CWMFC

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CWMFC is a novel technology that has been used for almost a decade for concurrent wastewater treatment and electricity generation in varying scopes of domestic, municipal, and industrial applications since its implementation in 2012. Its advantage of low-cost enhanced wastewater treatment and sustainable bioelectricity generation has gained considerable attention. Nevertheless, the overall efficiency of this novel technology is inclined by several operating factors and configuration strands, such as pH, sewage composition, organic loading, electrode material, filter media, electrogens, hydraulic retention time, and macrophytes. Here, we investigate the effect of the wetland plant component on the overall performance of CWMFCs. The macrophyte's involvement in the oxygen input, nutrient uptake, and direct degradation of pollutants for the required treatment effect and bioelectricity production are discussed in more detail. The review identifies and compares planted and unplanted CWMFC with their efficiency on COD removal and electricity generation based on previous and recent studies.

Keywords: electricity generation ; wetland plants ; wastewater treatment ; microbial fuel cell ; constructed wetlands

1. Introduction

Over the decades, many wastewater treatment technologies have been employed to address the wastewater environmental menace. Wastewater treatment technologies, which consist of trickling filters, activated sludge, reverse osmosis, and membrane filters, are currently being used to treat all types of organic and toxic wastewater from industrial and municipal sources. However, they are not very productive, with regards to the cost and energy demand required in their operation ^[1]. It is projected that USD 2 trillion will be required in the U.S.A over the next 20 years to construct, operate, and maintain wastewater and drinking water facilities ^[2]. In addition to the current annual costs of USD 25 billion, around USD 45 billion is expected for wastewater infrastructure upgrades, with over half of operating expenditures aimed at aeration of wastewater. Power production measured here only for aeration could provide much-needed energy in the U.S.A from industrial wastewater alone ^[3]. According to Gude (2015), some of these conventional wastewater treatment systems require 0.3–0.6 kW·h·m –3 for treatment, whereas inherent in the same wastewater is energy that is equivalent to 10 times that needed for treatment ^[4]. Hence, the concept of generating electrical energy from the inherent chemical energy (organic matter) in wastewater during the treatment process will help offset the financial burden of treatment and provide access to clean water throughout the world, which would be highly recognized as sustainable ^{[5][6]}.

In 1911, Michael C. Potter experimented and put forward the first microbial electrochemical technology (MET) and bioelectrochemical system (BES), established as microbial fuel cells (MFC), as a sustainable biotechnology ^{[Z][8]}. A microbial fuel cell is an innovative wastewater treatment technology that uses electrochemical active bacteria (EAB) as a biocatalyst to transform the chemical energy inherent in sewage directly into electrical production without any environmental footprint $^{[\underline{1}][8]}$. MFCs use wastewater as a feed substrate for EABs to produce bio-electricity, while concurrently treating waste $^{[\underline{1}]}$. According to, Singh et al. $^{[\underline{1}]}$, MFC as a technology holds great potential for a clean and green energy environment.

Constructed wetlands (CWs), on the other hand, are bio-physically assembled systems designed and built to take advantage of natural processes and interactions between wetland flora, soils, and associated microbial species to help regenerate wastewater $^{[9][10]}$. Wastewater from a wide variety of sources, such as municipal, agricultural, or industrial wastewater, are treated by CWs $^{[11]}$. They are easy to maintain and operate and can remediate many of the persistent pollutants that occur in conventional wastewaters into harmless by-products $^{[12]}$. As a result, they have emerged as a substitute to traditional intensified systems for wastewater treatment $^{[13][14]}$. A decade ago, researchers discovered that the embedded redox gradients, which naturally exist in wetlands, are highly compatible with the settings in microbial fuel cells, i.e., anaerobic zone in the inner–lower region and aerobic region at the air–water interface $^{[15]}$. This connection makes their incorporation very plausible by creating a synergy between these two technologies for enhanced wastewater regeneration and bioenergy generation $^{[16]}$.

2. Configuration of CWMFC

CWMFC is a hybrid system that seeks to integrate MFCs into built wetlands by leveraging the triple interaction of substrates, the plant and microorganisms' physical, chemical, and biotic elements for wastewater treatment and electricity production $\frac{17[18][19]}{19}$. This hybrid system syndicates the advantage of two systems in a way that is proficient in attaining high levels of wastewater reuse and bioenergy $\frac{18}{19}$. On the basis of researchers identifying a variation of dissolved oxygen (DO) along the vertical profile of CW's natural environment, this integration was conceived to be plausible, which creates a naturally prevailing stratified redox gradient similar to that of MFC in its two-chambered cell, as shown in **Figure 1** $\frac{161[20]}{21}$.

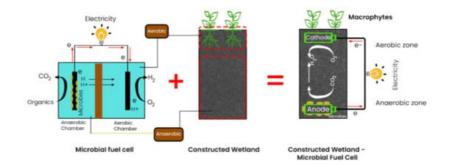


Figure 1. A graphical illustration of constructed wetland coupled MFC.

A typical CWMFC is, therefore, built similar to a traditional MFC with two major compartments—the lower anaerobic chamber and the upper aerobic chamber ^{[19][20][21][22][23]} with an anode electrode deeply buried within the anaerobic chamber and cathode electrode positioned at the air–water interface around the root zone of the plant, also called the aerobic or cathodic section ^[24]. These electrodes are then connected using titanium wires with an applied external resistance crucial for electricity generation. By positioning the anode at the lower anaerobic zone and inserting the cathode at the air–water interface, CW-MFC takes good advantage of the existing redox condition ^[23]. The optimization of this redox gradient or potential difference established betwixt the anode and the cathode is pivotal for power generation and contaminant removal in CWMFC ^[25]. Since the onset of this hybrid technology, carbon, and graphite materials have been widely used as electrodes, owing to their suitable surface microbial attachment and growth, high electrical conductivity, non-oxidative nature, and riveting characteristics for biofilm formation ^{[14][26]}.

A CWMFC reactor configuration comparable to a built wetland often has its lower anaerobic region filled with a layer of soil, gravel or some other recent substrates, such as activated carbon, zeolite, or alum sludge, as a supporting matrix for the anode electrode. This support matrix also creates the desired environment for the oxidation reaction by microorganisms for contaminant removal and electrons transfer processes [14][16][18][26]. All these components, as mentioned earlier, are essential in the configuration of CW-MFC bio-electrochemical systems. However, to maintain a highly aerobic upper cathodic chamber and increase the removal of pollutants, macrophytes that resource dissolved oxygen to the cathode through plant root respiration are planted in the upper cathode compartment, which contributes significantly to the reduction reaction. Aside from the maintenance of appropriate operating conditions, such as pH, temperature, organic loading rate flow regime, and hydraulic retention rate, the system's physical and biological components' performance is essential for the overall system efficiency ^[27]. The macrophyte components are recognized to play a pivotal role, as they interact with and influence the performance of all other required components, such as the substrate (filtration media), microorganisms, and electrode materials in CWMFC (see Figure 2). They also influence both the oxidation and reduction reactions. They act as biological filters and accumulators in the treatment process and as oxygenators to the cathode for electricity generation ^[15]. According to Fang et al. ^[28], the plants' presence promotes the cathode's oxygen concentration through their photosynthetic activities. In a study by Fang et al. [28], a CWMFC with plants produced an average voltage output of about 15% higher than an unplanted CW-MFC [29][30][31][32].

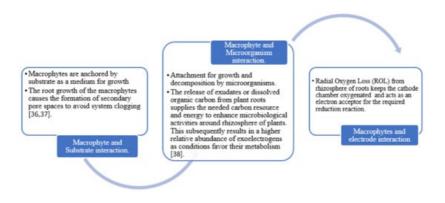


Figure 2. Interaction between macrophytes and other physical components of CWMFC.

3. Role of Macrophyte in CW-MFC Contaminant Removal

In many wastewater effluents, high COD levels, nutrients such as ammonium–nitrogen, nitrate–nitrogen, and phosphorus, and heavy metals are common pollutants. CWMFC as an eco-friendly technology can remove, transform, and immobilize these and many other wide ranges of contaminants ^[33]. The efficacy of CWMFC in wastewater treatment, however, depends on multifaced interacting processes that can be narrowly divided into three major categories—physical, chemical, and biological—as shown in **Figure 3** below ^{[27][29][34][33]}.

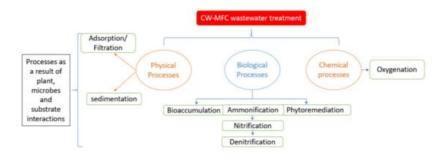


Figure 3. Interacting processes involved in contaminant removal.

The macrophyte component plays a versatile role in all of these processes to ensure the effective removal of wastewater contaminants. For example, in the bioaccumulation and phytoremediation process, aquatic plants have an important role in the absorption, assimilation, and storage of nutrients in their biomass, either directly or indirectly. They sequester soluble inorganic nutrients as a means of building their biomass [27][35][33][36]. Since these nutrients are necessary for their growth, the amount of nutrients from wastewater effluent can be maximized by choosing wetland plants with a high capacity for inorganic absorption and their subsequent conversion to organic plant biomass [37]. In addition, besides the release of oxygen (oxygenation) from plant roots to maintain a redox condition necessary to facilitate nitrification by aerobic microbes, the root system of submerged and emergent aquatic macrophytes releases exudates through a process called "rhizodeposition" [38][17][26][39]. These rhizodeposits act as an energy source for denitrifiers for the denitrification processes for the effective removal of nitrate in wastewater [38][39][40]. Organic rhizodeposits range from low molecular weight exudates to full roots used as energy sources for microorganisms in the CWMFC [41][33]. In a study conducted by Wen et al. ^[39] to assess the influence of macrophytes in ammonium nitrogen (NH₄⁺-N), nitrate, and total nitrogen removal, they used Canna indica, a typical wetland plant, and their results showed that the planted CW-MFC was 38% higher in removal efficiency than unplanted CW-MFC. This was mainly because the wetland plant enhanced the nitrification process. In a similar study, comparing planted CWMFC with unplanted CWMFC to investigate the role of plants (*Canna indica*) in the treatment of antibiotics and NH_4^+ -N, the presence of plants was observed to have accelerated the accumulation of sulfamethoxazole, tetracycline, and NH_4^+-N [42]. In addition to their inimitable role as bio accumulators, wetland plants also play an essential filtering and adsorption role by reducing wastewater's velocity and allowing finer particles to adhere to plants' biofilm surfaces. It is undoubtedly proven that the wetland plant species significantly affect pollutant removal in CWMFC [41][33][36][39]. In a study conducted by Liu et al. [43] to enhance the efficiency of CWMFC using plant photosynthate, the root exudates of Ipomoea aquatica were utilized as a part of the fuel in photosynthetic MFC to enhance denitrification [43]. Phragmites australis had better removal of NH4-N than Iris pseudacorus and was able to enhance the rhizosphere's nitrification process due to the more robust radial oxygen loss (ROL). A recent study by Oon et al. [34] using Elodea nutallii CWMFC operated under artificial aeration attained 98% COD removal efficiency. In another recently conducted experiment in South Africa by Oodally et al. [44], to examine the contribution of macrophytes used in CWMFC, they compared three indigenous South African species: Phragmites australis, Cyperus prolifer, and Wachendorfia thyrsiflora with an unplanted system as control. They obtained a COD

removal efficiency of 97 ± 1% for *Cyperus prolifer*, which was higher than *P. australis, Wachendorfia hyrsiflora*, and the unplanted with 94 ± 1%, 94 ± 1%, and 90 ± 2% removal efficiencies, respectively. The *Cyperus prolifer* species attained a higher orthophosphate removal efficiency (98 ± 0%) than the control experiment (72 ± 7%), *Wachendorfia thyrsiflora* (58 ± 6%), and *Phragmites australis* (81 ± 4%). Comparatively, *Cyperus prolifer* was noticed to be the most suitable indigenous wetland plant for electricity production and COD, ammonia, and phosphate removal among the three species ^[44]. These results also justify Greenway's ^[33] assertion that different macrophyte species differ in their removal efficiency, hence the need for a proper investigation in selecting macrophyte species to be incorporated into the CWMFC system. Furthermore, studies on plant effects of nitrogen, phosphorus, and heavy metal removal are scanty, compared to the COD removal efficiency. Although generally proven under constructed wetlands (CW), extensive studies are required regarding CWMFC ^[36]. This study may help optimize the integration of the plant component in CWMFCs and boost the development of CWMFCs for practical use (see **Table 1 and 2**).

Macrophyte	Initial COD (mg/L)	COD Removal (%)	HRT (hr)	Max. Power	Author
Canna indica	1500	74.9	96	15.7 mW·m ⁻²	[<u>16</u>]
Phragmites australis	1058	76.5	N. A	9.4 mW⋅m ⁻²	[45]
lpomoea aquatica	180	86	72	0.302 W⋅m ⁻³	[28]
Phragmites australis	250	80-100	N. A	0.15 mW⋅m ⁻²	[46]
lpomoea aquatica	193–205	94.8	48	12.42 mW⋅m ⁻²	[43]
lpomoea aquatica	300	72.5	72	0.852 W⋅m ⁻³	[47]
Phragmites australis	411-854	64	N. A	0.268 W⋅m ⁻³	[25]
Typha latifolia	314.8	100	N. A	6.12 mW⋅m ⁻²	[<u>48</u>]
Phragmites australis	583	64	N. A	0.276 W⋅m ⁻³	[26]
Taifa latifolia	624	99	24	93 mW⋅m ⁻³	[<u>49</u>]
Phragmite australis	323	60.6	62.4	131 mW⋅m ⁻²	[50]
Elodea nuttallii	643	97–98	24	184.75 mW⋅m ⁻³	[34]
Canna indica		78.71	72	31.04 mW⋅m ⁻³	[<u>51</u>]
Phragmites australis	200	90.45	48	0.20 W⋅m ⁻³	[52]
Phragmites australis		82	72	3714 mW⋅m ⁻²	[53]

Table 1. COD removal efficiency and power density between different macrophytes based on earlier studies.

In a CWMFC configuration, the appropriate selection of macrophytes is crucial for the system's success. The macrophyte component is one of the most conspicuous and versatile parts of the CWMFC bio-electrochemical system. The type of wetland plant installed in CWMFCs has some unique properties that make them play such an essential role in the contaminant removal processes and bioelectricity generation ^{[54][55]}. Therefore, a thorough selection of the type of macrophyte to be used is hugely imperative to the system's success. This decision can either enhance or retard CWMFCs efficiency significantly. Hence, an appropriate selection of wetland plants must be based on some unique characteristics, such as:

Table 2: Characteristics of Macrophytes and their relevance in CWMFC.

Macrophyte properties

Relevance in CWMFC

rapid growth and high biomass production

For winter insulation in cold and temperate regions, and particularly for the removal of nutrients by harvesting as nutrients are absorbed by macrophytes to build their biomass ^[55]. In addition, according to Yang et al. ^[56], species with high biomass production in CWMFC enhances the cell voltage and reduces the internal resistance of the system which often result in higher bioenergy production.

good natural adaptation to the local climate

Native species should be best preferred. According to Sierra (2017), CWMFC plants are selected based on the region's most common aquatic plants [27]. Oodally *et al.*, (2019), concluded that native species are best preferred due to their local climate adaptability. In their experimentation, the most common aquatic plants in the region showed improved performance in CWMFC than exotic species $\frac{[47]}{}$.

good root development

To provide a substrate for attached bacteria and oxygenation [55]. Also, the root development or maturity of the wetland plant affects oxygen release. In a sediment microbial fuel cell (SMFC) with wetland plant experiments conducted by Chen et al., (2012), their investigation has shown that young roots could excrete more oxygen than mature or aging species. Similarly, Stolzenberg et al. [57] also observed that plant species with good root development produced better oxygen which presented the highest voltage value than plants with smaller poor root systems. In addition, Mosqsud et al. operated a series of 6-CWMFC using Oriza sativa species. In their experimentation, they observed a reduction in power production as plants attained maturation. This was mainly because the maturation of the plant affected both oxygen release and exudate production. This signifies that the maturity of the root and its development is an essential factor in wetland plant selection [58].

High oxygen transfer capacity

Oxygen transfer capacity from the roots creates an aerobic environment. Due to the great diversity of flora, different species have different radial oxygen loss (ROL) [19].

nutrient absorption capacity

High nutrient absorption capacity helps in the effective removal of contaminants from the system. Species with high NAC use absorbed nutrients as a resource for their metabolism and growth ^{[33][59]}.

adaptation and ease of propagation

The ease in getting seedlings, seeds, or vegetative propagules must be well considered to ensure system sustainability.

Good Rhizodeposition; release of carbon sources as rhizodeposits from plant roots.

Rhizodeposition supports the growth and activities of microorganisms associated with bioelectricity production.

C4 Plants

The photosynthetic activity of plants is categorized into 3-phases: C3, C4, and CAM. In terms of oxygen production and CO₂ fixation, plants in each category have different photosynthetic pathways. Plants in the group of C4 are those with advanced photosynthetic activity than plants in C3 and CAM groups. Consequently, because they have a higher conversion rate of solar energy into bioelectricity, it is suggested to integrate C4 plants ^[60].

These factors should be primarily considered in the appropriate selection of macrophytes for CWMFC. Nevertheless, owing to the wide variety of aquatic flora, further investigation is needed to evaluate and select plant species with potentials for CWMFC for simultaneous wastewater regeneration and bioelectricity production.

Macrophytes, particularly emergent plants, can cause substantial water loss in CWMFC through evapotranspiration. As the volume of wastewater flowing through the system decreases due to water loss, the treatment efficiency in CWMFCs could be affected significantly when the evapotranspiration rate exceeds 2.5 mm/d ^[34]. Also, in the absence of light, plant cells and microorganism respiration will consume O_2 . Hence, the DO level in the reactor was reduced as DO consumption was more than production. The plant's photosynthesis and respiration altered the reactor's oxygen dynamics, ultimately leading to voltage fluctuations ^[61]. Therefore, macrophyte species that can help overcome this setback will be highly recommended.

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