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Integrated Constructed Wetland and Microbial Fuel Cell for the Treatment of Stabilised Landfill Leachate

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ABSTRACT

Stabilized Landfill Leachate (SLL) co-treatment with sewage was investigated using an integrated Constructed Wetland and Microbial Fuel Cell (CW-MFC). The CW and CW-MFC wetlands were filled with sand and gravel and planted with *Canna indica*. Additionally, carbon electrodes, comprising an anode and cathode, were incorporated into the CW-MFC setup. The SLL and sewage were combined in a 1:1 ratio and introduced as influent. The wetlands were operated in both batch and continuous modes. During batch operation at Hydraulic Retention Times (HRT) of 7, 5, and 3 days, the CW and CW-MFC achieved maximum Chemical Oxygen Demand (COD) removal efficiencies of 62±4% and 83±7%, respectively, at a 7-day HRT. For the continuous flow operation at a rate of 5 L/day, the systems displayed removal efficiencies of 75±3% and 81±5% for Biochemical Oxygen Demand (BOD5), 88±2% and 96±2% for COD, 54±6% and 61±4% for Total Nitrogen (TN), and 59±3% and 67±2% for Total Phosphorus (TP) for the CW and CW-MFC, respectively. Incorporating the MFC resulted in an 8% increase in COD removal efficiency. The CW-MFC produced an average voltage of 173 mV, with an average power density of 3.78 mW/m². However, the CW-MFC's low coulombic efficiency of 0.17% appeared to limit current production. These findings indicate that the CW-MFC system can treat landfill leachate more effectively.

Key words: Constructed wetland, Microbial fuel cell, Co-treatment, Leachate and sewage, Vertical flow wetland

INTRODUCTION

The concept of Microbial Fuel Cells (MFC), when integrated into a Constructed Wetland (CW), is referred to as a Constructed Wetland-Microbial Fuel Cell (CW-MFC). This innovative technology offers advantages for both CW and MFC systems and has been utilized to treat domestic and industrial wastewater (Zhu et al. 2023). CW-MFCs are recognized as a sustainable wastewater treatment solution that produces bioenergy and facilitates the biodegradation of contaminants (Doherty et al. 2015). An MFC typically consists of an anode and cathode regions, separated by a membrane and connected via an external circuit (Nam et al. 2010, Wen et al. 2010). The exoelectrogenic bacteria decompose the organic materials present in the wastewater, resulting in the release of protons and electrons. The electrons generated are drawn toward the anode, travel through the external circuit, and reach the cathode, while protons pass through the membrane layer to arrive at the cathode (Logan 2008). Hence, a redox zone is created within the chambers of the MFC.

Constructed wetlands are engineered systems designed to treat wastewater by replicating the natural processes that occur in wetlands. One important feature of CWs is the presence of distinct aerobic and anaerobic zones. The uppermost layer of a CW is typically aerobic due to its exposure to the atmosphere, while the bottom layer remains anaerobic because of limited oxygen penetration. In this anaerobic zone, microorganisms thrive, utilizing alternative electron acceptors such as nitrate, sulfate, or carbon dioxide for their metabolic processes (Wdowczyk et al. 2022). Introducing a cathode and anode in the aerobic and anaerobic regions can achieve conditions similar to those required for MFCs. The redox gradient naturally existing between the aerobic and anaerobic zones of the CW, which does not require any intermediate layer, resembles that of a conventional MFC and can be harnessed to generate bioelectricity. Similar to single chamber microbial fuel cells, the operation of CW-MFCs involves the production of protons and electrons through the breakdown of organic matter by microbial catalysts in the anodic zone. Protons are transported to the cathode via fluidized media, while exoelectrogenic bacteria transfer electrons to the anode, which ultimately flow to the cathode through an external circuit (Corbella et al. 2015, Debabov 2008). In constructed wetland-microbial fuel cells (CW-MFCs), microorganisms serve as the primary source of bioelectricity, facilitating the biodegradation of organic matter. Integrating constructed wetlands with microbial fuel cells addresses their respective limitations and enhances their strengths. A key benefit of CW-MFCs compared to traditional microbial fuel cells is the preexisting redox gradient within the system, which is essential for ion transfer and lowers the cost of fabrication by eliminating the need for an expensive membrane or separator (Lu et al. 2015). Dominant bacterial populations in MFCs and CW-MFCs include genera such as *Proteobacteria, Shewanella,* and *Pseudomonas*. Notable nitrifying bacteria in these systems include *Nitrosomonas* sp., *Aridibacter,* and *Nitrospira* (Nam et al. 2010), which utilize ammonia as a nitrogen source and convert it to nitrites or nitrates. Subsequently, these nitrites and/or nitrates are reduced to nitrogen gas (N_2) by various denitrifying bacteria, including *Thauera, Thiobacillus, Geobacter*, and *Nitratireductor* sp (Saeed et al. 2022b).

Stabilized Landfill Leachate (SLL) is a highly contaminated wastewater characterized by diverse organic and inorganic pollutants, nutrients, recalcitrant compounds, and various heavy metals. Constructed wetlands have effectively treated landfill leachate (Saeed et al. 2022b). Given the elevated levels of organic and inorganic nutrients, landfill leachate can be utilized in MFCs for power generation while concurrently treating wastewater (Ganesh 2012, Sonawane et al. 2017). Research has explored various aspects, including electrode configurations, different anode materials or substrates, aeration at the cathode, and various wetland plant species, all aimed at maximizing bioelectricity output and enhancing contaminant removal efficiency (Doherty et al. 2015, Zhao et al. 2013). Nonetheless, there have been limited attempts to integrate CWs with MFCs to treat a mixture of stabilized landfill leachate and sewage. In consideration of the above, in this study, two microcosms were constructed: a conventional Constructed Wetland (CW) and a Constructed Wetland-Microbial Fuel Cell (CW-MFC).

The objectives of this study are to evaluate the performance of CW and CW-MFC in treating stabilized landfill leachate. This evaluation will focus on parameters such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), heavy metals, and nutrient removal. Additionally, this study also monitored the power density and current density generated by the CW-MFC.

MATERIAL AND METHODS

Sample collection

SLL used in this study was collected from Perungudi dumpsite, Chennai, Tamil Nadu, India. Perungudi is located at 12.97°N 80.25°E. As per IS 1893-1975 this dumpsite falls under Zone II of the Seismic Zoning. This site is located in central northern part of Pallikkaranai depression. The sample was collected in PVC cans. Two wetlands were inoculated with activated sludge obtained from the Anna University Sewage Treatment Plant (STP) to promote the growth and cultivation of microorganisms. During the start-up phase, activated sludge mixed with sewage wastewater was introduced into the wetlands through an influent tank for 15 days. After this initial phase, the wetlands received incremental amounts of raw SLL, which was the influent for both wetland systems. Unfortunately, the *Canna indica* plants used in the treatments perished within a week. Consequently, a mixture of SLL and sewage in a 1:1 ratio was employed throughout the study. To prevent contamination, the samples were refrigerated at 4°C.

Influent and effluent characteristics

The SLL collected from the dumpsite, the sewage from the treatment plant and mixed wastewater (influent) and the effluent from the two wetlands were tested for various parameters. These included temperature, Dissolved Oxygen (DO), Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Total Solids (TS), salinity, pH, redox potential (ORP), turbidity, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD5), chlorides (Cl), sodium (Na), potassium (K), total phosphates, phosphates (PO_4^{3-}), total nitrogen, Total Kjeldahl Nitrogen (TKN), nitrates (NO_3^-), ammonium nitrate (NH_4^+-N), chromium (Cr), copper (Cu), lead (Pb), and cadmium (Cd). All parameters were tested using the guidelines set by APHA (Anonymous 2012). The collected samples were analyzed at the National Centre for Sustainable Coastal Management (NCSCM) at Anna University, Chennai.

Arrangement of wetlands

Two vertical downflow-constructed wetlands (CW and CW-MFC) were established using identical PVC containers, each with an internal diameter of 15 cm and a height of 60 cm. The wetlands were filled with sand (2-4 mm, 35% porosity) and gravel (5-8 mm, 42% porosity). In both wetlands, four *Canna indica* rhizomes of comparable size were planted at the top of the columns. The CW-MFC microcosm featured two carbon discs measuring 100 mm in diameter and 10 mm in thickness, which served as anode and cathode electrodes within the CW-MFC system. The anode electrode was positioned 15 cm from the bottom of the wetland, while the cathode electrode was located 15 cm from the surface. Both electrodes were connected using insulated copper wires. Glass wool was employed to separate the anode and cathode sections of the CW-MFCs, maintaining a distance of 30 cm between them. The anode and cathode were linked via an external resistance of 1000 Ω using copper wire and a digital multimeter (Fig. 1a, b). The CW without electrodes served as a control. Sample ports were installed in the anode chamber above the base of the columns. Both experimental setups were in an open area at Anna University, CEG (Chennai, India).The two wetlands were inoculated with activated sludge obtained from the Anna University Sewage Treatment Plant (STP) in order to grow and cultivate microorganisms. In the start-up phase, activated sludge mixed with sewage wastewater was added to the wetlands from the top through an influent tank. This was done for a period of 15 days. After the start-up phase, the wetlands were supplied with incremental amounts of raw stabilized landfill leachate (SLL) but the *Canna indica* plants were not able to sustain and died within a week. This may be due to the presence high recalcitrant pollutant in the SLL from the Perungudi dumpsite, an aged landfill around 30 years old. Hence raw sewage wastewater after preliminary treatment was collected from the STP of Anna University and mixed with SLL in the ratio of 1:1 and supplied as influent to the wetland. The system was replanted as earlier and the mixed influent was fed for a period of two months as a start-up phase. This was done to acclimatise the plants and allow it to grow. The experimental work was started after the two wetlands were stabilized.

Operation of the wetlands

After start-up period, a performance investigation of wetlands to treat leachate and generate bioelectricity, the wetlands were operated under batch and continuous mode. Initially the systems were operated in batch mode with a Hydraulic Retention Time (HRT) of 7 days followed by 5-day and 3-day HRT for five cycles each. Batch operation was done primarily to test the viability of the treatment process. Subsequently, the wetlands were

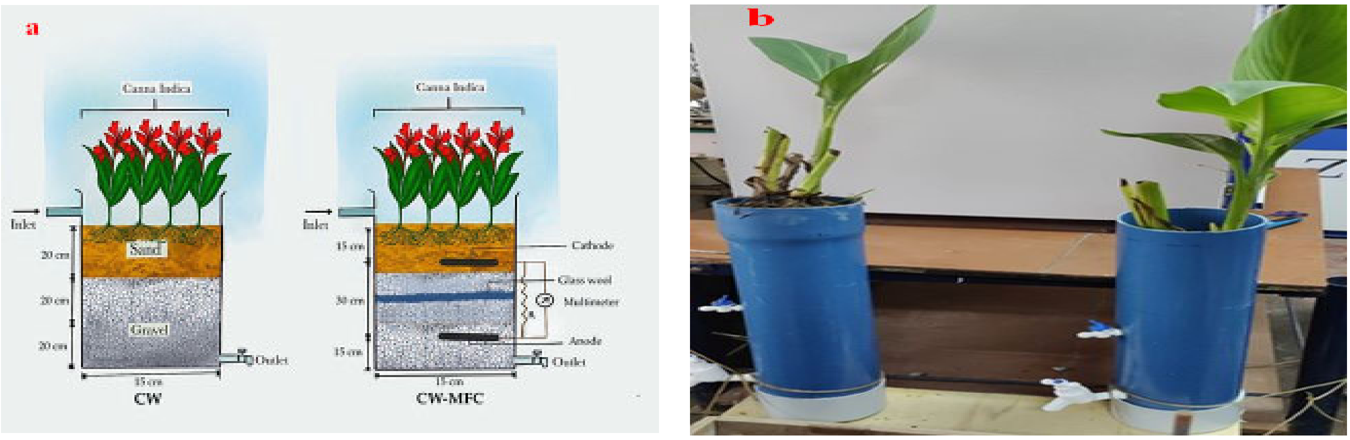

Figure 1. (a) Schematic arrangement of CW and CW-MFC system; (b) Photographic image of CW and CW-MFC system setup

switched to continuous mode, operating at a flow rate of 5 L/day for an additional two months. Throughout the study, voltage and current were recorded every eight hours. By dividing the power and current values by the surface area of the anode used in the constructed wetland microbial fuel cell (CW-MFC), the power and current density for the respective systems were calculated. The constructed wetland (CW) and CW-MFC systems were subjected to natural evapotranspiration as they were operated and exposed to the same open environmental conditions. It is important to note that this study did not account for or measure the water loss attributable to evapotranspiration.

Bioelectricity measurement

In the CW-MFC, bioelectricity is generated through microbial activity, making it essential to evaluate the system's effectiveness in converting biochemical energy into electrical energy. A digital multimeter measures the voltage drop (V), and power density is calculated based on the anode's surface area. Coulombic Efficiency (CE) is the ratio of the number of electrons utilized for electrical production to the total number of electrons generated during biodegradation. Assessing CE is crucial for understanding the CW-MFC system's capacity for bioelectricity generation, and it has been calculated using Equation (1) (Zhao et al. 2013).

$$CE = (\mathrm{MI})/(\mathrm{Fqb}\Delta\mathrm{COD}) \quad ....[1]$$

where CE is coulombic efficiency (%), M molecular mass of O_2 is 32 (g O_2/mol O_2), I is current (A), F is Faraday's constant (C/mol), which is 94,685, q is the flow rate (L/s). At the same time, b is the number of electrons donated per mole O_2, which is 4, and ΔCOD represents the difference in influent and effluent COD (g/L).

Another important parameter is Normalized Energy Recovery (NER), which gauges the effectiveness of the microbial fuel cell (MFC) system in generating bioelectricity. NER (Wh/kg COD) is calculated based on the volume of wastewater treated and the quantity of COD removed, as described in Equation (2) (Xiao et al. 2014).

$$\mathrm{NER}=(P_{avg}\mathrm{d})/(\Delta\mathrm{COD}\,\mathrm{Vww}) \quad ....[2]$$

where, ΔCOD = COD removed (kg/m^3), Vww = Volume of wastewater (m^3), P_{avg} = Average power (W (watts)), d = Time (days).

Statistical analysis

Statistical analysis was performed using the software SPSS Version 12.0 (SPSS Inc., Chicago, USA). The data were analysed through a one-way analysis of variance (ANOVA) to compare the pollutant removal performances of both systems. All results were expressed as mean values.

RESULTS AND DISCUSSION

Influent characteristics

Raw leachate characteristics

The characteristics of raw landfill leachate, sewage, and mixed influent (a combination of landfill leachate and sewage) are presented in Table 1. The composition of the leachate fluctuated throughout the experimental study, likely due to seasonal variations, the diverse types of waste present in the leachate, and the methods employed in landfilling (Wojciechowska 2017). Typically, leachate is assessed based on pH, chemical oxygen demand (COD), biochemical oxygen demand over 5 days (BOD5), suspended solids, nitrate, phosphate, and heavy metals. The pH of landfill leachate usually ranges from 6 to 8.5, influenced by biological activity. In this study, the pH was found to vary between 8.18 and 9, indicating a slightly alkaline nature of the leachate wastewater. Concentrations of dissolved solids ranged from 7,114 to 11883 mg/L. The elevated levels of dissolved solids observed in samples collected near the landfill site suggested that free ions were leaching from the deposited waste into the water (Soundaranayaki et al. 2022).

High electrical conductivity (EC) values of 6423±115 µS/cm indicate a significant presence of dissolved salts and other inorganic chemicals in the leachate. Generally, calcium, magnesium, potassium, sodium and phosphates are the main cationic constituents while nitrates, sulphates and chlorides account for the major anions in all types of wastewater. Redox potential (Eh) values of -164 mV and a Dissolved Oxygen (DO) level of 1.41 mg/L suggest an anoxic/anaerobic condition characterizes the raw leachate. The concentrations of biochemical oxygen demand over 5 days (BOD5) and chemical oxygen demand (COD) were found to be 601±23

Table 1. Characteristics of raw leachate, sewage and mixed wastewater

Parameter	Unit	Leachate (SLL)	Sewage	SLL+Sewage
Temp	°C	25.27±0.77	24.87±1.01	25.03±0.74
DO	mg/L	1.41±0.27	0.87±0.07	1.15±0.19
EC	µS/cm	6423±115	1375±271	3900±195
TDS	mg/L	9015±2527	883±132	4951±1332
TSS	mg/L	786±55	283±38	536±48
TS	mg/L	15307±4252	2277±426	8795±2645
pH	-	8.23±0.06	8.06±0.04	8.14±0.05
ORP	mv	-163.7±65.98	-85.43±32.6	-124.5±37
Turbidity	NTU	36±2	132±11	86±7
COD	mg/L	4507±185	727±42	2240±127
BOD_5	mg/L	601±23	368±13	490±20
Cl	mg/L	2045±87	472±114	1255±97
Na	mg/L	1459±819	235±80	851±452
K	mg/L	1558±307	73±4	816±155
TP	mg/L	99±6	11±2	56±4
PO_4	mg/L	215±67	136±24	178±47
TKN	mg/L	681±37	47±4	370±21
TN	mg/L	816±26	68±4	440±16
NO_3	mg/L	83±5	2.87±0.35	43±3
NH_4N	mg/L	670±25	36±5	349±17
Cr	mg/L	2.17±0.12	BDL	1.08±0.06
Cu	mg/L	132±145.61	BDL	0.08±0.01
Pb	mg/L	0.2±0.03	BDL	0.08±0.01
Cd	mg/L	0.1±0.03	BDL	0.06±0.01

mg/L and 4507±185 mg/L, respectively. In typical raw leachate, the BOD5/COD ratio diminishes from 0.7 to 0.04 as it ages (Sonawane et al. 2017). The calculated BOD5/COD ratio for this leachate was 0.13, indicating that the leachate has aged, is less biodegradable, and primarily contains recalcitrant compounds. Ammoniacal nitrogen concentrations and total phosphorus were measured at 670±25 and 99±6 mg/L, respectively. Notably, this leachate's average nutrient concentrations (nitrogen and phosphorus) were higher than those reported in other studies (Cano et al. 2020, Saeed et al. 2022a, Wojciechowska 2017).

Presence of heavy metals (chromium, copper, lead and cadmium) were also detected in the leachate. On feeding the raw leachate as influent to the two microcosms the wetland plants did not survive after a period of 15 days. Hence the leachate was diluted with sewage in the ratio of 1:1.

Sewage and mixed wastewater characteristics

The characteristics of sewage collected from the Anna University Sewage Treatment Plant are presented in Table 1. The BOD5/COD ratio for the sewage is 0.506, indicating a significant presence of biodegradable organic compounds. A higher BOD5/COD ratio suggests a substantial organic content in the sewage, serving as the primary carbon source for microorganisms (Table 1).

Chemical Oxygen Demand (COD) removal

The study investigates the COD removal efficiencies of two microcosms CW and CW-MFC. The systems were operated in batch mode with different HRTs of 3, 5, and 7 days. The influent exhibited a high COD concentration of 2240 ± 127 mg/L. At a 7-day HRT, the maximum COD removal efficiencies recorded were 62% for CW and 83% for CW-MFC, with corresponding effluent COD concentrations of 850

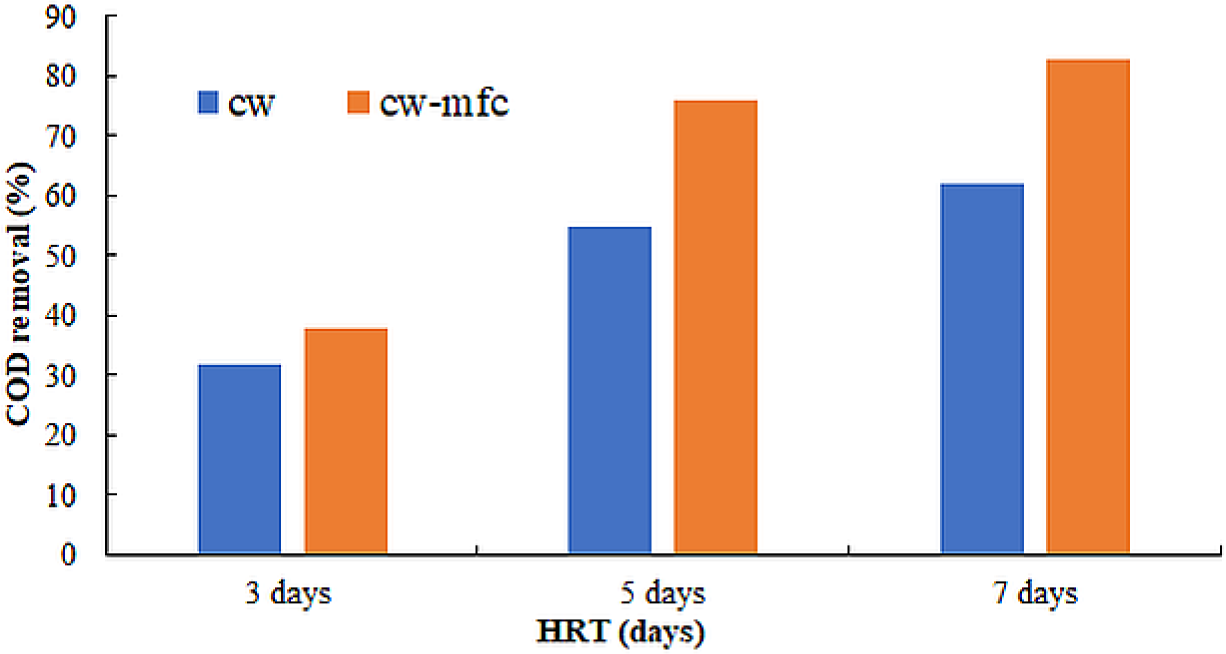

Figure 2. COD removal efficiency in CW and CW-MFC in batch flow

mg/L for CW and 380 mg/L for CW-MFC. In contrast, at a 3-day HRT, the minimum COD removal efficiencies were noted, with CW achieving 32% and CW-MFC attaining 38%. These findings indicate that treatment efficiency improves with longer HRTs, particularly in the CW-MFC, suggesting that extended retention time enhances organic removal performance. Wang et al. (2019) and Saeed et al. (2022a) noted that COD concentrations exceeding 1000 mg/L can hinder electrochemical organic decomposition at the anode, resulting in COD accumulation at the cathode. The differences in COD removal efficiencies between the two microcosms were statistically significant ($p < 0.05$), with the CW-MFC consistently outperforming the CW. These results underscore that the CW-MFC system is more effective than CW in treating leachate with high COD concentrations (Fig. 2).

In continuous mode of operation, the flowrate was maintained at 5 L/day and each microcosm treated wastewater for a period of 8 weeks. The treatment efficiencies were modest during the first week and gradually increased with more than 30% efficiency achieved during the second week. Both microcosms showed similar performance during this period, with the CW-MFC displaying a slight advantage. A significant divergence was observed from the third week onwards, with the CW-MFC consistently outperforming the CW microcosm. By the eighth week, treatment efficiencies reached 88 and 96% for CW and CW-MFC, respectively. The effluent COD values in the eighth week were recorded at 269 mg/L for CW and 90 mg/L for CW-MFC, indicating that the system can effectively treat complex wastewater. Including the MFC in the wetland resulted in an 8% increase in COD removal efficiency (Fig. 3). The presence of a closed loop electric circuit aids the COD removal. This is in line with earlier reports by (Doherty et al. 2015, Wang et al. 2019). These results affirm that CWs integrated with MFC can treat very high COD concentrations such as from recalcitrant leachate. Doherty et al. (2015) showed that the pathway for recalcitrant organics removal at the anode is as electrons acceptor while bio degradable organics removed at the anode as electrons donor. Though the pathways are different, these studies indicate that CW MFC can be used to treat high concentration leachate. Similarly, in case of BOD5, the influent concentration was 490+20 mg/L. A removal efficiency of 75% was obtained for CW microcosm while the CW-MFC had a removal efficiency of 81%.

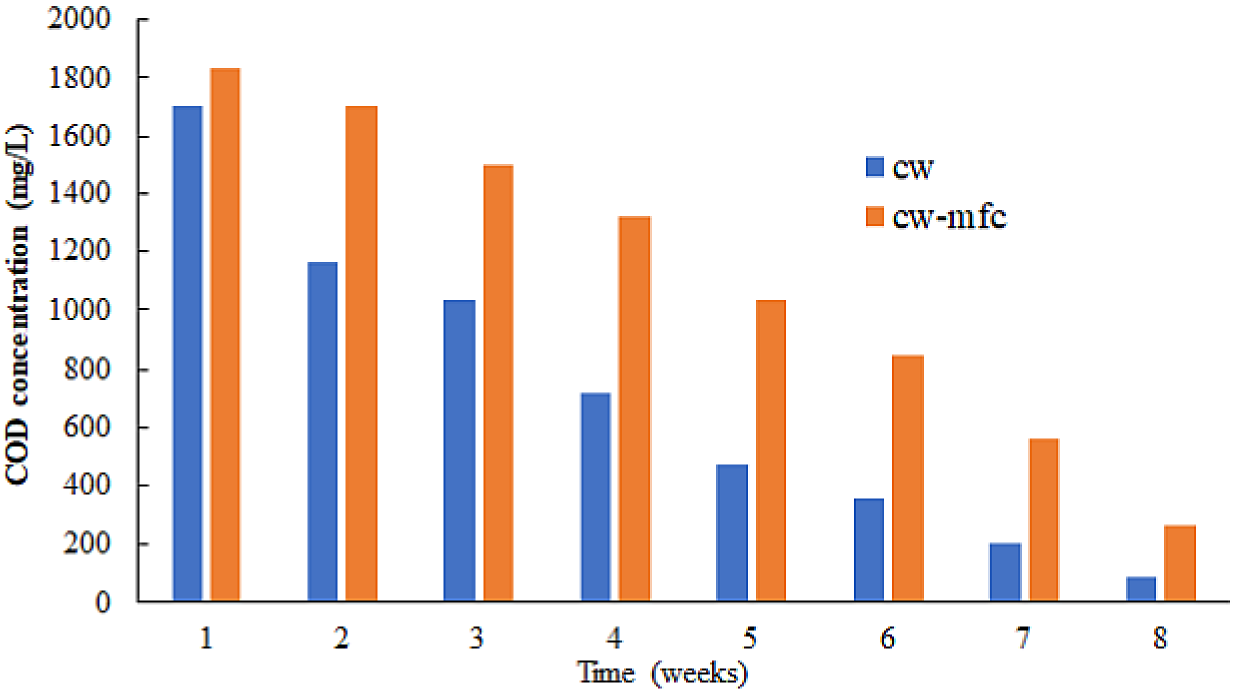

Figure 3. The concentration of COD in the effluent of CW and CW-MFC in a continuous flow

pH, DO and ORP

The influent pH during both batch and continuous modes of operation was slightly alkaline, with a notable reduction in pH observed in the effluent. These pH changes in constructed wetlands (CWs) can be attributed to alkalinity consumption and organic matter degradation. High Redox potential (Eh) of -125 mv with a low DO concentration of 1.15 mg/L indicating an anoxic/anaerobic condition in the influent (Fig. 4). In batch mode, with a 7-day hydraulic retention time (HRT), the effluent redox potential ranged from -32 to -40 mV, which still reflected anaerobic conditions, suggesting that a longer residence time was necessary for complete reduction at the anode. However, in continuous mode of operation, the effluent redox potential improved significantly, measuring between +64 to +67 mV, alongside an enhanced DO concentration of 4.4 to 5.1 mg/L observed in both systems during the eighth week. This increase in redox potential and DO in the effluent signifies that complete oxidation and reduction processes occurred at both the anode and cathode. The anode donates electrons to the cathode via the external circuit, while protons migrate to the cathode through the glass wool membrane to facilitate complete oxidation. A redox gradient is essential in a CW-MFC, as it creates the environment for pollutant removal and bioenergy generation.

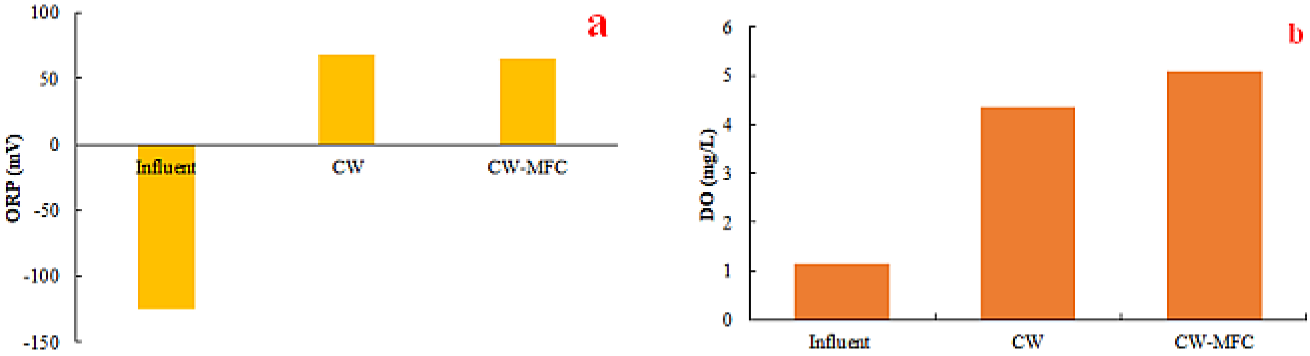

Figure 4. (a) Redox potential and (b) DO concentration in the influent and effluent of CW and CW-MFC

Previous studies have shown that planted CWs with continuous flow generate a more significant redox gradient than unplanted continuous or batch flow systems (Corbella et al. 2014). The primary pathways for oxygen in CWs include atmospheric diffusion and root exudates from plants, referred to as Radial Oxygen Loss (ROL). This seepage of oxygen acts as an electron donor at the cathode, playing a crucial role in the reduction reactions. An increase in the effluent's oxygen levels (DO) indicates a complete reduction at the cathode.

Removal of heavy metals

The comprehensive synergy of adsorption of media, plant uptake, microbial consumption, and electrochemical reactions is crucial in removing heavy metal pollutants in constructed wetland microbial fuel cells (CW-MFCs). In the leachate, heavy metals such as Chromium (Cr), Copper (Cu), Lead (Pb), and Cadmium (Cd) were identified, with influent concentrations recorded at 1.08, 0.08, 0.08, and 0.06 mg/L, respectively. The removal efficiencies for conventional constructed wetlands (CW) were 54% for Cr, 56% for Cu, 66% for Pb, and 50% for Cd. In contrast, the CW-MFC system achieved removal efficiencies of 63% for Cr, 64% for Cu, 68% for Pb, and 65% for Cd. These results demonstrate that the CW-MFC system exhibits slightly higher removal efficiencies for all four heavy metals than the traditional CW system.

Nutrient removal

The influent concentrations of BOD5, TN, TKN, and NO_3 were measured at 490 ± 20, 440 ± 16, 370 ± 21, and 43 ± 3 mg/L, respectively. In the constructed wetland (CW) microcosm, removal efficiencies of 75, 54, 54, and 61% were achieved for BOD5, TN, TKN, and NO_3, respectively. In comparison, the constructed wetland-microbial fuel cell (CW-MFC) demonstrated removal efficiencies of 81, 61, 59, and 68% for the same parameters (Fig. 6). In constructed wetlands, nitrogen removal through nitrification and denitrification is a significant process for treating wastewater. These processes involve complex biochemical reactions with various microorganisms and are influenced by environmental conditions. Nitrification occurs in two main aerobic steps. First, ammonium oxidation takes place, where ammonium nitrogen (NH_4–N) is converted to nitrite nitrogen (NO_2–N) by Ammonia-Oxidizing Bacteria (AOB). In the second step, nitrite oxidation occurs, in which nitrite is further oxidized to nitrate nitrogen (NO_3–N) by Nitrite-Oxidizing Bacteria (NOB), such as Nitrobacter (Soundaranayaki et al. 2020, Kannan and

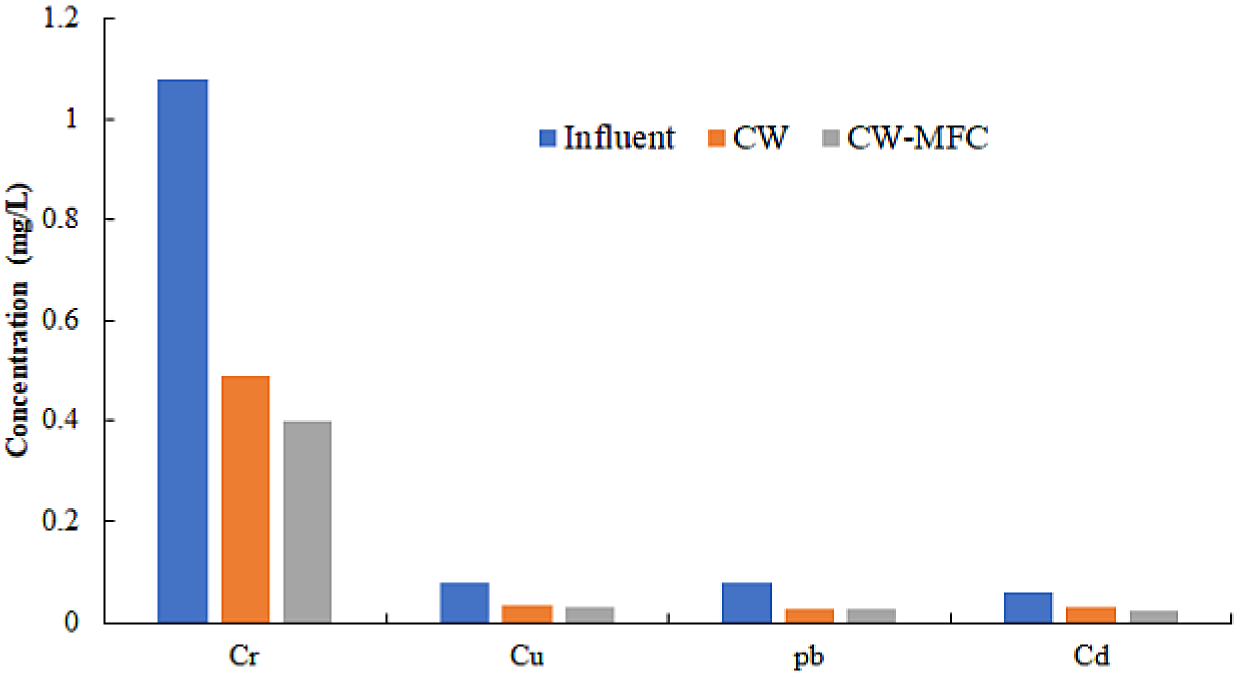

Figure 5. Heavy metal concentration in the influent and effluent of CW and CW-MFC

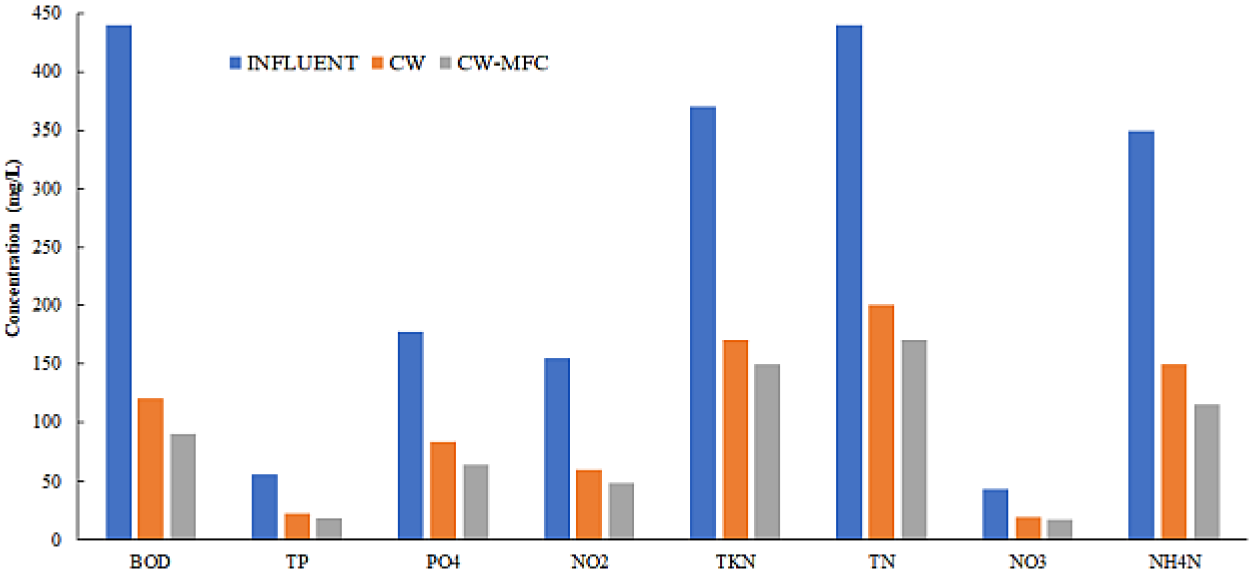

Figure 6. Concentration of Nutrients in the influent and effluent of CW and CW-MFC

Parameswaran 2021). The efficiency of nitrification depends on several factors, including the presence of oxygen, pH levels, temperature, and the availability of substrate (NH_4–N). Adequate oxygen levels are essential, as nitrifying bacteria are obligate aerobes that require oxygen for survival and metabolic function (Soundaranayaki et al. 2019). Macrophytes, or aquatic plants, transport oxygen from the atmosphere to their root zones. The oxygen released into the rhizosphere is referred to as Radial Oxygen Loss (ROL), an essential factor in promoting nitrification within constructed wetlands. The levels of ROL can range from 0.02 to 0.8 g O_2 /m², depending on factors such as plant species, root morphology, and environmental conditions (Vymazal 2011). Nitrate emerges as a viable candidate for use as an electron acceptor in constructed wetland microbial fuel cells (CW-MFCs), as MFCs can enhance both nitrification and denitrification processes (Wang et al. 2017). This approach offers an additional strategy for improving nitrogen removal in constructed wetlands. Integrating an MFC within a constructed wetland optimizes the nitrification and denitrification processes. In the cathodic region, oxygen seepage from the rhizosphere enhances ammonium oxidation, forming NO_3–N. When a sufficient carbon source is available, the produced NO_3–N can be eliminated through heterotrophic denitrification. In the CW-MFC, electrochemically active bacteria colonize the vicinity and surface of the anode, thereby accelerating the denitrification process via direct electron transfer (Corbella et al. 2015, Lu et al. 2015). In this study, the CW-MFC nitrate removal efficiency was 30% higher than that of the conventional wetland, demonstrating effective nitrification-denitrification processes for complete nitrogen removal. The influent's total phosphate and phosphate (PO_4) concentrations were recorded at 56 and 17811 mg/L, respectively, with removal efficiencies of 59% and 52% for CW and 67% and 64% for CW MFC. These results are comparable to the total phosphorus removal efficiencies typically observed in traditional vertical-flow CWs (59-71%) (Zhao et al. 2010). Effective phosphorus removal in constructed wetlands relies on media-based adsorption, where the media surface has the capacity to retain phosphorus, and plant uptake, where phosphorus is an essential nutrient for plant growth, are important phenomena for effective phosphorus removal in constructed wetlands (Ge et al. 2020, Saeed et al. 2022b). ANOVA results indicated that there was no statistically significant difference between the CW and CW-MFC systems (F = 2.28, p = 0.153). All variables were tested and confirmed to be normally distributed. Statistical significance was

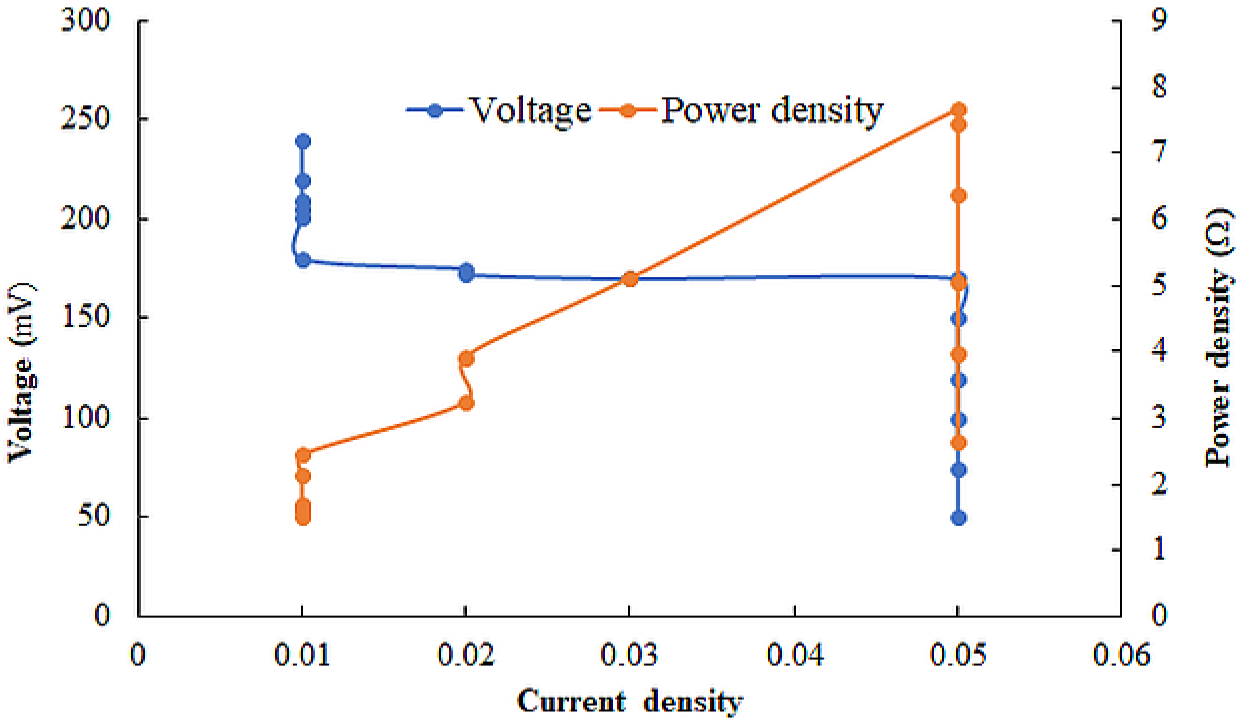

Figure 7. Polarisation curve for CW-MFC

determined at a threshold of $p < 0.05$.

Electricity generation and polarisation curve

During the experimental period with continuous flow, the mean output voltage from the CW-MFC was recorded at 173.545 mV, reaching a maximum of 240 mV (Fig. 7). The average power density, normalized to the anode area with an external resistance of 1000 Ω, was 3.78 mW/m^2, while the maximum power density reached 5.3 ± 1.2 mW/m^2. This average power density is comparable to findings from studies involving other types of wastewater (Zhao et al. 2013, Huang et al. 2021). The power output of the CW-MFC is influenced by various factors, including microbial activity, the type of wetland plants, hydraulic retention time (HRT), system arrangement, and materials used in the wetland setup (Saeed et al. 2022a). The polarization curve for the CW-MFC was established by varying the external resistance from 50 to 2000 Ω, during which the output voltage was measured. This curve exhibited distinct regions of active polarization at low power densities, significant ohmic losses at moderate current densities, and a marked voltage drop at high current densities (Fig. 7).

Although no relation can be seen between COD reduction and power density, the high COD content of the influent seems to have affected the power density. A notably low Coulombic Efficiency (CE) appears to impact current production (Fig. 8). It is crucial to find a balance between providing sufficient organics for oxidation at the anode and minimizing the amount of COD that reaches the cathode (Zhao et al. 2013). Liu et al. (2014) reported that increasing the COD levels beyond 1000 mg/L can decrease power density. Higher COD loading increases the likelihood of a significant amount of organic molecules arriving at the cathode, reducing oxygen availability in that region for reduction processes. An increase in COD at the cathode may potentially lead to the development of a heterotrophic biofilm on the cathode, which may limit the mass transfer processes (Freguia et al. 2008). Villasenor et al. (2013) observed that when COD levels exceed 560 mg/L, the dissolved oxygen (DO) concentration at the cathode drops to nearly zero, accompanied by a decline in redox potential. In scenarios where COD is above 560 mg/L, only 80-85% reduction occurs at the anode, with the remaining COD transferred to the cathode, leading to a decrease in CE. The

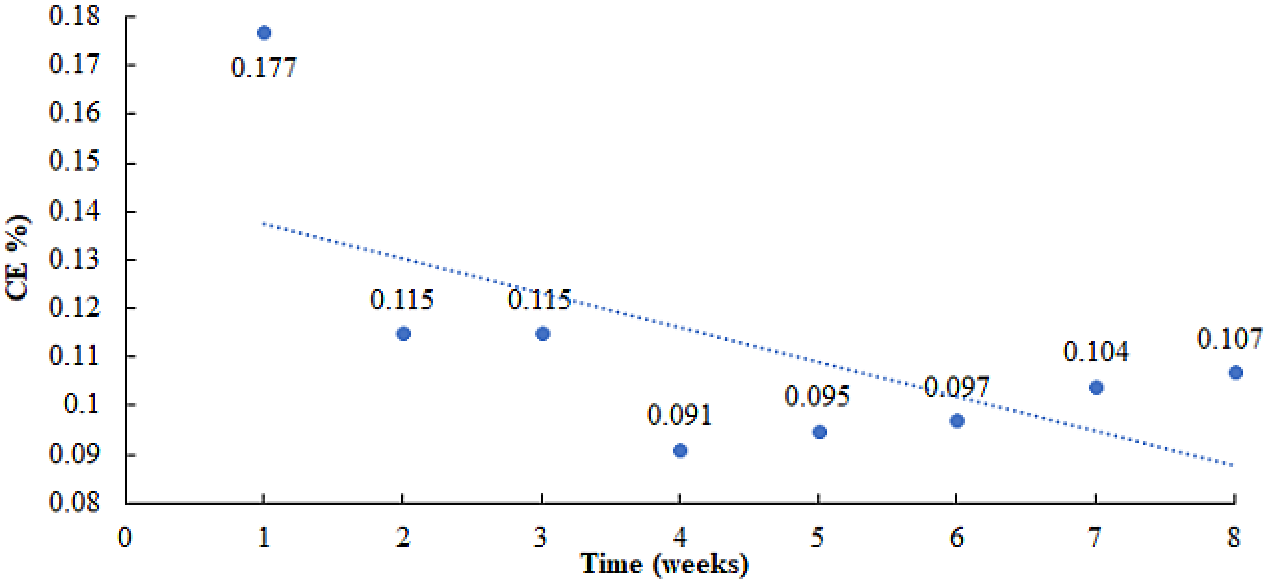

Figure 8. Coulombic efficiency (%) with time

presence of diverse microorganisms in complex wastewater may further diminish the system's CE (Doherty et al. 2015). These microorganisms decompose organic matter to produce electrons utilized in a CW-MFC for electricity generation.

Every single electron produced is utilized to generate energy, although some are lost due to processes such as aerobic respiration and methanogenesis, among various other biological activities. These processes typically result in a low Coulombic Efficiency (CE), ranging from 0.7 to 8.1% (Debabov 2008). These factors may have contributed to the reduced CE observed in this system. Nevertheless, the microbial fuel cell (MFC) has led to a 4% improvement in reducing chemical oxygen demand (COD) in this complex wastewater.

CONCLUSIONS

It was made to integrate constructed wetlands (CW) with microbial fuel cells (MFC) to assess their performance in treating landfill leachate compared to conventional CW methods. Unfortunately, the microcosms struggled, resulting in plant die-off within a week. This was probably due to the recalcitrant nature of the leachate with very high COD levels (4507±185 mg/L). To address this, the leachate was diluted with raw sewage at a 1:1 ratio and utilized as an influent for the research. Both systems demonstrated effective COD removal in batch trials, achieving removal efficiencies of 62% for CW and 83% for CW-MFC at a 7-day hydraulic retention time (HRT). Extending the resident time could enhance treatment efficiency. During continuous operation, both systems exhibited impressive treatment efficiencies of 96% for CW-MFC and 88% for CW.

The effluent COD values recorded were 90 mg/L for the constructed wetland (CW) and 269 mg/L for the CW-integrated microbial fuel cell (CW-MFC). These findings demonstrate the system's capability to treat complex wastewater. An increase of 8% COD removal efficiency was attained by including the MFC in the wetland. High removal efficiencies of 66 and 61% were noticed for sodium and potassium in CW and CW-MFC. The mean output voltage from the CW-MFC was 173.54 mV, with a peak of 240 mV. The average power density when normalised to the anode area was 3.78mW/m^2 with highest power density of 5.3mW/m^2. This performance is considerably lower than that observed in other constructed wetlands treating different types of wastewater, likely influenced by the high COD content of the influent. The very low coulombic efficiency of 0.17% has also hindered current production. Consequently, it is evident that COD loading significantly impacts CW-MFC performance. Striking a balance between providing adequate organic materials for oxidation at the anode and minimizing the COD reaching the cathode is crucial. Additionally, enhancing the electrode surface and increasing its area could improve the physical and chemical properties, optimizing microbial adhesion and electron transfer. Improved microbial attachment to the electrode facilitates the electron transfer process, which may enhance current production and the overall efficiency of the MFC. These results indicate that constructed wetlands can successfully treat high COD leachate, and integrating MFC with CW can modestly improve the treatment along with moderate power generation.

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