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A review of constructed wetland coupled with microbial fuel cell: A recently emerged technology

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Abstract
Natural assets for freshwater generation and energy production are exhausting at an unprecedented rate. It was expected that two-thirds of the overall population will face water condition problems by 2025. Further than this, primary energy utilization will also increase by 37%. This harsh situation has trigger research into developing sustainable scientific technology for water recycling and renewable energy generation. Microbial fuel cells (MFCs) have got marvelous attention for their potential to boost the degradation of some unmanageable pollutants and simultaneous energy production. Constructed wetland-coupled microbial fuel cell systems (CW-MFCs) incorporate an aerobic zone and an anaerobic zone is a new device to treat the wastewater and to generate electricity. It has more wastewater treatment volume and easy in maintenance than others MFCs. Based on the available research this review aims to present an appropriate and newest ideas and features of CW-MFC while investigating research findings and future problems.

Keywords: innovative constructed wetland, microbial fuel cell, energy generation, wastewater treatment

1. Introduction
Constructed wetlands (CWs) have been used to treat n number of wastewater that is ranging from domestic wastewater to urban wastewater and from agricultural wastewater to industrial wastewater. They have great efficiency for treating storm water runoff, leachates and mine drainage through various combinations like physical, chemical and biological process [1, 2]. They are comparatively low cost in terms of installation, operation and that too in maintenance. And all these qualities have increased its popularity in the last two decades [3, 4]. Microbial fuel cells (MFCs) are widely applied in the process of simultaneous sustainable wastewater treatment and bio electricity production [5, 6, 7]. It is a bio electrochemical system making use of biocatalyst for converting chemical energy into electricity, and it has been considered as one of the promising and sustainable technologies for power generation as well as waste management [8, 9]. Lately, MFCs have demonstrated as innovative devices that possess great potential in simultaneous wastewater treatment and bioelectricity generation. MFCs also successfully gained attention from many research groups worldwide [8, 10].
In recent years, microbial fuel cell (MFC) technology has been explored extensively for their innovative features and environmental benefits [8, 11, 12]. A microbial fuel cell coupled with constructed wetland (MFC-CW) is a latest technology which treat different wastewater and produce electricity which has more wastewater treatment capacity and easy maintenance as compared to others MFCs. Constructed wetland–microbial fuel cells (CW–MFCs) are novel devices with a delicate combination of artificial ecosystems (constructed wetlands) and bio electrochemical techniques (microbial fuel cells), in which electricity generation can be enhanced on account of rhizosphere effect of wetland plant [13, 14] and contaminants in the wastewater can be efficiently removed due to the synergistic effect of the 2 units [15, 16]. Both of the constructed wetland and the microbial fuel cell possess anaerobic and aerobic zones, where reduction and oxidation processes take place, and these similarities are the bases of the combination of the two units.
Yadav was the first research group that came up with the novel design of CW integrated with MFC. It is worth noting that some innovative hybrid systems were also developed recently based on the similarities between MFC and CW systems [16, 17, 18, 13, 19]. In this work, we explored the performances of the CW-MFC system in different operating conditions to reveal the bio electricity production of CW-MFCs.

2. Framework of CW-MFCs

Several designs for MFCs for wastewater treatment have been introduced. Broadly they can be divided into two categories: Dual chamber MFC and Single chamber MFC.

2.1 Dual chamber MFC

Dual chamber MFC consists of an anaerobic anode chamber and an aerobic cathode chamber which are usually separated by a proton exchange membrane (PEM). Substrate is oxidized by bacteria generating electrons and protons at the anode chamber. The protons travelling through the PEM and the electrons travelling through the external circuit are combined with electron acceptors at the cathode chamber. The anode is inoculated with a mixed solution of anaerobic sludge and substrate like glucose. On the other hand, cathode is inoculated with aerobic sludge.

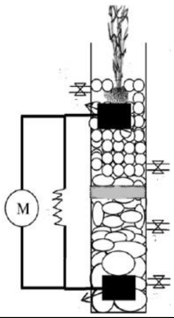
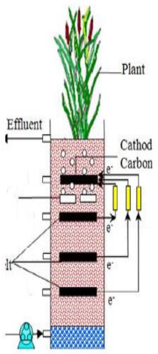
2.2 Single chamber MFC

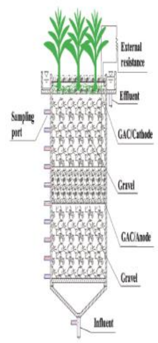
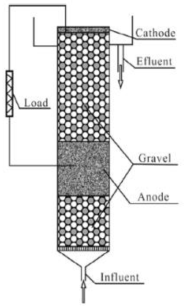
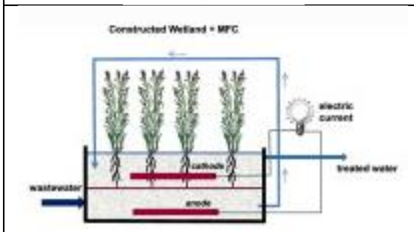
Single compartment MFC offers simpler design and cost savings. It typically consists of an anode chamber with a microfiltration membrane air-cathode. The cathode was exposed to air on one side and water on the other side (Inside). There is no proton exchange membrane. The microfiltration membrane is applied directly onto the water-facing side of the cathode.

Generally, CW and MFC systems consist of aerobic and anaerobic regions where reduction and oxidation processes take place respectively [14]. The bottom region of the system is in anaerobic condition, which is used as anodic chamber. The organic matter was oxidized by bacteria and denitrification also takes place at this region. While the upper region is in aerobic condition, which is suitable for biodegradation of unutilized organic matter from lower region, nitrification and mineralization of aromatic amines [20].

In order to maximize the redox gradient (as it is an essential factor in producing an electrical current in MFCs) most CW-MFCs have been operated under up flow conditions with a buried anode and a cathode at the surface and/or in the plant rhizosphere. This arrangement minimizes the dissolved oxygen (DO) at the anode while ensuring maximum availability in the cathode region.

Table 1: Different setups of constructed wetland-microbial fuel cells

Set-up	Mode	Electrode	Reference
	Batch mode	Graphite	15
	Continous up flow	Activated carbon (GAC)	21
	Continous up flow	Carbon	20

	Continous upflow	Stainless steel mesh (GAC)	16
	vertical subsurface flow	stainless steel mesh (SSM) carbon cloth (CC) granular activated carbon (GAC)	18
	horizontal subsurface flow	Graphite plate	13

3. Operation of CW-MFC

The similarity between CW and MFC contribute to the idea of developing an integration of both systems[14]. MFC integrated into CW is a possible and economical way to achieve the objectives of both wastewater treatment and electricity generation [15]. As for the mechanism of MFC, the organic matter is oxidized and the electrons and protons are released at the anodic compartment. Electrical current is generated when the electrons migrate to cathode through an external circuit. The electrons from anode also react with oxygen or other electron acceptor at the cathode to produce water as well as other reduced compound [22]. A microbial fuel cell (MFC) consists of an anode and cathode electrode similar to any battery. The voltage difference between the anode and cathode, together with the electron flow in the outer circuit, generate electrical power. Conventional two-chamber MFC consists of aerobic (cathode) and anaerobic (anode) compartments separated by a proton exchange membrane or salt bridge. In an MFC, electrochemically active bacteria oxidize the biodegradable organic matter present in the anodic chamber which generates electrons (e−) and protons (H+). The transfer of electron occurs through the electrode (anode) which is integrated with an external circuit to the cathode. Proton diffuses through the proton exchange membrane (PEM) into the cathode chamber, where it combines with O_2 and electrons to form water. The organic substrates utilized at the anode may vary from the ordinary carbohydrates such as glucose and acetate, to more complex compounds such as starch, complex wastewater, sediments and various other organic and inorganic constituents. The bacteria play a major role in the MFC. The electron transfer and the electrochemical reactions put together comprise the MFC. Redox mediators are compounds that can increase speed of the process called electron transfer from a main electron donor to a terminal electron acceptor, which may increase the reaction rates by one to several orders of magnitude [23].

Research suggested that wetland plants can promote the cathode performance of MFCs [13]. Initially a glass wool separator was used by [15] and [17] to provide a 'sharp' redox profile. In previous studies it shows that the Ipomoea aquatic grown in cathode enhanced the bio electricity production by enhanced the cathode potential of the CW-MFC [16. 13] integrated MFC technology into a horizontal flow constructed wetland using a bentonite layer to separate the lower anaerobic anode compartment and upper aerobic cathode compartment. The bottom layer (20-cm high) and the middle layer (20-cm high) were filled with gravel. Activated carbon (GAC) was widely used as MFC electrode material by [2]. Biodegradation of organic matter, nitrification and denitrification was investigated by [24] further in his study he used gravel with average size of 5.43 mm as supporting material and Glass beads with diameter of 10 mm were filled at the bottom of the column up to 5 cm to ensure even distribution of influent. Both electrodes were connected with stainless steel and insulated copper wires across a 1000 Ω resistor in his experiment. An ultra filtration membrane with a molecular cutoff weight of 5 kD was applied directly onto the water-facing side of the cathode. Anode and cathode were connected using titanium wire to an external resistor of 500 X by [25].

Azo dyes are bio refractory compounds containing one or more –N¼N– groups and have been widely used in industry [26, 27]. The –N¼N– groups which can be found in all of azoic compounds are hard to break because of their stable chemical properties. However studies have shown that –N¼N– groups can be reduced as electron-acceptors in anaerobic conditions (Dos Santos *et al*. 2007). MFCs anodes can provide anaerobic conditions and electrons for the reduction of –N¼N– groups, and Azo dyes usually been used as an excellent model contaminant for MFCs [28].

Table 2: Source inoculums used in microbial fuel cells

S. No.	Source inoculum	Concentration (mg/L)	Reference
1.	Mixture of aerobic and anaerobic sludge	300	(29)
2.	Microbial consortium	0.06–0.24	(30)
3.	Klebsiella pneumoniae strain L17 from subterranean forest sediment	0.016	(14)
4.	Anaerobic sludge	100	(31)
5.	Proteus hauseri ZMd44	450–560	(32,33)
6.	Mixture of aerobic sludge and anaerobic sludge	300	(34)
7.	Microbial consortium	75	(35)
8.	Anaerobic sludge	10–20	(36)

4. Performance of CW-MFCs

4.1 Functioning of CW regarding wetland plants

The roles of plants in CW were frequently discussed in CW study. The foremost roles of the macrophytes are to alleviate the surface beds, supply excellent state for physical filtration, prevent clogging in vertical flow systems and provide huge surface area for attached microbial growth [37]. Many studies also relate the important of plant with regards to the treatment efficacy [38, 37, 39, 40]. According to [37], macrophyte transfers oxygen to the rhizosphere through roots system and enhances the aerobic degradation of organic matter and nitrification.

To evaluate the effect of location of plant roots on the performance of the CW–MFC, three types of CW–MFCs were set up: a Rhizosphere-anode CW–MFC with plant roots placed on the anodic compartment, a Rhizosphere-cathode CW–MFC with plant roots placed on the cathodic compartment and a non-planted CW–MFC as control, and they were operated under the same conditions. Three adult plants of Ipomoea aquatica with a similar weight were planted both in the Rhizosphere-anode CW–MFC and the Rhizosphere- cathode CW–MFC (planting density about 32 plants m^{-2}) [18].

4.2 Functioning of CW regarding microbes

Most of the microbes are electrochemically inactive. The electron transfer from microbes to the electrode is faciliated by conciliator such as methyl viologen, humic acid, methyl blue, thionine, neutral red and so on [41]. Such MFCs are called mediator MFC. Most of the mediators available are expensive and toxic. On the other hand, mediator-free MFCs use electrochemically active bacteria to transfer electrons to the electrode and thus do not require a mediator [11]. referred to such microbial communities as adapted anodophilic consortia. To date, discrete entities of bacterial species of genus Geobacter [42], Enterobacter [43], Shewanella [44] and Bacillus [45] have been tested with respect to their generation or maximization of the power output in MFCs.

Table 3: Microbes used in MFC

Microbes	Application
Actinobacillus Succinogenes Aeromonas Hydrophila Desulfovibrio desulfuricans Clostridium butyricum Escherichia coli	Neutral red or thionin as electron mediator (46) Mediator-less MFC (47) Sulfate/sulfide as mediator (48) Fermentative bacterium (49) Mediators such as methylene blue needed (48)

4.3 Functioning of CW regarding organic load

COD loading greatly affects the performance of CW-MFCs. A balance is necessary between providing sufficient organics for oxidation at the anode and limiting the amount of COD arriving at the cathode. In a vertical upflow CW-MFC designed by [18] an increasing trend in power densities was observed as influent COD was increased from 50 mg/L to 250 mg/L. However, further increases in concentration to 500 mg/L and 1000 mg/L resulted in average power densities of 33.7 mW/m2 and 21.33 mW/ m2, respectively, compared with 44.63 mW/m2 for influent COD concentrations of 250 mg/L. Additionally, an increase of COD at the cathode can promote the development of a heterotrophic biofilm on the cathode limiting the mass transfer of reactants to, and products from, the electrode [50]. Other compounds in the wastewater will affect the ability of electrogenic bacteria to produce power. Operating under batch mode [15] noted that as dye concentration increased from 1000 mg/L to 1500 mg/L the average power density more than halved due to the toxic effect of the dye. Similarly, [21] reported that as the proportion of ABRX3 dye (measured as COD) increased incrementally from 10% to 90% the maximum power density, obtained from the power density curves, fell from 0.455 W/m^3 to 0.138 W/m^3.

4.4 Effect of redox conditions

Optimising the redox gradient between the anode and cathode is crucial in CW-MFC development [19]. Reported that maximum redox gradients were found between the surface and bottom of the wetland. Continuous flow, planted wetlands provided the largest average redox gradient of 407.7 mV compared with unplanted continuous flow (401 mV) and discontinuous flow (326.2 mV). The presence of macrophytes had a greater effect on redox conditions between the top and middle layer with the planted wetland producing a redox gradient 20% larger than the unplanted CW-MFC

Table 4: Reported performance of CW–MFCs

Type	*Liquid volume* (L)	Electrode material	Initial COD (mg/L) and (% removal)	Max. power	References
Vertical flow	5.4	Anode – graphite plate Cathode – graphite plate	1500 (74.9)	15.7 mW/m2	(15)
Vertical up flow	3.7	Anode – graphite plates Cathode – graphite plates	1058 (76.5)	9.4 mW/m2.	(17)
Vertical flow	12.4	Anode – granular activated carbon Cathode – granular activated carbon	180 (86)	0.302 W/m3	(16)
Horizontal subsurface flow	96	Anode – graphite plates Cathode – graphite plates	250 (80–100)	0.15 mW/m2	(13)
Vertical flow	12.4	Anode – granular activated carbon Cathode – granular activated carbon	193–205 (94.8)	12.42 mW/m2	(14)
Vertical flow	–	Anode – granular activated carbon Cathode – granular activated carbon	300 (72.5)	0.852 W/m3	(21)
Vertical up flow	8.1	Anode – granular graphite Cathode – granular graphite	411–854 (64)	0.268 W/m3	(51)
Vertical up flow	–	Anode – carbon felt Cathode – carbon felt	314.8 (100)	6.12 mW/m_2	(24)

5. Limitations and future prospects

These shortcomings are reduced by choosing a suitable coating of polymer on the microfiltration membrane, which is impermeable to air [52]. Before MFC technology is used in practical applications, substantial efforts are required to optimize its performance, particularly to address the problems of low power output and high cost. Among the various factors which contribute to the overall MFC performance, electrode design and the use of noble metals, such as platinum as catalysts, present a great challenge.

A recently developed biocathode that uses microorganisms as catalysts to assist in electron transfer eliminates the use of noble metal, such as platinum, and eliminated the need for replenishment of the electron mediator, resulting in greatly improved MFC sustainability. Granular activated carbon-biocathode (GAC) can be an excellent alternative to Pt and other chemical catalysts. GAC offers high surface area for biofilms which is crucial for high activity of the MFC system.

Strategies such as adding graphite flake to the sediment [53], increasing the projected electrode area [54] or using multi-electrodes [55] have improved the power produced in SMFCs. Similar strategies and optimizations should be applied to CW-MFCs. Methane production can be postponed by incorporating a PMFC into a rice microcosm [56]. The anodes of PMFCs [57] and CW-MFCs [16] offer a more favorable electron acceptor and limit the growth of methanogens. Exchange of solar energy into electricity can be achieving by coupling wetland plant with the microbial transformation of organics to electricity in CW-MFC system.

6. Conclusion

Proper treatment of wastewater is important to human health and societal development. Thus, new treatment technologies with low energy consumption and possible recovery of valuable resources (e.g., energy and water) from wastewater become of strong interest. Among the recently developed concepts, microbial fuel cells (MFCs) appear to be very eye-catching because of direct electricity generation from waste by taking advantage of microbial metabolism with electron acceptors or donors. The coupled system can recover useful energy, compared to constructed wetland that does not generate any energy.

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