Research Article

Power Generation Enhancement by Utilizing Plant Photosynthate in Microbial Fuel Cell Coupled Constructed Wetland System

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Received 27 June 2013; Accepted 31 August 2013

Academic Editor: Manickavachagam Muruganandham

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In the present study, a new technology that coupled constructed wetland (CW) with microbial fuel cell (MFC) (CW-MFC) was developed to convert solar energy into electricity on the principles of photosynthetic MFC by utilizing root exudates of *Ipomoea aquatica* as part of fuel. The maximum power density of 12.42 mW m^{-2} produced from the CW-MFC planted with *Ipomoea aquatica* was 142% higher than that of 5.13 mW m^{-2} obtained from the unplanted CW-MFC. The maximum power output for the planted CW-MFC could be divided into two parts: the maximum power yield from COD_R in the water body was $66.05 \text{ KJ Kg}^{-1} \text{ COD}_R$, and the maximum power transformation from plant photosynthesis was $2.31 \text{ GJ ha}^{-1} \text{ year}^{-1}$. The average COD removal efficiencies were 92.1% and 94.8% in the unplanted CW-MFC and planted CW-MFC, respectively; the average TN removal efficiencies amounted to 54.4% and 90.8% in the unplanted CW-MFC and planted CW-MFC. This research demonstrates that planting *Ipomoea aquatica* in the CW-MFC achieved a higher power density and nutrient removal of nitrogen simultaneously.

1. Introduction

A microbial fuel cell (MFC) is a bioelectrochemical 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 [1–3]; especially, in the past decade, there has been a remarkable promotion of MFC performance through a large variety of methods, including advancement of fuel cell configuration [4, 5], selection and modification of electrode material [6–8], and adoption of cheap proton exchange membrane with high conductivity efficiency [9, 10]. Besides, novel technologies in generating power by integrating photosynthesis with microbial fuel cells (photosynthetic MFC) have been researched and significant progress has been made [11–14]. The photosynthetic MFC operates to generate sufficient electric current from sunlight with either electrocatalysts or heterotrophic bacteria on the anode to convert photosynthetic products indirectly [15], and the photosynthesis could be carried out by plants, algae, or

some photosynthetic bacteria. The photosynthetic MFC can produce electricity without the external input of exogenous organics or nutrients, but it is often restricted by sunlight and its power density is still too low for practical applications.

Wetland treatment of wastewater has been widely practiced in several countries for many years due to its easy maintenance, low cost, and good self-purification capacity; moreover, it provides great quantities of biomass production by photosynthesis [16]. A well-designed microbial fuel cell inside a constructed wetland system may combine the advantages of the photosynthesis of wetland plants and electricity generation of electroactive microorganisms to transform solar energy into electricity. The first lab-scale CW-MFC was designed and operated to evaluate the effect of configuration on power production [17], and it also showed good wastewater treatment effect with simultaneous power generation. As the constructed wetland has the ability of degradation of refractory organic matter, the CW-MFC system had great advantages in treating dye containing wastewater [18].

The concept of CW-MFC is based on constructed wetland and plant MFC (one form of photosynthetic MFC), of which all contain plants. The role of plants is important in the CW-MFC system, including their role in excreting oxygen and organic matter into the rhizosphere [19], supporting a wide range of microbes and providing a surface for bacterial attachment [20]. These unique characteristics may make the CW-MFC system an ideal approach to generate electricity at sites and reduce globing warming as they can decrease methane emissions. However, the effect of plant photosynthesis and plant rhizosphere microorganisms on the power enhancement for the CW-MFC has not been studied fully yet.

In this study, we built a single-chamber, membrane-free, continuously feeding upflow microbial fuel cell coupled with constructed wetland, in which the cathode is located in overlying water to use oxygen from air for reduction reactions, and the anode is submerged in a support matrix near the rhizosphere to obtain organic substrates in the influent or deprived from wetland plants root as fuel. The aim of this study was to evaluate whether or not the wetland plant (*Ipomoea aquatica*) can improve power generation in a CW-MFC system and to explore the bacterial population in the electrode biofilm in response to MFC performance. Meanwhile, investigations of the removal efficiencies of chemical oxygen demand (COD) and total nitrogen (TN) were carried out.

2. Experimental

2.1. CW-MFC Construction. As schematically shown in Figure 1, two CW-MFC reactors were constructed in the same way using a polycarbonate plastic cylinder (30 cm in diameter and 50 cm in height). The bottom 20 cm was support matrix composed of gravel (gravel diameter 3–6 mm), and then upwards it consisted of anode, support matrix (20 cm gravel), and cathode. The anode was constructed from 10 cm thick granular activated carbon (GAC, a diameter of 3–5 mm, the specific area of 500–900 m² g⁻¹ and the filling density of 0.45–0.55 g cm⁻³). GAC was pretreated by soaking in 1 M NaOH and 1 M HCl to eliminate possible oil stain and metal ion contamination, respectively. The cathode was made from stainless steel mesh (a diameter of 25 cm, thickness of 0.3 cm, 12 mesh) buried in 2 cm thick layer of activated carbon particle. The electrode spacing was 25 cm (center of the anode to the face of the cathode). Electrodes were connected to a circuit using titanium wires across an external resistance of 1000 Ω , and epoxy was used to seal metals exposed to the solution. Nine adult plants of *Ipomoea aquatica* were planted through the upper layer of one CW-MFC device (planting density about 32 plants m⁻²), and the other CW-MFC was a control with no plants. The volume of the whole container was 35.3 L with a total liquid volume of 12.4 L.

2.2. CW-MFC Operation. The CW-MFCs were inoculated with the anaerobic sludge from a wastewater treatment plant located in Jiangning Development Zone (Nanjing, China) and operated by continuous feeding at a flow

FIGURE 1: Schematic of the CW-MFCs used in the experiment.

rate of 4.31 mL min⁻¹ corresponding to a hydraulic retention time (HRT) of 2 d. The feed solution consisted of 50 mM phosphate buffer solution (PBS) with pH 7.4, glucose (0.20 g L⁻¹), NH₄Cl (0.15 g L⁻¹), KCl (0.13 g L⁻¹), NaHCO₃ (3.13 g L⁻¹), and 1 mL L⁻¹ trace essential elements solution (contained per liter: 5.6 g (NH₄)₂SO₄, 2 g MgSO₄·7H₂O, 200 mg MnSO₄·H₂O, 3 mg H₃BO₃, 2.4 mg CoCl₂·6H₂O, 1 mg CuCl₂·2H₂O, 2 mg NiCl₂·6H₂O, 5 mg ZnCl₂, 10 mg FeCl₃·6H₂O, and 0.4 mg Na₂MoO₄·2H₂O). All experiments were carried out in a 12:12-h light/dark cycle at 26 ± 2°C under greenhouse conditions. The ambient light was provided by artificial illumination using (light-emitting diode LED) Grow Lights (14 W, GC-ZW225S-P, Gechuang Electronics Co., Ltd, Shenzhen, China), and the average light intensity was 1000 lux during the light phase.

2.3. Fluorescent In Situ Hybridization (FISH). FISH analysis was applied to investigate the quantity of microorganisms on the anode and cathode in our study. Granular activated carbon with attached biofilm (wet weight of 0.5 g) was multisampled (parallel samples) and suspended in 5 mL sterile deionized water, and microorganism cells were detached from the GAC and uniformly dispersed in the solution with ultra-sonic oscillations treatment. About 0.5 mL supernatant

TABLE 1: Probe name and probe sequence used for FISH analysis.

Probe	Target microflora	Probe sequence	References
EUB338	<i>Bacteria</i>	GCTGCCTCCCGTAGGAGT	[21, 22]
GEO2	<i>Geobacter sulfurreducens</i>	GAAGACAGGAGGCCGAAA	[23]
HGEO2-1	Helper probes for GEO2	GTCCCCCCTTTTCCCGCAAGA	[23]
HGEO2-2	Helper probes for GEO2	CTAATGGTACGCGGACTCATCC	[23]
BET42a	<i>Betaproteobacteria</i>	GCCTTCCCACTTCGTTT	[24]

after ultrasonic oscillations was shifted and suspended in phosphate-buffered saline solution (PBS, pH 7.4) consisting of 8 g L^{-1} NaCl, 0.2 g L^{-1} KCl, 1.44 g L^{-1} Na_2HPO_4 , and 0.24 g L^{-1} K_2HPO_4 in distilled water. Then the samples were fixed with 4% paraformaldehyde (in PBS) at 4°C for 24 h. The fixed samples were washed twice with PBS, and suspended in a solution of 50% PBS, and 50% ethanol and stored at -20°C . For FISH, $10 \mu\text{L}$ of the fixed sample was applied on a glass slide dried for 2 h at 37°C and subsequently dehydrated with ethanol at 50, 80, and 96% (v/v, in 10 mM Tris-HCl, pH 7.5) during 3 min at each concentration. To start hybridization, $24 \mu\text{L}$ of hybridization buffer and $1 \mu\text{L}$ of fluorescently labeled probe (50 ng mL^{-1}) were added. The hybridization was conducted for 5 h at 46°C in a humidified chamber. Slides were then washed in a buffer solution (60 mM NaCl, 20 mM Tris-HCl, pH 8.0, 0.1% SDS) at 45°C for 20 min.

In the FISH procedure, target microflora and oligonucleotide probes used were shown in Table 1. Hereinto, *Geobacter sulfurreducens* and *Betaproteobacteria* have been evaluated for the potential for current production. Microscopy was performed on an Olympus BX50 microscope, equipped with filters HQ-CY3 (Analysentechnik AG, Tübingen, Germany). The bacterial number on each image was counted, and then the bacterial density (D_b) of each biofilm cathode was calculated from the following equation:

$$D_b = \frac{1000NS_1}{MS_2}, \quad (1)$$

where S_1 , S_2 , and M represent the coating area, the image area, and the sample weight (g), respectively, and N is the average bacterial number on each image (cells). All cell density data shown in this paper were statistical average values.

2.4. Measurement and Analysis. The cell voltage was recorded every 30 min by a data acquisition system (USB120816, Hytek Automation, Inc., Shanghai, China). The cell potentials were measured against a saturated Ag/AgCl (S) electrode. Polarization curves were obtained in the daytime (high peak voltage) by varying the external resistor over a range from 5Ω to $10^5 \Omega$ (10^5 , 4000, 3000, 2000, 1000, 800, 600, 400, 200, 100, 75, 50, 25, 10, and 5Ω) to monitor the output voltage. The current (i) was calculated from Ohm's law as shown in (2), and the power density (P , area power density) was calculated as shown in (3), where E is the voltage, R is the external resistance, and A is the anode area. The ohmic resistance (R_Ω) of each system was determined using the current interrupt technique [25], and R_Ω was calculated as shown in (4).

E_R is a steep potential rise when the current is interrupted, and E_{OCV} is the open circuit voltage:

$$i = \frac{E}{R}, \quad (2)$$

$$P = \frac{E^2}{RA}, \quad (3)$$

$$R_\Omega = \frac{E_R}{i} = \frac{(E_{OCV} - E)R}{E}. \quad (4)$$

Chemical oxygen demand (COD), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), nitrite nitrogen ($\text{NO}_2^-\text{-N}$), and nitrate nitrogen ($\text{NO}_3^-\text{-N}$) were performed in accordance with the Standard Methods of American Public Health Association (APHA, 1998), and all the samples for chemical analysis were filtered through a $0.45 \mu\text{m}$ pore diameter syringe filter to remove particles. Total nitrogen (TN) concentration was calculated as the sum of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$. Dissolved oxygen (DO) concentration was measured *in situ* by the DO probe (ORION 3 STAR, Thermo Co., USA). All measurements were made at least three times and the average values with standard deviations are presented in the figures.

Specific power yield (SPY) was obtained by dividing power generated (P_V , volume power density) with the substrate (COD) removed as shown in (5) [26], where V is the total liquid volume of the CW-MFC, COD_{in} the influent COD and COD_{out} the effluent COD. The power yield (PY) was calculated as shown in (6), and it implicates the power output per kilogram of organic substrate (COD_R) in the water body:

$$\text{SPY} = \frac{P_V}{\text{COD}_R} = \frac{E^2}{(\text{COD}_{in} - \text{COD}_{out})RV}, \quad (5)$$

$$\text{PY} = \text{SPY} \times \text{HRT}. \quad (6)$$

3. Results

3.1. Power Output. The two CW-MFCs were operated for more than 1 month to obtain a stable performance before the determination of cell voltage. Figure 2(a) shows voltage outputs from the planted CW-MFC and unplanted CW-MFC electricity-generating systems from May 3 to June 10. At the initial stage (1–8 days), the trough voltages of the planted CW-MFC (0.51–0.53 V) were close to the mean voltage of the unplanted CW-MFC (0.50 V). As *Ipomoea aquatica* was adapted to the experimental environment, the peak and trough voltages of the planted CW-MFC increased gradually (8–26 days) and remained stable (26–40 days).

FIGURE 2: Continuous records of voltage with a fixed external load of $1000\ \Omega$ for the planted CW-MFC and unplanted CW-MFC. (a) A daily record of voltages at 0:00 (night through time) and 12:00 (day peak time) from May 3 to June 10; (b) half-hourly records of voltages from June 12 to June 16.

As shown in Figure 2(b), the voltage for the planted CW-MFC was characterized by diurnal oscillations with clear fluctuations, but no such circadian oscillation was observed for the unplanted CW-MFC. As temperatures were relatively stable throughout the experiments, the observation implied that the cyclical fluctuation of voltage for the planted CW-MFC was closely related to the sunlight. From June 12 to June 16, the electric output was stable, and the average voltages in the planted CW-MFC and unplanted CW-MFC were 0.64 and 0.49 V, respectively. Therefore, it was calculated that the average power outputs for the planted CW-MFC and unplanted CW-MFC were 0.129 and $0.076\ \text{GJ ha}^{-1}\ \text{year}^{-1}$, respectively. Taking into account the consistency of the influent condition and the culture environment in the two CW-MFCs, the power output about $0.053\ \text{GJ ha}^{-1}\ \text{year}^{-1}$ was generated from plant photosynthetic products in the planted CW-MFC.

3.2. Fuel Cell Behavior. The performance of the planted CW-MFC was depicted and compared with the unplanted CW-MFC in terms of power density curves and polarization curves. It can be seen from Figure 3 that planting *Ipomoea aquatica* in CW-MFC effectively enhanced the electricity generation. The open circuit voltages of the planted CW-MFC and unplanted CW-MFC were 0.74 and 0.62 V, respectively, and the maximum power density of the planted CW-MFC was $12.42\ \text{mW m}^{-2}$, 2-folds more than that of the unplanted CW-MFC ($5.13\ \text{mW m}^{-2}$). Maximum power outputs of the planted CW-MFC and unplanted CW-MFC were 3.92 and $1.61\ \text{GJ ha}^{-1}\ \text{year}^{-1}$, respectively. According to (3), the internal resistances of the planted CW-MFC and unplanted CW-MFC were 156 and $256\ \Omega$, respectively.

3.3. Relation of Electrode Potentials and Cell Density on the Electrode. It was demonstrated that the catalytic activity of the electrode positively correlates with biomass [27]. To verify the hypothetical inference, electrode potentials and cell densities in various GAC electrodes zone were determined (Figure 4). The average cathode potential ($299\ \text{mV}$) of the planted CW-MFC was higher than that of the unplanted

FIGURE 3: Polarization curves of the planted CW-MFC and unplanted CW-MFC (solid symbols for the cell voltage and open symbols for the power density).

CW-MFC ($202\ \text{mV}$) (Figure 4(a)), and the average anode potential ($-341\ \text{mV}$) of the planted CW-MFC was lower than that of the unplanted CW-MFC ($-288\ \text{mV}$) (Figure 4(b)). As shown in Figure 4(a), the average *bacteria* density in cathodic biofilms of the planted CW-MFC ($3.85 \pm 0.61 \times 10^7\ \text{cells g}^{-1}$) was higher than that of the unplanted CW-MFC ($2.43 \pm 0.40 \times 10^7\ \text{cells g}^{-1}$). From Figure 4(b), it was clearly observed that cell densities of *bacteria*, *G. sulfurreducens*, and *Betaproteobacteria* in anodic biofilms of the planted CW-MFC ($8.66 \pm 1.01 \times 10^7\ \text{cells g}^{-1}$, $1.22 \pm 0.18 \times 10^7\ \text{cells g}^{-1}$, and $0.91 \pm 0.13 \times 10^7\ \text{cells g}^{-1}$) were also higher than that of the unplanted CW-MFC ($5.13 \pm 0.86 \times 10^7\ \text{cells g}^{-1}$, $0.67 \pm 0.11 \times 10^7\ \text{cells g}^{-1}$, and $0.48 \pm 0.09 \times 10^7\ \text{cells g}^{-1}$). The results indicated that the cathode potential showed a positive correlation with the microbial amount,

FIGURE 4: Electrode potential and cell density in electrodes zone for the planted CW-MFC and unplanted CW-MFC: (a) cathode zone and (b) anode zone.

but a negative correlation between the anode potential and microbial amount was observed.

3.4. Waste Treatment. Throughout the experimental stage, the influent chemical oxygen demand (COD) and total nitrogen (TN) reached to the ranges of $193\text{--}205 \text{ mg L}^{-1}$ and $31\text{--}39 \text{ mg L}^{-1}$, respectively. More or less, the same COD removal efficiency (planted CW-MFC, 94.8%; unplanted CW-MFC, 92.1%) was noticed with both the CW-MFCs, but SPY (planted CW-MFC, $0.178 \text{ W Kg}^{-1} \text{ COD}_R$; unplanted CW-MFC, $0.107 \text{ W Kg}^{-1} \text{ COD}_R$) and PY (planted CW-MFC, $30.67 \text{ KJ Kg}^{-1} \text{ COD}_R$; unplanted CW-MFC, $18.51 \text{ KJ Kg}^{-1} \text{ COD}_R$) showed that the CW-MFC planted with *Ipomoea aquatica* had higher power productivity efficiency. Unlike the COD removal efficiency, a great difference in the TN removal efficiency (planted CW-MFC, 90.8%; unplanted CW-MFC, 54.4%) was observed.

In order to ascertain the reason for the difference of TN removal efficiencies between the CW-MFCs, the concentration of DO and various forms of nitrogen along the reactor height were investigated in the day time. DO had a “V” type change in both the planted CW-MFC and unplanted CW-MFC (Figure 5). The concentration of DO decreased gradually with the increase of reactor height till it reached 30 cm due to the consumption of O_2 , and then it increased with the increase of reactor height because of the reoxygenation. The lowest concentrations of DO were in the anode zone, and they were $0.15\text{--}0.38 \text{ mg L}^{-1}$ and $0.11\text{--}0.31 \text{ mg L}^{-1}$ for the planted CW-MFC and unplanted CW-MFC, respectively. The maximum differentiation of DO occurred at height of 40 cm, and the concentrations of DO were 3.10 mg L^{-1} and 1.37 mg L^{-1} for the planted CW-MFC and unplanted CW-MFC, respectively. The effluent had

FIGURE 5: The change of DO in the planted CW-MFC and unplanted CW-MFC.

the highest DO of 4.56 mg L^{-1} and 3.79 mg L^{-1} , respectively, for the planted CW-MFC and unplanted CW-MFC. Furthermore, diurnal variation of DO in cathode zone for the planted CW-MFC was higher ($4.31 \pm 0.18 \text{ mg L}^{-1}$) in the day and lower ($3.85 \pm 0.14 \text{ mg L}^{-1}$) at night.

Figures 6 and 7 present the change curves of different forms of nitrogen in the planted CW-MFC and unplanted CW-MFC, respectively, over a period of 13 days. The concentration of TN and $\text{NH}_4^+\text{-N}$ declined continuously with water flows in both the two CW-MFCs. TN concentrations

FIGURE 6: The change of different forms of nitrogen in the planted CW-MFC.

FIGURE 7: The change of different forms of nitrogen in the unplanted CW-MFC.

decreased drastically from 35.00 mg L⁻¹ to 3.22 mg L⁻¹ in the planted CW-MFC, but there was a less decrease from 35.00 mg L⁻¹ to 15.96 mg L⁻¹ in the unplanted CW-MFC. Comparing the change curve of TN for the two CW-MFCs, there were similarities that TN removal was less in the bottom region (0–20 cm) and more in the central region (20–30 cm), but there was a great difference in the top region (30–50 cm) that TN removal in the planted CW-MFC (from 22.50 mg L⁻¹ to 3.22 mg L⁻¹) was much higher than that in the unplanted CW-MFC (from 21.70 mg L⁻¹ to 15.96 mg L⁻¹). The removal efficiencies of NH₄⁺-N for the planted CW-MFC and unplanted CW-MFC were 96.51% and 64.86%,

respectively. In the planted CW-MFC, there were two sharp descending regions for NH₄⁺-N removal: NH₄⁺-N decreased from 35.00 mg L⁻¹ to 26.30 mg L⁻¹ at the bottom of 0–10 cm and from 19.80 mg L⁻¹ to 4.30 mg L⁻¹ at the top of 30–40 cm. However, in the unplanted CW-MFC, NH₄⁺-N only decreased sharply from 35.00 mg L⁻¹ to 25.60 mg L⁻¹ at the bottom of 0–10 cm, and then it began to descend smoothly.

In the planted CW-MFC, the accumulated NO₂⁻-N concentration gradually increased from 0 mg L⁻¹ in the influent to the maximal 6.30 mg L⁻¹ at height of 10 cm, but it decreased slowly to 0.70 mg L⁻¹ in the effluent. The same change rules of NO₂⁻-N were observed in the unplanted CW-MFC, but the concentration of NO₂⁻-N in the effluent was slightly higher about 1.56 mg L⁻¹. The change of NO₃⁻-N can be divided into four stages in the planted CW-MFC, taking on the trend of rising first, dropping, then rising and dropping, namely, two inverse “V” type curves, and the maximal NO₃⁻-N concentrations were 3.5 mg L⁻¹ and 5.7 mg L⁻¹ at the height of 20 cm and 40 cm, respectively. However, only a flush of NO₃⁻-N concentration from 0 mg L⁻¹ to 3.70 mg L⁻¹ was observed in the bottom region in the unplanted CW-MFC, and then the concentration gradually decreased to 1.70 mg L⁻¹ at the height of 30 cm, and it changed little in the top region.

Under aerobic conditions, NH₄⁺-N could be oxidated to NO₂⁻-N and NO₃⁻-N by nitrococcus and nitrobacteria, and the increase in NO_x⁻-N concentration (sum of NO₂⁻-N and NO₃⁻-N) and the decrease in the NH₄⁺-N concentration were significantly correlated with DO in the bottom region both in the two CW-MFCs ($P < 0.01$). But the increase in NO_x⁻-N concentration and the decrease in the NH₄⁺-N concentration at height of 30–40 cm in the planted CW-MFC were generally correlated with DO ($P < 0.05$).

4. Discussion

4.1. Comparison of Power Output of the Planted CW-MFC and Unplanted CW-MFC. When *Ipomoea aquatica* was planted in CW-MFC, the bacteria density in anode and cathode both increased, cathode potential became larger, and anode potential become more negative (Figure 4), thus generating more power. Here, the grown *Ipomoea aquatica* is generally very important feature because it can improve the catalytic activity of anode and cathode mainly due to the enhancement of the microbial density, activity, and diversity in the plant's rhizosphere [28]. Furthermore, root exudates that comprise carbohydrates, carboxylic acids, and amino acids are highly degradable to microorganisms and the most responsible for electron donation [29]. In addition, the internal resistance of the planted CW-MFC accounted for only 61% of the unplanted CW-MFC, and the cause of such difference may lie in the quantity of current-producing bacteria (such as *G. sulfurreducens* and *Betaproteobacteria*), which are able to generate electrically conductive pili or nanowires that assist the microorganism in reaching more distant electrodes. The power densities in the two CW-MFCs were consistent with the change of the internal resistances. It is generally known that the maximum power output occurs when the internal

FIGURE 8: The principal reactions for the overall process of the CW-MFC. (1) Plant roots secrete O_2 and $(CH_2O)_n$. (2) Electrons are produced at the anode from the anaerobic degradation of $(CH_2O)_n$ and $C_6H_{12}O_6$. (3) NH_4^+ was converted to NO_3^- by Nitrifying bacteria in the rhizosphere. (4) O_2 and NO_3^- were electron acceptors at the cathode.

resistance is equal to external resistance [25]; thus, the decrease in internal resistance is one reason for the improvement in power generation performance for the planted CW-MFC. The improvement in power generation for the planted CW-MFC resulted from three different factors: increased biomass in anode and cathode, a decrease in the internal resistance, and more available fuel secreted from plant roots.

4.2. High Nitrogen Removal in the Planted CW-MFC. The removal of nitrogen (including nitrate, nitrite, and ammonia) in MFC has been reported in recent years. In a MFC, nitrate and nitrite can be removed as electron acceptors in the cathode through electrochemical reduction or autotrophic denitrification [30–32]. A high level of ammonia removal from 198 ± 1 to 34 ± 1 $mg\ L^{-1}$ (83% removal) was obtained from swine wastewater in a single-chamber air cathode MFC system [33]. However, subsequent research demonstrated that the removal of ammonia occurred primarily by physical-chemical mechanisms due to ammonia volatilization with conversion of ammonium ion to the more volatile ammonia species as a result of an elevated pH near the cathode [34]. In this study, effective TN removal efficiency obtained in the planted CW-MFC might be attributed to *Ipomoea aquatica* uptake of NH_4^+ or NO_3^- as their N source for growth and yield [35]. In this experiment, the influent N was sufficient and dominated by NH_4^+ . Many researches indicate that aquatic plant roots can release oxygen (O_2) in constructed wetland [36, 37]; thus, the rhizosphere was aerated and the nitrification process was promoted by microbial activity, and the NH_4^+ was converted into NO_3^- via NO_2^- by

the ammonia oxidizing bacteria and nitrite oxidizing [38], whereas the produced NO_3^- ($E^{\theta} NO_3^-/N_2 = 0.74$ V) could be used as the final electron acceptor in the cathode (Figure 8). Although the electric production of MFC with nitrate as electron acceptor is inferior to other types of MFC (e.g., O_2 as the electron acceptor), realizing the biological denitrification in the cathode is crucial and significant for the total nitrogen removal in the CW-MFC system.

4.3. Comparison of the Planted CW-MFC with Similar Published MFCs. Because of the alternating phases of light and dark, the electric output generated from plant photosynthetic products may show diurnal oscillations with clear fluctuations between the trough and the peak values [39, 40]. Similarly, in this study, the voltage outputs of the planted CW-MFC were cyclically fluctuant depended on the day/night cycle. In the planted CW-MFC system, the fuel source consisted of glucose fed from waste water and a certain amount of organic compounds released by *Ipomoea aquatica* roots (Figure 8). Generally, the photosynthates produced during the day may have led to increased exudates production availability for the anode in the planted CW-MFC. When operated in the light, the CW-MFC could use photosynthates and glucose as fuel generating more electricity. Moreover, roots of *Ipomoea aquatica* (20 ± 2 cm length but most distributed in the upper part) released more oxygen in the day and created more suitable aerobic conditions in the cathode zone, which induced the improvement of electric output. So the high peak voltages for the planted CW-MFC in the day were attributed to sufficient fuel available in the anode and favorable oxygen condition in the cathode.

The CW-MFC system can utilize the organic substrate in the influent and plant photosynthate as fuels, so its power output could be divided into two parts: power yield from COD_R in the water body and power transformation from plant photosynthesis. In current study, the maximum power output for the planted CW-MFC was $3.92 \text{ GJ ha}^{-1} \text{ year}^{-1}$ (12.42 mW m^{-2}), the maximum power yield from COD_R in the water body was $66.05 \text{ KJ Kg}^{-1} \text{ COD}_R$, and the maximum power transformation from plant photosynthesis was $2.31 \text{ GJ ha}^{-1} \text{ year}^{-1}$. A maximum power density of 15.73 mW m^{-2} for a CW-MFC system planted with canna indica was achieved during the treatment of wastewater containing 1000 mg L^{-1} methylene blue [18], and it was about 26% higher than that generated in this study. Our CW-MFC device is constructed with a large anodic geometric surface area about 706.50 cm^2 , that is, 17 times higher than the CW-MFC planted with canna indica (40.93 cm^2); moreover, the substrate concentration (200 mg L^{-1} glucose) in the influent is relatively low in our CW-MFC, so these differences may make the power density slightly less. Besides, many similar MFCs generated power from plant photosynthate have been reported, and the maximum power outputs vary in different systems, such as $1.89 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of plant-MFC in a rice paddy field [39], $4.55 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of rice-paddy MFC [41], $0.41 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of sediment MFC with a biocathode in the rice rhizosphere [19], $70.01 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of plant MFC planted with *Spartina anglica* [42], $119.83 \pm 5.99 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of Direct Photosynthetic Plant Fuel Cell by using *Lemna minuta* duckweed [43], and $0.98 \pm 0.06 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of vascular plant biophotovoltaics planted with *Oryza sativa* [40]. Through comparison and analysis for the previously reports, the power outputs were mainly affected by plant species, plant area (anode surface area), and internal resistance. As MFC tests have been demonstrated that increasing the anode surface area resulted in a slight increase in volumetric power density [4], there would be a huge drop in area power density if the anode surface area were too large. Our device had relatively large anode surface area (706.50 cm^2) and high internal resistance (156Ω), so the power output was much lower than some of the plant MFCs (for instance, $119.83 \pm 5.99 \text{ GJ ha}^{-1} \text{ year}^{-1}$ of Direct Photosynthetic Plant Fuel Cell with anode area only 15.75 cm^2 and interresistance 91Ω). The current power generated by CW-MFC is not competitive; however, the CW-MFC technology possesses potential advantages in removing contaminants in wastewater and reducing greenhouse gas emission, which will attract attention and may worth applying in the future. In this study, the CW-MFC system operating with cheap GAC anode and cathode with no use of precious metals was low cost and had large volume (35 L), so its application is more possible in the future.

5. Conclusions

Conversion of solar energy into electricity can be fulfilled by coupling wetland plant photosynthesis with the microbial conversion of organics to electricity in CW-MFC system.

The CW-MFC planted with *Ipomoea aquatica* produced a much higher power than that from unplanted CW-MFC, because plant root can improve electrode activity and provide more organic compounds available for fuel. Moreover, the root of aquatic plants could uptake ammonia nitrogen and part of the pollutants to promote the degradation of contaminants in the wastewater and reduce the greenhouse gas. These results show that developing CW-MFC could provide significant prospects for wastewater treatment and bioenergy recovery. Further studies are necessary to investigate the impact of CW-MFC on the rhizospheric environment and aquatic plant physiology as well as the microbial community.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (Grant no. 21277024).

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