Bioelectricity generation from air-cathode microbial fuel cell connected to constructed wetland

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ABSTRACT

The aim of this study was to investigate the different performance of bioelectricity generation and wastewater treatment between constructed wetland (CW) respectively coupled with air-cathode microbial fuel cell (ACMFC) and microbial fuel cell (MFC) under a fed-batch mode. During a 75-day-operation, the voltage of CW-ACMFC and CW-MFC ranged from 0.36 to 0.52 V and from −0.04 to 0.07 V, indicating that the bioenergy output of CW-ACMFC was significantly higher than that of CW-MFC system. In addition, the maximum of power density of CW-ACMFC and CW-MFC was 4.21 and 0.005 mW m^{-2}. Notably, the chemical oxygen demand (COD) and NH_3-N removal efficiency of CW-ACMFC was slightly higher than that in CW-MFC, which resulted from a higher voltage accelerating the transport of electron donors and the growth of microorganisms and plants. This study possesses a probability of using ACMFC coupled with CW to enhance the pollutant removal performance in CW system.

Key words | bioelectricity generation, constructed wetland, microbial fuel cell, wastewater treatment

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INTRODUCTION

The domestic sewage treatment in rural areas of developing countries is an increasing pollution burden due to the lack of adequate sewage treatment facilities. Pollutants, including ammonia nitrogen, organic matter and heavy metals, may affect significantly the self-purification capacities of water bodies. This is the primary reason for the higher rates of water eutrophication in these areas of developing countries. Typically, the cost of electricity account for 5% to 30% of total operating costs in municipal wastewater treatment (Chae & Kang 2013). Hence, the low-cost operation and maintenance, sustainable and energy-efficiency constructed wetland (CW) has been considered as a worldwide technology for domestic sewage and industries treating in small communities. Recently, the bioenergy recovery from organic matter in the process of wastewater treatment has been got focused by integrating microbial fuel cell (MFC) technology into CW.

In anode of MFC, organic matter is degraded by microorganisms especially electrochemically active microorganisms (EAM) to generate electrons (e^-) and protons (H^+). Protons shuttle through proton exchange membrane (PEM) into the cathode chamber, and electrons under the effect of potential gradient transfer from the anode electrode to the cathode, where they combine with protons and oxygen to produce water (Yadav *et al.* 2012). However, the application of MFC usually showed a low power density, current density and coulombic efficiency, especially under fed-batch mode (Liu *et al.* 2013). To ameliorate MFC performance, air-cathode microbial

doi: 10.2166/wst.2018.471

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fuel cell (ACMFC) has been frequently observed in organic matter degradation with a higher bioelectricity generation (Cheng *et al.* 2011; Campo *et al.* 2014; Kim *et al.* 2014).

The variation of dissolved oxygen (DO) and oxidation reduction potential (ORP) in CW provide a natural habitat for the growth of microorganisms with different metabolic functions (Ciria *et al.* 2005; Ojeda *et al.* 2008). In this regard, CW can be designed, by ameliorating operational parameters, to act as MFC for wastewater treatment and bioelectricity generation simultaneously (Yadav *et al.* 2012). These considerations make it more excitable that CW-MFC has been developed for treating various types of wastewater under different operational conditions (Liu *et al.* 2013; Zhao *et al.* 2013). By integrating MFC into CW (Zhao *et al.* 2013), the CW were in suit to observe with a peak power density of 12.83 $\mu W\ m^{-2}$ and 71.5% removal performance of chemical oxygen demand (COD). In a CW-MFC developed by Liu *et al.* (2013), the power density of 12.42 $mW\ m^{-2}$ was observed with *Ipomoea aquatic*. In addition, in an ACMFC designed by Cheng *et al.* (2011), the maximum power density of 1,070 $mW\ m^{-2}$ was obtained. Hence, the application of ACMFC into CW might be useful for the enhancement of bioelectricity generation.

In this study, a comparative study on the bioelectricity generation performance of CW-ACMFC and CW-MFC was operated under a fed-batch mode. To assess the efficiency of two kinds of reactors, the maximum power density, COD and ammonia nitrogen removal performance were measured in each cycle.

MATERIAL AND METHODS

System construction, inoculation and operation

Two polyvinyl chloride tanks (0.6 L × 0.4 W × 0.4 H m) filled with quartz sand (φ 4–6 mm; porosity 37%) with an average thickness of 0.35 m were used to simulate the laboratory-scale CW-MFC. The containers were planted with disease-free *Cannas indica* of initial stem lengths 25 ± 3 cm. *Cannas* were transplanted into every wetland under a density of 17 rhizomes per square meter and propagated for 30 days' acclimation.

As schematically shown in Figure 1, an anode electrode (graphite felt, 0.6 L × 0.36 W × 0.003 H m) was placed 0.15 m near to the bottom. The larger surface of the electrode could provide a habitat for the growth of microorganisms that will benefit the process of electron production of EAM. A similar graphite felt (dimensions of 0.6 L × 0.08 W × 0.003 H m) was placed 0.05 m near to the top of the microcosm to form a good aerobic condition. The difference between CW-ACMFC (System 1) and CW-MFC (System 2) was that the cathode electrode of CW-ACMFC was placed at the top of influent level, while cathode chamber of CW-MFC was filled with wastewater during the influent process. The total volume of System 1 and 2 was 84 L with a liquid volume of 28.8 L and 33.6 L, respectively. The anode to cathode electrode was connected through an insulated electric wire (copper) and an external electrical resistance of 2,000 Ω. Each microcosm was inoculated with equal volume (15 L) activated sludge, which was collected from Songjiang sewage treatment plant, Shanghai, China.

The main composition of synthetic wastewater is listed as follows (in $mg\ L^{-1}$): glucose·H_2O (112.33), NH_4Cl (48.59), KH_2PO_4 (7.69), $Na_2HPO_4 \cdot 12H_2O$ (17.73), $MgCl_2 \cdot 6H_2O$ (17.67), $ZnCl_2$ (7.54), $CaCl_2$ (17.64), CH_3COONa (100.20). This study was performed for a total of 75 days (from September 28 to December 12, 2014), which consisted of 30 days' acclimation for the growth of biofilm and wetland plants. During the experiment, both reactors were worked under a fed-batch mode with the hydraulic retention time (HRT) of 24 h. The collection of influents and effluents were manipulated at 16:00 every day.

Water quality analysis

The COD solution of water sample was digested by a HH-6 COD meter and measured by HACH DR900 Spectrophotometer (USA). The concentration of NH_3-N was analyzed by HANNA HI 93733 instrument (Italy). Water temperature, pH and DO were calculated by a multi-parameter meter (HQ40d, HACH, USA). ORP was measured by an HI 9135, HANNA equipment.

Bioenergy output determination

The voltage between the edge of external electrical resistance of two reactors were registered every 5 min by an automatic recorder intelligent instrument. To obtain the polarization curve of Systems 1 and 2, the current and voltage were recorded by a digital multimeter (VICTOR 86E, Shenzhen) through the variation of external electrical resistance from 40,000 to 5 Ω every 3 min on Day 65. The current and power density were calculated by the following formula: $J = U/SR_{ex}$, $P = UI/S$, where the J ($mA\ m^{-2}$), U (V), R_{ex} (Ω), S (m^2), P ($mW\ m^{-2}$) and I (A) is current density, cell voltage,

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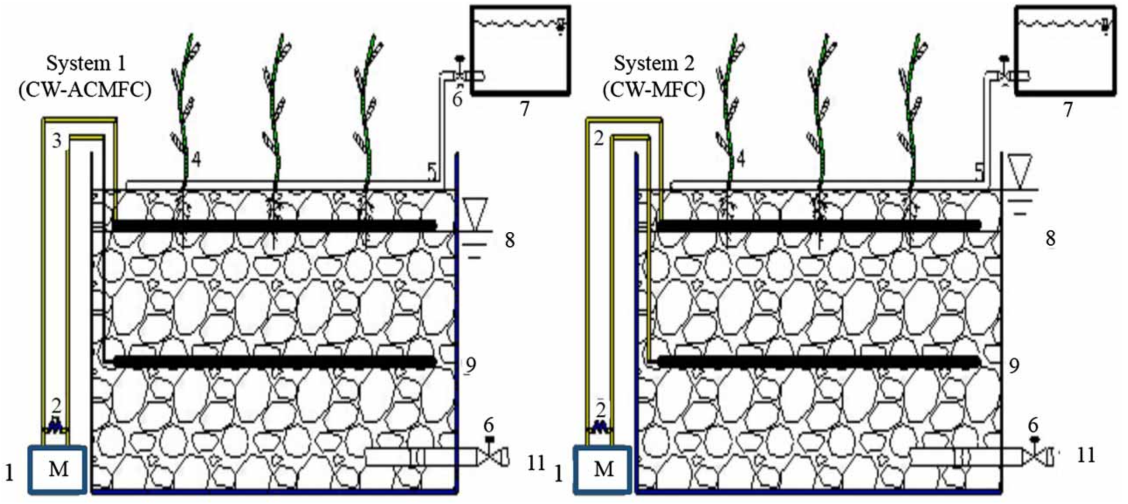

Figure 1 | Configuration of the air-cathode microbial fuel cell and microbial fuel cell coupled with constructed wetland system. (1) multimeter, (2) external electrical resistance, (3) copper wire, (4) *Cannas indica*, (5) cathode, (6) pipe valve, (7) wastewater tank, (8) surface of water level, (9) anode, (10) water outlet, (11) sampling ports.

external electrical resistance, cathode surface, mean power density and current, respectively.

Statistical analysis

DO, COD, and ammonia nitrogen removal by the CW-ACMFC and CW-MFC reactor under similar operational condition was statistically analyzed with the one-way analysis of variance (ANOVA) method in SPSS 22.0 software, and $p < 0.05$ were considered as the significant level.

RESULTS AND DISCUSSION

DO and ORP profile

DO and ORP of the effluent samples are presented in Figure 2(a). In general, ORP values of Systems 1 and 2 were obviously affected by DO level. In System 1, the values of effluent ORP and DO were −170 mV and 1.2 mg L^{-1}, respectively, while effluent ORP and DO were obtained with value of −180 mV and 1.1 mg L^{-1} in System 2. A previous study in CW found similar results, indicating that DO concentration of the effluent at CW are usually maintained at a low level (García *et al.* 2010). Notably, the concentration of these parameters showed a relatively obvious fluctuation at the middle and end of the experiment. It was well recognized that the drop of average air temperature (from 19 to 14 °C in Days 55–60, and from 16 to 5 °C in Days 60–75, respectively) and might result in the instability of DO and ORP of both reactors. In addition, average pH of Systems 1 and 2 were maintained at 6.79 and 6.85, respectively.

COD and NH_3-N removal performance

As shown in Figure 2(b), the average COD concentration of influents were 198.4 mg L^{-1}, and the average COD concentration of effluent samples collected from Systems 1 and 2 were 59.8 and 67.2 mg L^{-1}, respectively. The average COD removal efficiencies of Systems 1 and 2 were respectively 69.9 and 66.0%. In addition, the maximum efficiency of COD was found to be 79.13% in System 1, indicating that an anode of MFC integrated into the CW was beneficial for the COD removal (Fang *et al.* 2013). From a previous study, a higher voltage output might stimulate the growth of microorganisms and plants (the synthesis of chlorophyll), which resulted in a better COD removal performance in System 1 (Song *et al.* 2011). In addition, the present data also revealed that the COD removal was limited to the fluctuation of air temperature, the first drop of air temperature (from 19 to 14 °C, at Days 55–60) was more obvious than that of the second drop (from 16 to 5 °C, at Days 60–75) during the experiments. A decrease of air temperature could reduce the process of oxidation reaction in the anode chamber of the reactor.

Figure 2(c) shows the performance of NH_3-N removal efficiency in these reactors. Average NH_3-N concentration of influents was 14.9 ± 0.2 mg L^{-1}, and average NH_3-N concentration of effluent sampled collected from Systems 1 and 2 were found to be 9.5 ± 0.5 mg L^{-1} and 10.0 ± 0.3 mg L^{-1}, respectively. This suggested the NH_3-N removal efficiency of

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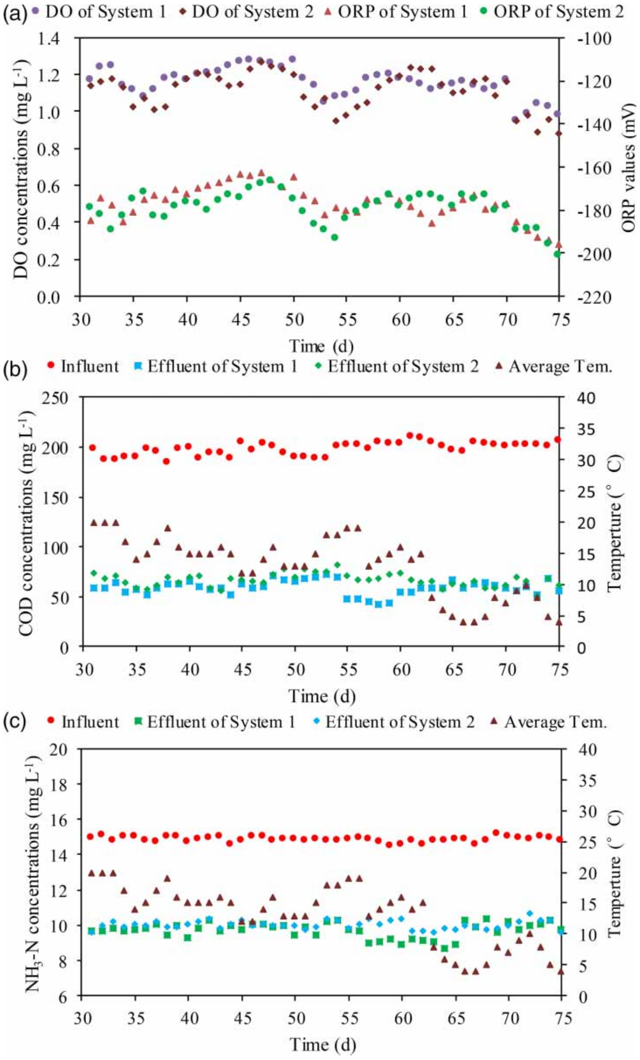

Figure 2 | Variation of pH and ORP in effluent sample of CW-ACMFC and CW-MFC (a); COD (b) and NH_3-N (c) concentration of influent and effluent samples collected from CW-ACMFC and CW-MFC.

CW-ACMFC and CW-MFC was 36.2% and 32.8%, respectively. Notably, the ammonia nitrogen removal efficiency in both reactors was not high.

The mechanisms of nitrogen removal in CW were plant adsorption, ammonia-volatilizing and simultaneous nitrification–denitrification (Bigambo & Mayo 2005; Song *et al.* 2011). A generally accepted cause of low efficiency wastewater treatment was the DO concentration of wetland under a lower level during the biodegradation of pollutants (Horne 2002), which showed a significant influence on the efficiency of nitrification. The DO concentration of these reactors were maintained at a relatively lower concentration. In addition, the presence of electrons production under higher cell voltage of CW-ACMFC might promote removal of NO_3-N or NO_2-N. However, Song *et al.* (2011) indicated that a large sum of NH_3-N could be transformed into NO_3^-N in the circumstance of DO exceeding 1.5 mg L^{-1} in a horizontal subsurface-flow (HSSF) CW for high concentration ammonia nitrogen wastewater treatment. With a DO concentration lower than 1.5 mg L^{-1}, the efficiency of nitrification has been inhibited. Hence, the average NH_3-N removal efficiency of CW-ACMFC and CW-MFC was observed with a value below than 35%. However, some studies reported that the integrating micro-electric field (MEF) into CW could stimulate the production of chlorophyll, the permeability of cells membrane and transporting capacity of plants (Song *et al.* 2011). A higher voltage found in CW-ACMFC system might be beneficial for microorganism and plant growth. Therefore, the average ammonia nitrogen removal efficiency of System 1 was higher than that in System 2.

Bioelectricity generation performance

After stabilization, the cell voltage of Systems 1 and 2 is presented in Figure 3(a) and 3(b) with 45 cycles. As described in the section 'System construction, inoculation and operation', two reactors were carried out in a fed-bath mode, the feeding time of wastewater was performed at 16:00 every day, so the starting point of each cycle of cell voltage was plotted at same time. The cell voltage of Systems 1 and 2 were immediately rising at feeding time, which was largely driven by wetland MFC were fed with new substrate. After the feeding time, stable voltage of both reactors was obtained, the voltage of CW-ACMFC varied in the ranges of 0.36 to 0.52 V, while the voltage of CW-MFC changed from −0.04 to 0.07 V. For example, on Day 56, stable voltage of System 1 was approximately constant with a value around 0.5 V, whereas the voltage of System 2 was approximately constant values of 0.06 V after the replacement of substrate. The constant voltage produced by System 1 was 8.3 times higher than that of System 2, indicating a significant difference on the bio-electricity generation between the in two reactors. When the wastewater dropped from wetland MFC, cell voltage of Systems 1 and 2 was also descended sharply to about 0.0 V, resulted from the lack of fuel substrate in the reactors.

The air diffusion could enhance oxygen concentration in the cathode of wetland MFC, where the electrons produced by EAM combine with protons and oxygen to form water: $4e^- + 4H^+ + O_2 = 2H_2O$. In addition, plants also could promote the oxygen concentration in the cathode through their photosynthesis that had been indicated in

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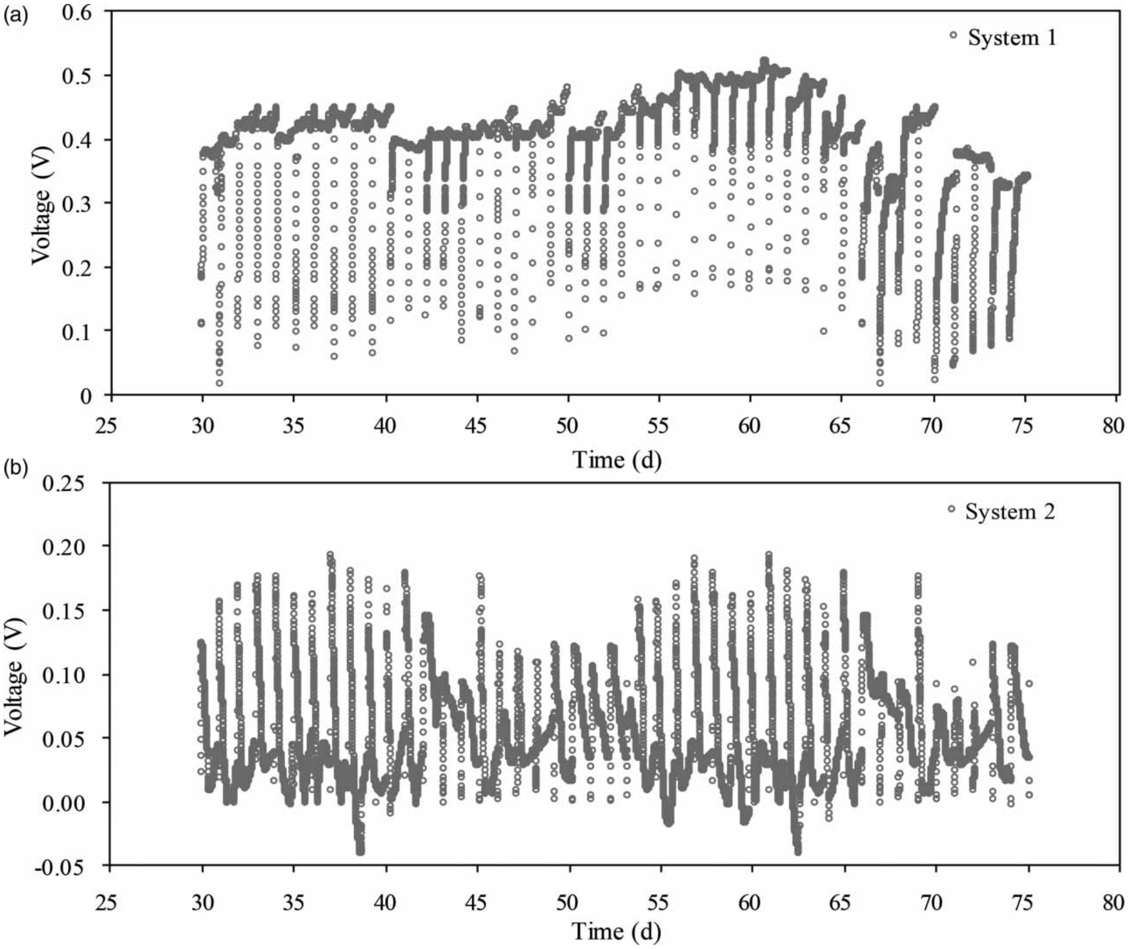

Figure 3 | The performance of bioelectricity generation in CW-ACMFC (a) and CW-MFC (b).

the experiment designed by Fang *et al.* (2013). The average voltage output of CW-MFC with plants was about 15% higher than that of unplanted CW-MFC. Furthermore, the continuous mode and high substrate concentration are beneficial to the amplitude of bioenergy output in CW-MFC (Zhao *et al.* 2013; Liu *et al.* 2014). The CW-MFC designed by Zhao *et al.* (2013) produced its peak voltage of 58 mV with initial average COD concentrations of 1,058 ± 421 mg L^{-1} under the sequencing batch mode. By integrating CW into MFC, Villaseñor *et al.* (2013) observed that an average cell voltage of CW-MFC was approximately maintained at 240 mV, at COD concentrations of 250 mg L^{-1} under a continuous mode. Therefore, a higher efficiency of recycling the bioenergy contained in organic matter was found with CW-ACMFC by changing the configuration of CW during wastewater treatment.

In addition, the cell voltage performance of System 2 was unstable, especially in the night cycle, which resulted from root exudates of plants consuming parts of oxygen around the rhizosphere. According to previous studies, there are numerous factors, such as air temperature, photosynthesis, affecting on macrophytes releasing low-molecular weight organic compounds into the soil or filler according to previous studies (Vancura & Hanzliko 1972; Carvalhais *et al.* 2011). The release of dissolved organic carbon (DOC) from *P. australis* was 9.0 ± 0.9 μg g^{-1} root dry mass h^{-1} (Zhai *et al.* 2013). Also, organic carbon released by roots would cut down because of the descendant efficient photosynthesis during the night cycle (Jonasson *et al.* 1999). However, because of negative value of voltage were obtained for several days, the release of DOC from plants might have had a deep influence on the bioelectricity generation in CW-MFC.

Cell voltage of Systems 1 and 2 had dropped from 0.81 to 0.64 V and 0.74 to 0.35 V when the external resistance was reduced from 40 to 6 kΩ, whereas the cell voltages of Systems 1 and 2 had dropped from 0.50 to 0 V and 0.01 to 0 V when the external resistance was reduced from 2,000 to 5 Ω, respectively (Figure 4). The maximum power density

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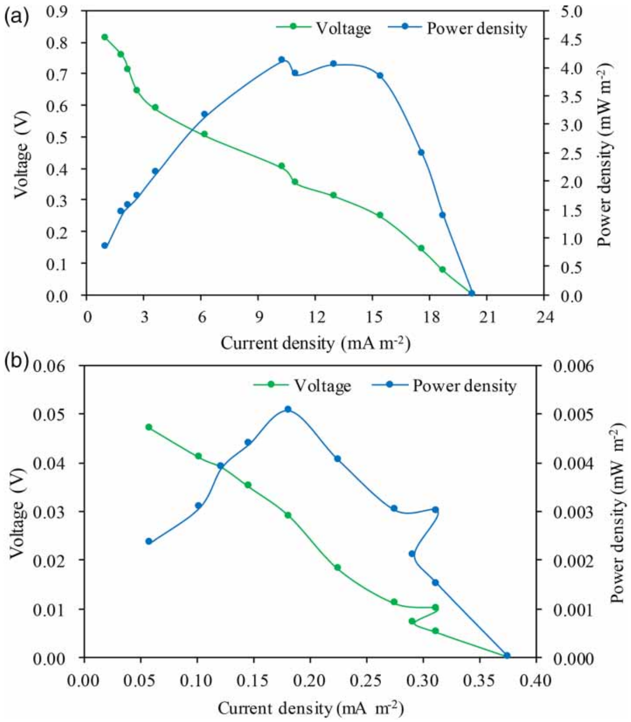

Figure 4 | The polarization curve of CW-ACMFC (a) and CW-MFC (b) at the end of experiment.

and current density of System 1 was obtained to be 4.21 mW m^{-2} and 20.30 mA m^{-2}, while the maximum power density and current density of System 2 was obtained to be 0.005 mW m^{-2} and 1.47 mA m^{-2}. This suggested maximum power outputs of Systems 1 and 2 were 362.93 and 0.43 J m^{-2} d^{-1}, respectively, and the maximum power density of System 1 was 842 times higher than that of System 2. It was observed that the power density of Systems 1 and 2 increased to a peak value with an external electrical resistance of 1,000 and 4,000 Ω. This indicated that CW-MFC with air-cathode was conducive to the loss of internal resistance in MFC. Similar results were found in a previous study with the air-cathode MFC having 18% less ohmic resistance than the two-chamber reactor (Cheng *et al.* 2011).

CONCLUSION

In this study, the performance of bioelectricity generation in CW-ACMFC and CW-MFC was compared under an operational mode of fed-batch. In general, the bioenergy output in CW-ACMFC was significantly higher than that of CW-MFC. The peak power density (4.21 mW m^{-2}) was observed in CW-ACMFC. In addition, the removal efficiency of COD and NO_3-N in CW-ACMFC was slightly higher than that of CW-MFC, which might be resulted from the growth and metabolism of microorganisms and plant stimulated by a higher voltage produced in former reactor. In this study, it was demonstrated that the CW-ACMFC system was an advantageous technology for the harvest of bioelectricity from organic matter during wastewater treatment.

ACKNOWLEDGEMENTS

This study was supported by the Chinese National Natural Science Foundation (91547209, 51679041 and 41571037).

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First received 5 April 2018; accepted in revised form 2 November 2018. Available online 14 November 2018

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