarly, applications such as biosensing tool face stability challenges and yet need to be explored with real wastewaters for futuristic applications. The CW-MFCs have shown delayed clogging phenomenon compared to CW, however, the long-term field studies are yet to come up and prove it. The plentiful literature on proof-of-concept and state of the art of CW-MFC are available. The future CW-MFC research should explore its role in emerging pollutants remediation, enhancement of bioelectricity and storage for use, development of biosensing techniques, and designing the field-scale model for the applications as well as full-scale long term treatment performance studies. Thus, large scale-controlled trials and long-term operation and monitoring of CW-MFCs along with holistic impact assessment are the next steps to be achieved in order to validate its commercial success.

3. Maturity and readiness level assessment for the field-scale application

To comprehend and differentiate the maturity and readiness of different technologies, technology readiness level (TRL) is a globally accepted and valuable parameter (Fruehauf et al., 2020). It is a multicriteria-based measurement system used to assess the maturity of any technology at different levels and confirm its readiness for real-world implementation. TRL has 9 different levels, out of which TRL1-3 pertains to proof-of-concept studies, basic and applied research at lab scale, TRL 4 & 5 regards to industrial research, TRL 6 refers to the demonstration of the technology in the relevant operational environment and is represented by large lab/semi-pilot scale studies, and TRLs 7-9 are classified as commercial development levels which includes pilot scale studies (Fruehauf et al., 2020; Roy et al., 2022). To achieve high TRL levels for the above-discussed wastewater treatment and electricity generating technologies, different benchmarks should be accomplished, which include scalability, longevity, high treatment efficiency, economic viability, and bioelectricity generation at pilot scale i.e., >1000 L volume (Roy et al., 2022; Tan et al., 2021). However, in today's era, green, clean, and sustainable aspects of technologies should also be emphasized to reduce environmental impacts. The continuous effort by the research community has helped to achieve variable TRLs for MFC and its inspired or integrated variants, S-MFC, P-MFC, and CW-MFC, which are discussed here.

Microbial fuel cell is some 100 years old technology that started from micro and milli-litres volumes in the lab and has covered the milestones

to scale up to hundreds of litres of volume i.e., <1 L to pilot scales i.e., up to 1000 L (as shown in Table 1). Wherein, single chamber MFC expansion was carried out till the volume capacity of 200 L and beyond this volume, stacking of MFC cells was adopted. This is because enlargement of individual MFC faced issue with declining power density ascribed to increasing volumetric ohmic resistance together with inactive reactor volume (Mahmoud et al., 2022). Nevertheless, some handful of research publications on pilot-scale microbial fuel cells have appeared so far, which signifies the difficulty in its upscaling. Until 2009, no research publication was reported on pilot scale MFC. Later, one of the large lab-scale MFCs was demonstrated by Logan (2010) group at Penn State University which could operate a small electric fan for around 1.5 years but eventually its functioning deteriorated due to cathode biofouling. Subsequently, the other two known attempts for piloting the MFC systems were brought by two different research groups. One of them was tested for brewery wastewater treatment at Foster's brewery in Yatala, Queensland (Australia), by the Advanced Water Management Centre at the University of Queensland, and second tested by University of Connecticut researchers and their collaborators (Fuss & O'Neill, and Hydroqual Inc.) at a site in the USA for treating wastewater containing COD 300-600 mg L⁻¹ (Jiang and Li, 2009b; Logan, 2010; Seelam et al., 2016). However, limited information was disclosed including electrical performance and long-term operation and failure. Several semi-pilot and pilot scale stacked MFC studies were reported displaying low power output, mainly due to voltage reversal and mass transport limitations (Jadhav et al., 2021b), as illustrated in Table 2. To avoid the impact of voltage reversal most stacked MFCs were equipped with several controlling systems for maintenance of artificial environment, ultimately increasing the complexity and cost of stacked MFCs operation (An et al., 2015; J. Li et al., 2017; Sugnaux et al., 2017). Thus, the feasibility and real-world applicability of the technology remained challenged in terms of cost benefit ratio.

Ieropoulos et al. (2016) reported the first study on the pee power urinal, a stacked modular MFC assisted with energy storage system, used for internal lightning demonstrated at University campus (8 modules, 288 MFCs, 200 L volume, >90 % COD removal achieved) and music festival (12 modules, 432 MFCs, 300 L volume, 30 % COD removal achieved). Blatter et al. (2021) report that 1000 L capacity stretched MFC produced power with the assistance of maximum power point tracking and 0.015 kWh m⁻³ of electricity was generated consistently with peak performance of up to 0.06 kWh m⁻³. The energy efficiency of MFC was 5.8-12.1 % which is the highest value reported so far with municipal wastewater, however, it was affected by voltage reversal. Further, Das and Ghangrekar (2019) tried the concept of integrating MFC into septic tank for its utilization as bioelectric toilet with 1500 L volume, demonstrated to treat human waste at student campus for three years and it was the first successful long term assessment story of pilot scale MFC. It effectively treated human waste, illuminated the toilet premises at night time, and provided reclaimed water for flushing. The bioelectric toilet system consisted of hexagonal structure including a middle settling tank, five air cathode MFCs, and last chlorination tank as an aqueous chamber for disinfection. Each air cathode MFC contained smaller membrane electrode assemblies made up of ceramic membranes sandwiched between catalyst-coated carbon felt anode and cathode. The MFC stacks were connected to supercapacitors for energy storage. Thus, bioelectric toilet contributed in feasible ways towards field application of MFC technology for sanitation applications with cost effective solutions and its commercialization. Nevertheless, in terms of the bioelectricity generation perspective, being the oldest technology, it can only be used in powering small electronic devices until now (Uria-Molto et al., 2022). Municipal wastewater contains a considerably huge amount of energy (1.9 kWh m⁻³) but power recoveries achieved so far are between 0.015 and 0.024 kWh m⁻³ (Blatter et al., 2021). Therefore, focussed effort on electricity generation application is needed. Furthermore, in terms of environmental impact, recently, Chin et al. (2021), has performed the environment impact study of 5 different configurations of MFCs with 1 L of treatment capacity and 10 years of operation i.e., MFC1 (single chamber air-cathode), MFC 2 (H-type dual chamber), MFC 3 (U-type single

Table 2
Recent semi-pilot and pilot scale studies on MFC and CW-MFC describing their upscaling potential.

Reactor type (stacked units)	Wastewater type	HRT (h)	Volume (L)	Power density	COD removal	References
Microbial fuel cells						
Tubular MFC (18 modules)	Domestic	43	700	195 mW m ⁻³	87 %	(Linares et al., 2019)
Air cathode MFC (6 modules)	Domestic	18, 36	720	85 mW m ⁻³	78.5-87.3 %	(Das et al., 2020)
Stretched MFC (64 modules)	Domestic	–	1000	650 mW m ⁻³	34.4-95.4 %	(Blatter et al., 2021)
Air cathode Single MFC	Septage	84	125	31.8 W m ⁻³	5.6-9.3 %	(Nath and Ghangrekar, 2020)
Stack MFC (12 modules)	Urine	11.7	57.6	7.31 W m ⁻³	48 %	(Walter et al., 2018)
Stack MFC (24 modules)	Urine	24	104, 124	8.3 W m ⁻³	82 %	(Walter et al., 2020)
Stack MFC (12 modules)	Swine	4	110	905 mW m ⁻³	65 %	(Babanova et al., 2020)
Air cathode MFC (17 modules)	Domestic	12	850	0.043 W m ⁻²	49 ± 15 %	(Rossi et al., 2022)
Self-powered MFC and potentiostatically controlled MFC (16 modules)	Municipal	144	1200	ND	38.4 ± 3.1 and 41.6 ± 3.5 mg L ⁻¹ day ⁻¹	(Mohamed et al., 2021)
Constructed wetland integrated microbial fuel cell (CW-MFC)						
Vertical flow CW-MFC	Synthetic	36	420	0.8 mW m ⁻²	76-81 %	(X. Wang et al., 2019a)
Vertical flow CW-MFC	River water	96	69	0.575 mW m ⁻²	–	(Yu et al., 2020)
Vertical flow CW-MFC	Synthetic	72	20.35	19.53 mW m ⁻²	94.2 %	(Di et al., 2020)
Horizontal CW-MFC	Synthetic domestic wastewater	66	270.25	–	100 %	(Villaseñor Camacho et al., 2017)
Vertical CW-MFC	Synthetic	24	19	18.5 mW m ⁻²	97-99 %	(Oon et al., 2017)
Vertical CW-MFC	Synthetic	36	420	3.25 mW m ⁻²	–	(X. Wang et al., 2019b)
Vertical CW-MFC	Swine	48	40	210 mW m ⁻²	88.07 %	(Liu et al., 2020)
Vertical CW-MFC	Synthetic	72	320	–	64.02 %	(Shen et al., 2018)
Horizontal CW-MFC	Synthetic	158.4	143.26	33.76 mW m ⁻²	95.4-98.9 %	(Srivastava et al., 2020b)
Intermittent and continuous CW-MFC	Domestic sewage	–	316	106 mW m ⁻²	66.67 %	(Yang et al., 2022)
CW osmotic MFC	Synthetic	600	25	59.53 ± 10 mW m ⁻²	84.69 %	(Bhagat et al., 2022)

chamber), MFC 4 (flat single chamber), and MFC 5 (modularized dual chamber). The study revealed that MFC 4 configuration has highest environmental burden amidst all attributed to high HRT for wastewater treatment and rest possesses 60 % low environmental burden. Whereas, the discharged effluent creates 31-86 % of environmental load by reason of high ammonium and nitrogen content in the treated effluent. Moreover, the operational stage induces 60-90 % high environmental loads mostly from electricity generation than the construction stage (Chin et al., 2021). However, no single pilot study so far has reported on its long-term operational feasibility, techno-economic assessment during field trials, normalized land footprint, life cycle assessment (LCA) and environmental impact assessment (EIA) which are crucial for technology commercialization. Thus, the sustainability and longevity evaluation of MFCs technology remains missing and poses the biggest challenge for MFC commercialization.

On the contrary, variants of MFCs operating in natural environments, have been in progressive research to upscale them. Numerous approaches have been adopted to scale up S-MFCs such as (i) series connection of multiple S-MFCs and (ii) enhancing electrode surface area corresponding to connecting multiple S-MFCs units in parallel. However, the former approach was impracticable since each electrode will be submerged in the same solution. Similarly, the latter was also infeasible as it demanded a 100-folds increase in electrode surface area to double the power output of S-MFCs. To resolve these issues, the concept of PMS was introduced (Donovan et al., 2008) in S-MFCs, and later several large lab scale/semi-pilot scale S-MFCs were studied such as: 100 L S-MFC assisted with PMS operated for 2 years generating 18.3 mW m⁻³ utilized for charging batteries and commercial electronic devices (Yang et al., 2015); benthic microbial electrochemical system (B-MES) of 195 L with natural river sediment powering 9 LEDs with power density 81 mW m⁻² (H. Li et al., 2017); S-MFC of 68 L operated to power a wireless temperature sensor with highest current 12.6 mA (F. Zhang et al., 2011); 36 S-MFCs operated parallelly with energy storage of 5.02 V and 72 S-MFCs were proposed to charge a cell phone in 26 h (Prasad and Tripathi, 2021). Numerous others have also evaluated the performance of S-MFCs with either real or synthetic wastewater at different volume capacities ranging from 1 L to as high as 200 L (Abbas et al., 2017; Ewing et al., 2014; Xu et al., 2015). However, the inherent limitation in most S-MFCs is the large internal resistance, which limits their electrical energy generation, thus constraining their implementation at the field scale (Xu et al., 2015). Besides this, there are several large lab/

semi-pilot scale studies, but maximum power densities were obtained with the studies considering synthetic wastewater and results in low energy production in field conditions with real wastewater (Fang et al., 2013, 2015; Liu et al., 2014; Villaseñor et al., 2013), thus again deviating from real field pilot scale implementation. Along with this, none of these studies have assessed the parameters like techno-economic assessment, LCA, ECA, and technology readiness level, which are prerequisites for commercializing S-MFCs. Although from our understanding after thoroughly studying the journey of S-MFC, it can be stated that S-MFC has come out of the lab scale but not yet fully established and implemented at industrial research level, thus defining its TRL level in the range of 3-4.

Further, P-MFCs have been evaluated with numerous plants species with longer lifespan and high biomass, additive improvised cathodes and anodes to maximize electricity generation (Deng et al., 2012; Kabutey et al., 2019b). However, P-MFCs consistently encountered the limited bio-electricity generation as a major challenge. Therefore, researchers have also integrated the energy harvester and storage systems with P-MFCs. With this approach numerous studies were executed including: single P-MFC based energy harvester system (P-MFC-EH) developing 5 mA m⁻² to power low-power wireless sensor networks systems (de La Rosa et al., 2019); floating type P-MFC to supply power for intermittent LED light, buzzer and transmitted data remotely at low speed (Schievano et al., 2017); parallel P-MFC array generating 1.75 V for operating wireless sensor node (Osorio-De-La-Rosa et al., 2021); P-MFCs generating 0.114 mW m⁻² utilized for sensing water content in green roofs (Tapia et al., 2018). Nevertheless, P-MFC are still at their infancy stage with most of the work being conducted at lab scale and lack of information on energy demand, cost investment, EIA, LCA and TRL level. Accordingly, our take on TRL achievement by P-MFC will be just TRL 3 based on our comprehensive understanding of P-MFC technology from cover to cover. Therefore, hereafter extensive work is required to make P-MFCs commercially feasible (Maddalwar et al., 2021; Nitisoravut and Regmi, 2017).

CW-MFCs has been extensively researched at a large scale and as an outcome out of total CW-MFC publications, 1/9th of studies are on upscaled/pilot scale CW-MFC systems, as it can be observed in Fig. 4. These studies have shown promising results in scaled-up setups in natural environments (as represented in Table 2) with the least maintenance and low energy requirements. A horizontal pilot plant CW-MFC was developed with a volume capacity of 120 L for the treatment of urban wastewater, which exhibited

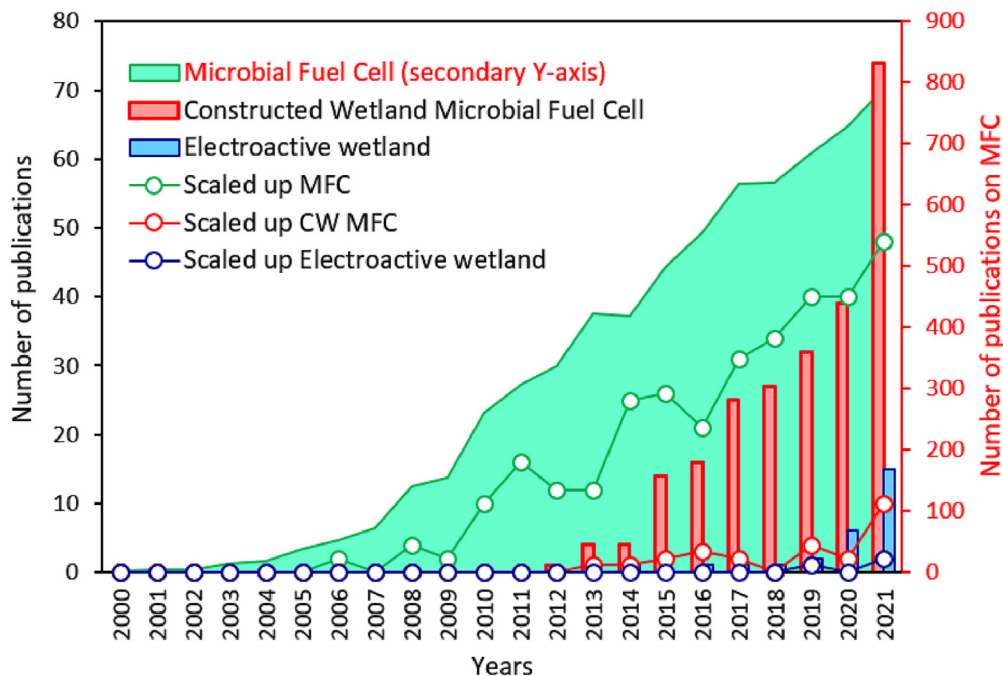


Fig. 4. Assessment of MFC and CW-MFC & Electroactive wetland by comparison of Web of Science data on total number of publications and number of publications on upscaling (i.e., >1000 L volume) over a period of two decades (2000-2021). Upscaling includes the search keywords: pilot, large upscale and full scale. Other search keywords are: “microbial fuel cell”, “constructed wetland + microbial fuel cell” and “electroactive + wetland”.

COD removal of 61 % and $\text{NH}_4^+\text{-N}$ removal of $98 \pm 2\%$ with electricity generation of 14.5 mW m^{-2} (Corbella et al., 2016). Further, a pilot scale horizontal CW-MFC with a capacity of 270.25 L and graphite plate as anode and cathode electrodes has achieved nearly 100 % of COD removal with the simultaneous maximum power density of 43 mW m^{-2} and current density of 37.1 mA m^{-2} (Villaseñor et al., 2013). Subsequently, Shen et al. (2018), operated *Hydrilla verticillate* planted vertical CW-MFC with enclosed carbon fiber brushes as electrodes at a high volume capacity of 320 L, achieving 93.54 %, 88.92 %, 77.90 %, and 64.02 % of total phosphorous, $\text{NO}_3\text{-N}$, $\text{NH}_4^+\text{-N}$ and COD, respectively. Later in 2019, 420 L of pilot scale vertical CW-MFC was operated with *Canna indica* vegetation treating synthetic domestic wastewater and displayed the potential of removing 76-81 % of COD, 60-85 % of total nitrogen and generating 0.8 mW m^{-2} power density (Wang and Kong, 2022; X. Wang et al., 2019a). Furthermore, on a similar reactor, the influence of COD/TN ratio was studied and high total nitrogen removal efficiency of 90.30-91.46 % was observed at the ratio ≥ 3 , evidencing a reduced dependence on organic carbon for denitrification even at field scale (X. Wang et al., 2019b). Meanwhile, Srivastava et al. (2020b) achieved 11.67 mW m^{-3} power density and 17.15 mA m^{-3} current density in horizontal pilot scale CW-MFC of 143.26 L treating 99 % COD from synthetic wastewater.

Likewise, with the prospect of achieving maximum treatment efficiency by advantageously regulating electron flow in the wetland bed Aguirre-Sierra et al. (2016) researched on snorkel configuration of bio-electrochemical wetlands and termed it METland. The METland functions as an electroactive wetlands similar to a scenario where conductive material is utilized throughout the filter bed of CW-MFCs and electrons are hypothesized to flow in a short circuit path throughout the bed (Srivastava et al., 2020d). It has shown application in different climatic, geographical, and demographic conditions, as it was assessed through multicriteria evaluation-based methodology (Peñacoba-Antona et al., 2021a). A full-scale METland version of CW-MFC with 24 m^2 surface area was installed in Spain in a community of 2500 inhabitants treating urban wastewater with the highest loading rate of $5.59 \text{ m}^3 \text{ day}^{-1}$ in vertical unsaturated flow mode requiring $0.6 \text{ m}^2 \text{ PE}^{-1}$ (Aguirre-Sierra et al., 2016; Peñacoba-Antona et al., 2021b). Besides this, similar replicated pilot-scale METlands biofilters were also installed in Denmark, Argentina, and Mexico (Wastew

et al., 2018). These METland version of CW-MFC have shown significant COD and TSS removal ranging between 80 and 87 % and 85-96 % despite of 3.5-fold increase in the organic loading rate from recommended organic loading rate for vertical flow CWs i.e., $20 \text{ g BOD m}^{-2} \text{ day}^{-1}$. Moreover, METlands necessitate low energy consumption of 0.18 KWh m^{-3} to operate $1 \text{ m}^3 \text{ day}^{-1}$ treatment capacity system (Yadav et al., 2022). These full-scale implementation studies of METlands in real fields indicate their readiness for commercialization as low-cost intensified wastewater treatment facilities for variable climatic, geographical, and demographic locations. Thus, CW-MFCs/METlands/electroactive wetlands have shown high potential for wastewater treatment at the pilot scale, thus achieving the primary purpose of CW-MFCs, but still lagging in terms of electricity generation. The primary reason is internal resistance development during large-scale implementation which further needs exploration (Fang et al., 2017; Huang et al., 2021; H. Li et al., 2017). Furthermore, conversing in the context of environmental impact, CW-MFCs stand out to function as ecological restoration technology while field scale implementation by significantly reducing the greenhouse gas (GHGs) emissions by suppressing the methanogenesis and enriching the electrochemically active exoelectrogenic bacteria (Saba et al., 2019; X. Wang et al., 2019a; H. Xu et al., 2021; Zhang et al., 2021).

Techno-economic perspective of the technology is one of the crucial parameters and needs consideration while employment of technology at the field scale (Saz et al., 2018). MFCs generally incur the high cost of installation i.e., capital expenditure (CAPEX), and operation i.e., operational expenditure (OPEX) because of expensive proton exchange membranes, catalytic cathodes, current collectors, and electrodes (Jadhav et al., 2020; F. Xu et al., 2018b). For example, different configurations of MFC can cost 720 USD (for a single chamber MFC of 20 L), 1956.36 USD (for 1 dual chamber of 10 L) to as high as 288,910 USD (two dual chamber MFC in series with a total volume of 2000 L) (Jadhav et al., 2021b). Despite this, according to economic analysis, MFCs are more economically viable and profitable (energy and resource recovery) in comparison to conventional commercialized activated sludge process membrane bioreactors, moving bed biofilm reactors, and sequential batch reactors for wastewater treatment (Trapero et al., 2017; Yadav et al., 2022). As an analogy, the energy consumption to operate a treatment facility of $1 \text{ m}^3 \text{ day}^{-1}$ fall within

the range of 0.27–1.89 KWh m^{-3} , whereas MFC requires low energy demand of 0.18 KWh m^{-3} to operate the identical treatment capacity system (Yadav et al., 2022). On the other hand, if we consider power output compared to the cost incurred then according to a study, 1 m^3 laboratory scale MFC equipped with carbon foam, hard felt and graphite brush as anode electrode would cost \$1995, \$220, and \$503 with a capital cost of \$33.3, \$3.45, and \$9.09 per mW of power density (Kumar et al., 2022). Thus, a reduction in MFC's overall cost investment (CAPEX + OPEX) was necessary to bring it into the viable cost-benefit ratio (Jadhav et al., 2020). A merger of CW with MFCs could be a potential alternative solution with reduced CAPEX and OPEX components as it utilizes a low-cost separator or membrane such as glass wool and non-conductive material i.e., gravels between anode and cathode. Even membrane-less CW-MFCs configuration was also successfully investigated through the benefit of the inbuilt natural redox gradient of CW-MFCs. Adding to this, CW-MFCs also use low-cost anode and cathode electrodes such as stainless-steel mesh, graphite rod, foamed nickel, and carbon fiber felt (Gupta et al., 2021a; Trapero et al., 2017; Xu et al., 2018a). In fact, the cost to benefit ratio (CBR; where cost and benefit i.e., revenue is calculated in terms of (USD ($W m^{-2}$) $^{-1}$ day $^{-1}$)) model was developed for comparing MFCs with CW-MFCs based on cost per unit power and revenue per unit power. The study revealed significantly lower CBR for CW-MFCs compared to other MFCs and a faster increase in revenue per unit power compared to the cost per unit power increase for CW-MFC compared to MFCs. The CBR for raw water treating MFC lies in the range of 4790–6566, whereas the CBR range for CW-MFC is significantly lower, i.e., 249–1388 under both experimental and practical conditions (F. Xu et al., 2018b). This signifies that scaling up of CW-MFCs is more economically beneficial than MFCs and comprehensive research and development is needed to improve and increase the number of pilot-scale CW-MFCs. Furthermore, till today, if we attempt to correlate the two technologies based on their TRL achievement and cost involvement then it can be certainly stated that CW-MFC has achieved higher TRL (i.e., 6–7) in low-cost involvement compared to TRL achieved by MFC (i.e., 5–6). This indicates CW-MFC has higher field scale feasibility at a low cost compared to MFC. Furthermore, for a better understanding of the readiness of technology on a real field, a comparative assessment has been drawn in Fig. 4, showcasing the increase in the number of scaled-up studies in the field of MFCs and CW-MFCs/electroactive wetlands relative to lab scale studies in past 20 years. There are around 7000 studies on MFC, but only 1/20th of studies have demonstrated full-scale MFC. Whereas CW-MFC/Metlands is a relatively young technology with >250 total publications, around 30 publications have showcased the full-scale operation of CW-MFCs/Metlands technology that shares 1/10th part of CW-MFCs/METlands research. Thus, deriving the same conclusion which has been discussed earlier asserts easy scalability and operational feasibility of newly emerged integrated technologies i.e., CW-MFC/wetlands at pilot scale compared to classical MFC system.

Conclusively, with the foregoing comparative assessment between different MFC-based technologies, it can be learned that every technology has its own constraints and struggles for implementation to pilot scale/real field scale. Nonetheless, CW-MFCs have shown a greater potential to scale up MFCs to the point where they can be implemented in real-world environments with minimal cost, and less complexity and maintenance in the field of wastewater treatment with simultaneous bioelectricity as opportunistic products. Moreover, CW-MFCs, compared to standalone MFCs are commercially viable, sustainable, greener technology with reduced environmental footprint and can simultaneously function as ecological restoration technology. Further, to develop a better understanding, a comparative table was drawn (Table 2). It is evident from the table that CW-MFCs have evolved as an alternative option to make MFC competent with current wastewater treatment technologies.

4. Conclusions

The MFCs represent a sustainable and energy generating technology. The microbial electrochemical reactions function to simultaneously

generate electricity and remediate wastewater. However, several constraints and challenges associated with volumetric increase in MFC have limited its use for electricity generation at large scale or large scale wastewater treatment. Considering the feasibility of microbial electricity generation and upscaling of MFC, sediments (S-MFC) and plant rhizosphere (P-MFC) were recognized as fuel substrate for optimum natural hosts for building MFCs. Later, MFCs were incorporated in constructed wetlands to accelerate its treatment efficiency along with energy recovery opportunistically. Nevertheless, each technology has limitations of its own kind, and they need to be assessed on multiple parameters before meaningful practical implementation. The multicriteria assessment of classical MFC and its variant technologies, based on bioelectricity generation efficiency, wastewater treatment efficiency, energy demand, cost investment and scale up potential, has placed CW-MFC at TRL 6–7, MFC at TRL 5–6, S-MFC at TRL 3–4 and P-MFC at TRL 3. Among the MFC and CW-MFCs, MFCs have high cost of installation i.e., CAPEX and OPEX because of fabrication parts. The operational energy demand of both MFCs and CW-MFCs are at par i.e., 0.18 KWh m^{-3} , though on the cost to benefit ratio, CW-MFC ranked high compared to other MFCs. The other sustainability criteria that shall be considered for commercialization of these technologies are life cycle assessment and environmental impact assessment. Furthermore, in the context of environmental harmony, CW-MFCs stand out for its functioning as expedite ecological restoration technology.

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CRedit authorship contribution statement

Supriya Gupta: Conceptualization, design of the work, data collection and interpretation, drafting the article. Ashmita Patro: data collection and interpretation, drafting the article. Yamini Mittal: data collection and interpretation, drafting the article. Saurabh Dwivedi: data collection and interpretation, drafting the article. Palak Saket: data collection and interpretation, drafting the article. Rupobrata Panja: data collection and interpretation, drafting the article. Dr. Tanveer Saeed: Conceptualization, critical revision of the article. Dr. Fernando Martínez: Conceptualization, critical revision of the article. Dr. Asheesh Kumar Yadav: Conceptualization, design of the work, data collection and interpretation, critical revision of the article and final approval of the version to be published.

Data availability

The authors do not have permission to share data.

Declaration of competing interest

The authors have no relevant financial or non-financial interests to disclose.

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