

Synergy of Electricity Generation and Waste Disposal in Solid-State Microbial Fuel Cell (MFC) of Cow Manure Composting

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A small-scale, composting, microbial fuel cell (MFC) system was constructed that used cow manure as the reduced carbon energy source. The system was a single-chamber, air-cathode MFC with a reactor, resistance box and data processing unit. Factors such as moisture content, concentration of phosphate buffer solution (PBS), catalyst addition and electrode area were investigated. Moisture contents of 80%, 70% and 60% resulted in maximum power densities of 349 ± 39 , 36 ± 9 and 12 ± 2 mW m⁻², respectively. A moisture content of greater than 80% is suitable for generation of current in the composting MFC. Addition of 0.1 mg Pt cm⁻² catalyst resulted in 10-fold greater maximum power density with an output voltage twice as great as that generated in the absence of the catalyst. A concentration of 100 mM PBS resulted in maximum power density and output voltage. The power per unit area of electrode was inversely proportional to surface area of the electrode. Quantification of carbon, hydrogen and nitrogen (CHN) content indicated enhanced degradation of organic compounds in addition to production of the electric current. The diversity of the microbial community, as determined by denaturing gradient gel electrophoresis (DGGE) was directly proportional to content of water, but inversely proportional to concentration of PBS. The results of this study demonstrated that the composting MFC can be used to treat wastes while generating electric current.

Keywords: Electricity; Bacterial; Microbial; Community; Optimum; Current density; denaturing gradient gel electrophoresis (DGGE)

1. INTRODUCTION

Microbial fuel cells (MFC) are a new method of simultaneously generating electricity from organic matter while degrading waste, organic matter [1]. Initially generation of electricity in MFCs was fueled by pure compounds, such as acetate [2], glucose [3], sucrose [4], or a protein [5]. MFC technology has also been applied to treat and generate power from mixtures as substrates, including waste food [6] and waste water [7]. However, until now, most MFCs were operated in a liquid state environment, which was thought to be more favorable for transport of ions, but MFCs have also been applied to solid-state media, such as soils and sediments [8, 9]. Power densities of MFCs vary among substrates and conditions of operation. For example, maximum power density was 494 mW m^{-2} when glucose was used as the substrate compared to 146 mW m^{-2} , when domestic waste water was used as the substrate under otherwise equivalent conditions [10]. However, the flexibility of microorganisms to use a range of fuels as substrates, indicated that compost, such as cow manure, might be used in MFCs for generation of electricity while treating organic wastes [11-14]. The combined action of multiple species of microbes working in concert as a consortium has been reported to be necessary for producing greater current densities in MFCs. For example, the power density in a MFC using wastes from processing of foods was $371 \pm 10 \text{ mW m}^{-2}$ [15], while that generated from kitchen garbage was 682 mW m^{-2} [14]. In the composting process, greater biomass and diversity of microbial communities both facilitate the generation of electrical current in MFCs. Three different isolation media under aerobic conditions have been used to culture microbial communities in an electrode biofilm enriched from seawater with representatives of the classes as: *Alphaproteobacteria*, *Gammaproteobacteria*, *Firmicutes*, the family of *Flavobacteriaceae* and the phylum *Actinobacteria* in MFCs [16-18]. Since exoelectrogenic bacteria can generally utilize a limited range of substrates, more diverse microbial communities were needed to oxidize more complex organic matters [19].

Composting MFC can generate electric current while disposing of wastes in systems of little maintenance and producing no waste water. It has been proven that MFC could be conducted successfully in a solid fermentation process of food waste [20]. Production of current in MFCs depends mainly on the type and concentration of the mediator, ionic strength and surface area of the cation exchange in contact with the anode and cathode chambers. All these factors need to be optimized for maximum generation of electric current in MFCs [14]. In a composting MFC, parameters such as moisture content, electrode area, substrate composition, proton exchange capability and oxygen availability also need to be optimized to maximize efficiency of the system. In the study, the results of which are reported here, factors that influenced generation of electric current in a new MFC that used cow manure as the composting substrate were investigated and the most efficient combination of values for the key factors were determined. The design of the system allows aerobic in the upper side to enhance degradation of the solid waste while the lower part is anaerobic to maximize generation of current. It is the first time cow manure is used as substrate for composting MFC although cow manure slurry was used in a liquid state in another research [21]. Degradation of organic matter was determined and the composition of the microbial community in the anode was characterized and the relationship between generation of electricity and composition of the substrate and diversity of the microbial consortium was analyzed.

2. EXPERIMENTAL

2.1 Composting materials

Cow manure was obtained from a farm near the city of Tianjin, China. The manure contained 9% inorganic matter, 4% cellulose, 20% hemicellulose, 30% lignin and 37% other organic matter. The pH was 8.76. Before composting, manure was air dried, crushed and mixed thoroughly. In some tests, a phosphate buffer solution (PBS) was added to the solution at several concentrations. The 50 mM PBS solution contained in 1 L: KCl, 0.13 g; $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 3.32 g; $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 10.32 g; NH_4Cl , 0.31 g.

2.2 Construction of composting MFC

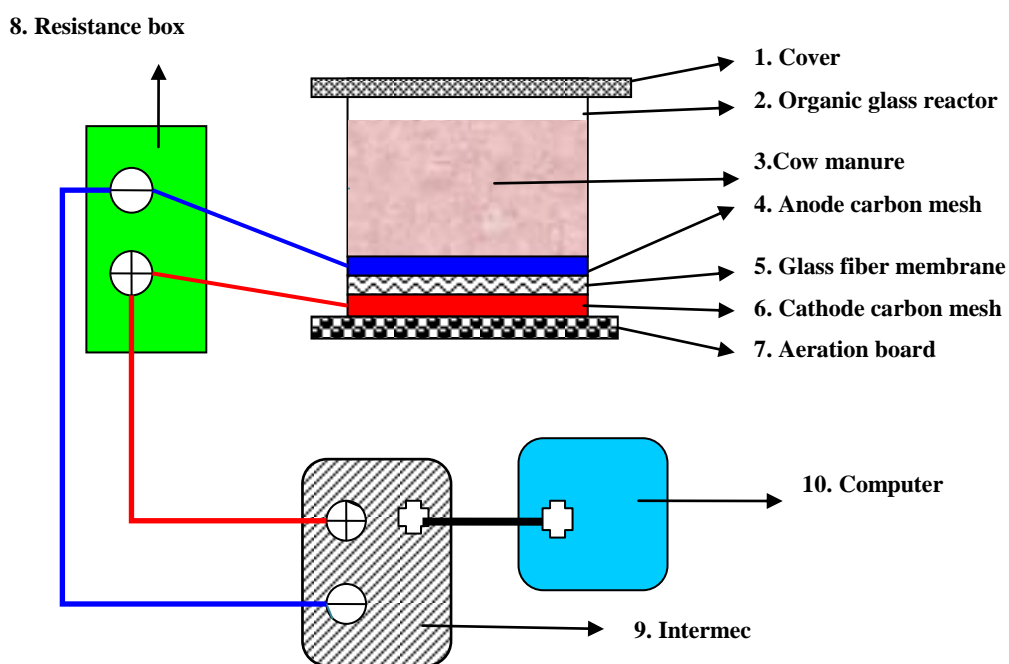


Figure 1. Schematic representation of the composting MFC system using cow manure as the substrate.

A single-chamber, air-cathode MFC was constructed (Figure 1) with a reactor, resistance box and data processing module. External resistance was fixed at 1000Ω except as indicated. The anode area was 113 cm^2 . The upper part of the reactor consisted of a circular vessel, which was made of polymethyl methacrylate with a diameter of 120 mm with a height of 120 mm. A 120 mm diameter piece of carbon mesh was placed in the bottom of the vessel to act as the anode. The design of system allows the aeration in the upper of compost and anaerobic condition in the bottom near anode, which is necessary for electricity generation. Two layers of glass fiber with a diameter of 130 mm were inserted below the carbon mesh. Because of its open structure and weave, the carbon mesh minimized biofouling [22]. To realize full contact with the reactor vessel and to prevent short circuit during

operation, a glass fiber separator that was larger in size than the diameter of the vessel was placed in the bottom of the reactor. Below the glass fiber was a 113 cm² piece of carbon mesh containing Pt catalyst (0.1 mg cm⁻²). The air-cathode was prepared according to previously described methods for soil MFCs [23]. Under the carbon mesh was a 140 mm disc with uniformly punched holes. To prevent the leakage of water from the system, the side of the cathode that faced the air was coated with four PTFE diffusion layers. The cathode consisted of a disk of carbon mesh with a diameter that was greater than that of the reactor for connection of wires from a clamp. To ensure circulation of air, the vessel was placed on a layer of polyfoam. Electrodes were placed on opposite sides of the cylindrical chamber and connected to the external circuit with copper wires. The internal resistance was calculated (Equation 1).

$$\text{Internal resistance } (R) = (OCV - U) / I \quad (1)$$

Where: *OCV* = open circuit potential; *U* represents output voltage.

2.3 Factors affecting performance of the composting MFC

Four factors that could affect functioning of the MFC, including moisture content, concentration of PBS, presence or absence of catalyst and area of the electrode were investigated singly or in combination (Table 1). Cow manure (20 g) was used as the reduced carbon source in the form of compost. Moisture content was determined by gravimetric method and adjusted with distilled water to 60%, 70% and 80% in run1, run2 and run3, respectively and with PBS solution. The cathodic carbon mesh was coated with 0.1 mg Pt cm⁻², and electrode area was 28 cm² and 113 cm² in runs 3 and 5, respectively. Effects of electrode area were determined in runs 3 and 5.

Table 1. Conditions for composting MFC with cow manure as the substrate.

Run	Moisture content (%)	PBS concentration (mmol/L)	Catalyst (mg/cm ²)	Electrode area (cm ²)
1	60	100	0.1	28.26
2	70	100	0.1	28.26
3	80	100	0.1	28.26
4	80	100	0	28.26
5	80	100	0.1	113.04
6	80	200	0.1	28.26
7	80	50	0.1	28.26

No catalyst was applied in run 4, the results of which were used to check for effects of Pt on performance of the composting MFC as compared to run 3. Concentrations of PBS used were 50, 100 or 200 mmol L⁻¹ in runs 7, 3 and 6, respectively. In order to determine reproducibility of each measurement, all the experiments were conducted in duplicate.

2.4 Analysis methods

Carbon, hydrogen, nitrogen (CHN) analyses were conducted by use of a EuroEA3000 CHNS-O Analyzer (EuroVector S.p.A, Milan, Italy) after grinding dried samples to pass 50 mesh. The microbial community in the anode was characterized by denaturing gradient gel electrophoresis (DGGE) method by use of previously described methods [24]. The anode was taken out of the reactor and biofilm removed by use of a sterilized pipet tip. DNA was extracted by use of the ZR Soil Microbe DNA KitTM (Orange, CA). 16S rDNA genes of compost microorganisms were amplified by use of PCR with the following primers: 357f-GC clamp and 518r. The denaturing gradient of the polyacrylamide gel ranged from 30% to 60%. Electrophoresis was performed in an electrophoresis cell D-codeTM system (Bio-Rad Laboratories, Hercules, CA, USA) at 60 °C and with 200 V for 4 h. The DGGE bands were analyzed by Quantity One (Bio-Rad Laboratories, Hercules, CA, USA).

3. RESULTS AND DISCUSSION

3.1 Effect of moisture content

Moisture content influenced electromotive force and resistance of the composting MFCs. Water plays a key role in performance of MFCs. When moisture contents were 80%, 70% and 60%, respectively, cell voltages were 544 ± 26 , 180 ± 12 and 115 ± 8 mV under a fixed resistance of 1,000 Ω (Figure 2A). Electrons transfer from anode to cathode through copper wire, while protons transfer from anode to cathode through solution and composting substrate. Greater contents of water facilitated formation of a more electron-mobile solution, and promoted transfer of electrons to the cathode. A 10% greater content of water in the MFC resulted in 3-fold greater output voltage. Moisture also influenced maximum output power density of the MFCs powered by cow manure (Figure 2C). When moisture contents were 80%, 70% or 60%, respectively, maximum power densities were 349 ± 39 , 36 ± 9 or 12 ± 2 mW m⁻², respectively. These values are less than 494 mW m⁻², which was generated when 0.6 g glucose L⁻¹ was used as the substrate [10]. A water content of 80% in the MFC that used manure as a substrate, produced more power than that that used domestic wastewater, which resulted in a power density of 146 mW m⁻² (200–300 mg COD L⁻¹) [25]. When moisture contents were 80%, 70%, or 60% respectively, electromotive forces were 626 ± 12 , 222 ± 12 and 140 ± 7 mV (Figure 2B), while resistances were 99 ± 7 , 125 ± 10 and 148 ± 6 Ω . Moisture content had little influence on the resistance of MFC, relative to the greater effect on electromotive force. Moisture content can be from 60% to 80% in general composting process used to treat solid waste [26]. Organic, solid wastes such as manure and sewage sludge have water contents greater than 80%, which can be used as suitable substrates in a composting MFC process to realize energy recovery and waste disposal at the same time.

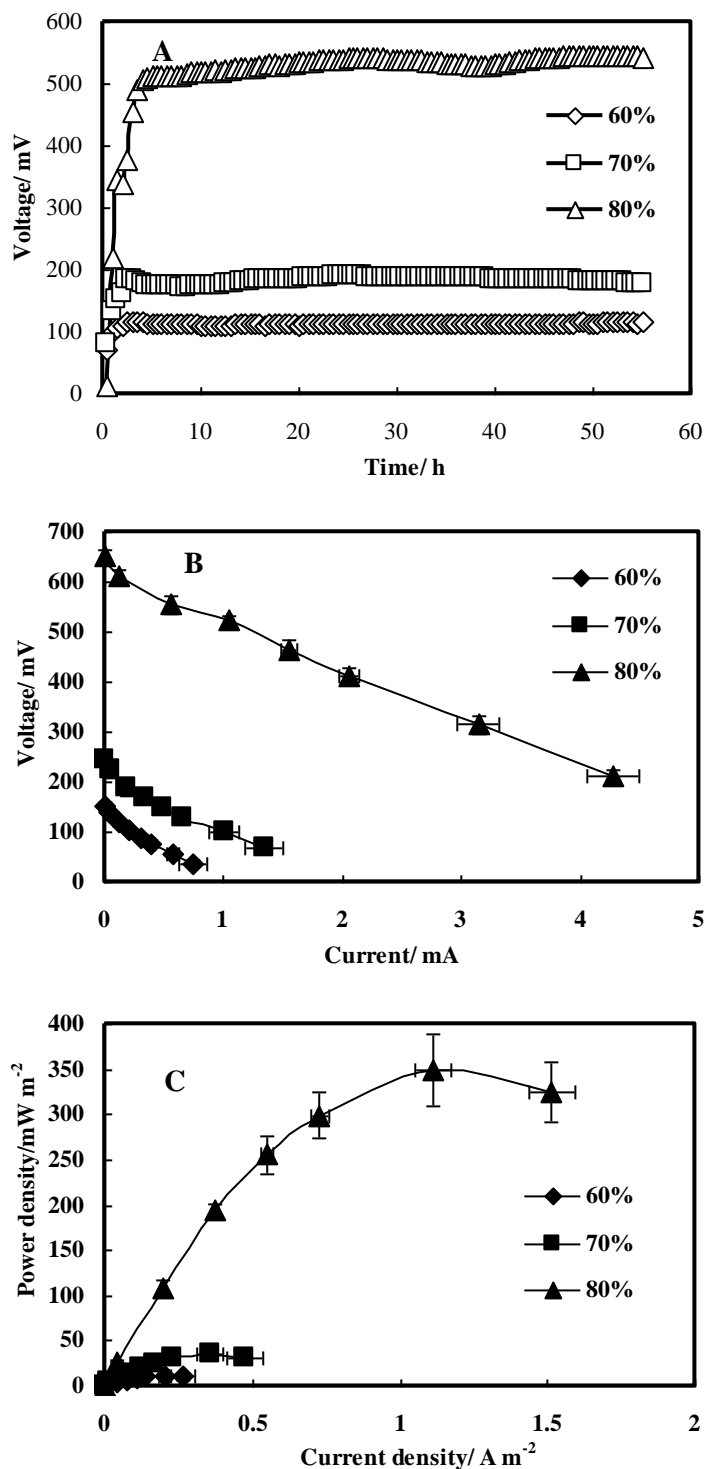


Figure 2. Effect of moisture content on performance of the composting MFC. A: Voltage generation; B: Voltage-current curve; C: Power density curve. The error bars indicate standard deviation.

3.2 Effect of catalyst content

MFC has been a novel technology for direct bioelectricity generation from biomass for many years. The efficiency of MFC systems has been a key factor limiting practical application which

related to the catalyst in cathode of MFCs was the major cost of production [27]. Therefore, cathode catalyst is important for improving effectiveness and cost of MFCs. When catalyst content of Pt was 0.1 mg cm^{-2} , maximum power density was 349 ± 39 relative to 23 ± 0.7 without Pt and output voltage output was $544 \pm 26 \text{ mV}$ compared to 223 ± 3 in the absence of catalyst (Figure 3).

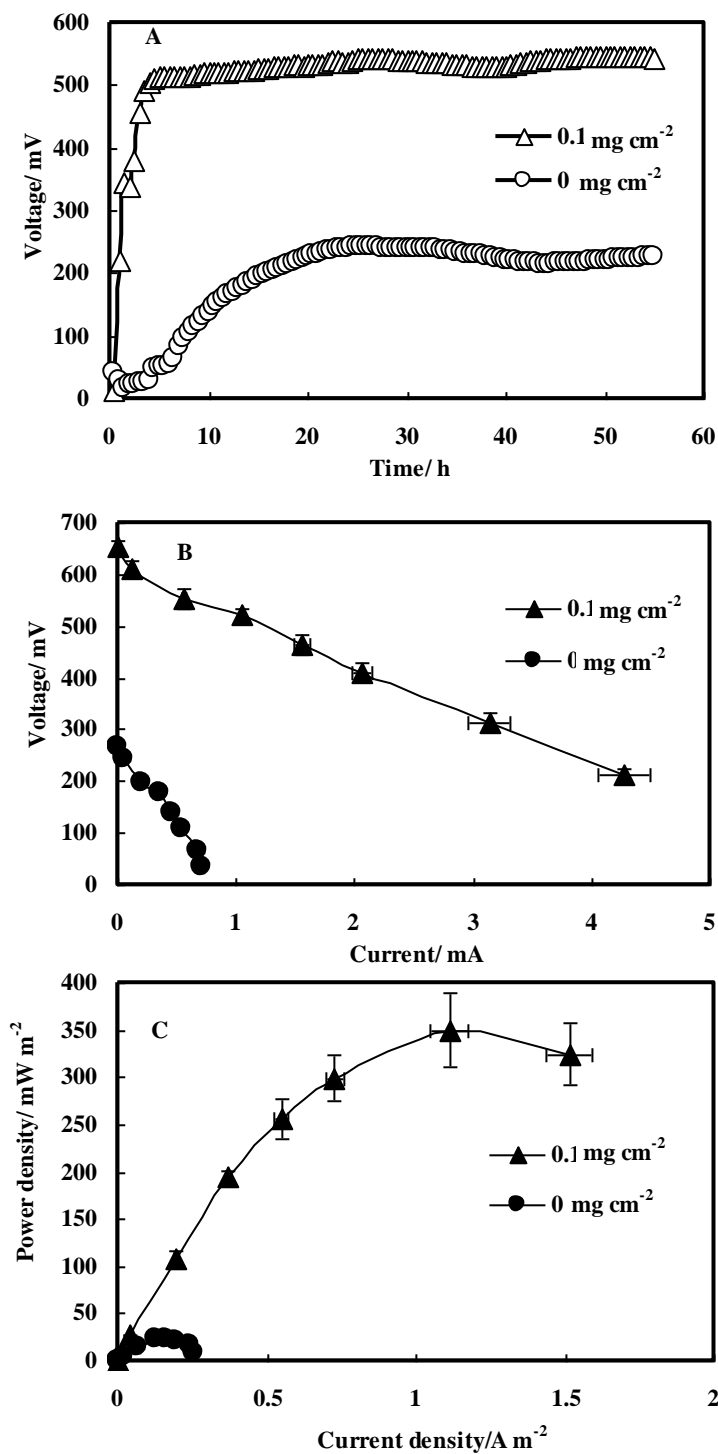


Figure 3. Effect of catalyst on function of the composting MFC. A: Voltage generation; B: Voltage-current curve; C: Power density curve. The error bars indicate standard deviation.

Catalyst content also influences electromotive force and internal resistance of MFC in composting. When $0.1 \text{ mg Pt cm}^{-2}$ catalyst was used, electromotive force was 626 ± 12 , relative to $266 \pm 10 \text{ mV}$ in the absence of Pt and internal resistance was $99 \pm 7 \ \Omega$ in the presence of catalyst compared to $296 \pm 11 \ \Omega$ in the absence of Pt as catalyst. Addition of the $0.1 \text{ mg Pt cm}^{-2}$ Pt catalyst increased maximum power density 10-fold and voltage output by 2-fold, relative to that in the MFCs without Pt catalyst.

Since the platinum used in the catalyzed electrode is expensive, studies have been conducted to find an alternative for platinum-catalyzed electrode and the inexpensive activated carbon, air cathode was proposed [28]. In MFCs using $1.0 \text{ g acetate L}^{-1}$ as the substrate, an activated carbon cathode produced a maximum power density of 1220 compared to 1060 mW m^{-2} obtained with a carbon cloth cathode catalyzed with Pt. Alternatives to Pt also include 0.6 or $1.2 \text{ mg CoTMPP cm}^{-2}$ and $1.0 \text{ mg iron phthalocyanine cm}^{-2}$) [29-31]. Manganese dioxide (MnO_2) can also be used to improve cathode performance [31]. Catalyst content also influenced time to initial production of current in MFCs. Output voltage was stable after 5 h when $0.1 \text{ mg Pt cm}^{-2}$ was used as a catalyst, compared to 20 h without catalyst.

3.3 Effect of PBS concentration

The concentration of buffer influenced maximum power density, voltage output, electromotive force and resistance (Figure 4). Maximum power densities were 203 ± 10 , 349 ± 39 and $129 \pm 9 \text{ mW m}^{-2}$ when buffer concentrations were 50, 100 and 200 mM, respectively. Output voltages were 228 ± 13 , 544 ± 26 and $210 \pm 10 \text{ mV}$ at a fixed external resistance of $1,000 \ \Omega$. Electromotive forces were 536 ± 10 , 626 ± 12 and $522 \pm 9 \text{ mV}$, and resistances were 215 ± 11 , 99 ± 7 and $118 \pm 12 \ \Omega$.

Since a liquid solution is a major conductive material in composting of solid waste, it is difficult to determine conductivity in the absence of such a liquid medium. Conductivity of MFC for beer brewery wastewater was 3.23 mS cm^{-1} , which was less than that of other complex waste sources such as corn stover hydrolysates [32]. In the studies, the results of which are presented here, addition of PBS resulted in conductivities of 7.65 mS cm^{-1} when 50 mM was used and 14.6 mS cm^{-1} when 200 mM was used. In solid waste composting, maximum power density and output voltage were observed when the concentration of PBS was 100 mM. Conductivity was maximized and resistance minimized in the MFC with a buffer concentration of 100 mM PBS. When the buffer concentration was 200 mM, the ion concentration was too great to maintain proper microbial activity and resulted in lesser production of electricity in the composting MFC. Addition of PBS, while not necessary for the MFC to function, enhanced production. These results indicate that economically viable system can be used to generate electrical current while reducing the volume of organic wastes. At the same time, the N, P and K in the PBS might actually improve the value of the compost as a soil amendment.

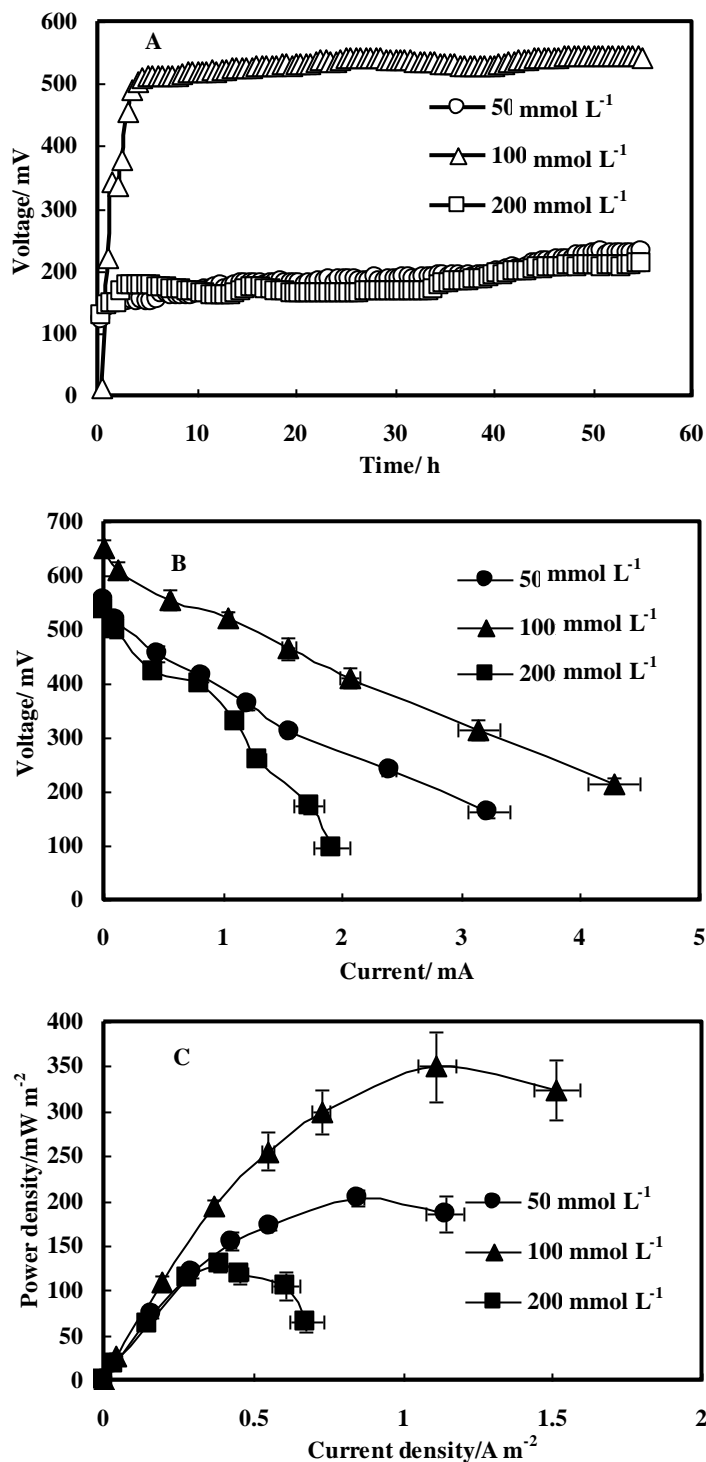


Figure 4. Effect of buffer solution on performance of the composting MFC. A: Voltage generation; B: Voltage-current curve; C: Power density curve. The error bars indicate standard deviation.

3.4 Effect of electrode area

Effect of electrode area on performance of the composting MFC is shown in Figure 5. When the area of the electrode was 113 cm², maximum power is 1.39±0.5 mW, which was greater than the

value of 0.95 ± 0.3 mW observed for an electrode area of 28 cm^2 . However, maximum power density of the MFC with electrode area of 28 cm^2 was $349 \pm 39 \text{ mW m}^{-2}$, which was greater than that of $100 \pm 11 \text{ mW m}^{-2}$ observed when the area of the electrode was 113 cm^2 . Electromotive force and internal resistance of the MFC was $660 \pm 25 \text{ mV}$ and $100 \pm 9 \Omega$ when the larger electrode was used, but only $626 \pm 12 \text{ mV}$ and $99 \pm 7 \Omega$ when the smaller electrode was used.

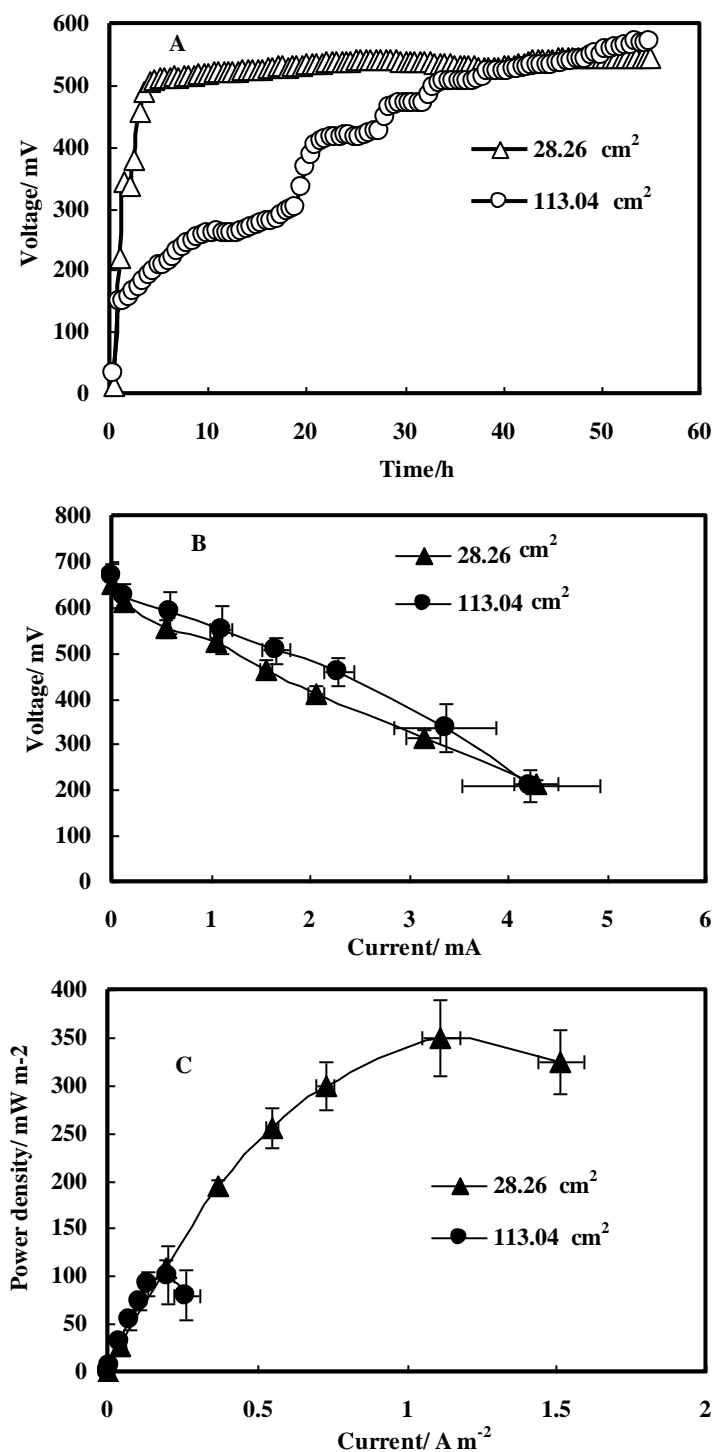


Figure 5. Effect of electrode area on performance of the composting MFC. A: Voltage generation; B: Voltage-current curve; C: Power density curve. The error bars indicate standard deviation.

Although total energy produced by the MFCs was greater with the larger electrode, the power per unit area of electrode was less. The reason for the lesser production of current when the larger electrode was used could be due to the greater concentration of O₂ due to diffusion to the anode when the larger cathode area was used [33]. In addition, exoelectrogenic bacteria could have come into contact with greater amounts of organic matter and thus produce electricity more efficiently when the electrode area was smaller. When corn stover was used as the substrate in a MFC, and cathodes were carbon cloth with an electrode area of 4.9 cm², maximum power density was 331 mW m⁻² [34]. When an air-cathode MFC was used with a substrate of brewery wastewater, and electrodes were placed on a cylindrical chamber with area of 7 cm², its power density was 187 ± 8 mW m⁻² [35]. In the study reported on here, a longer lag time is needed to reach a stable power out using MFC with larger electrode area. Thus, utilizing several MFCs with smaller electrode area would be more efficient than using fewer MFCs with larger electrode areas.

3.5 Change of C, N and C/N ratio

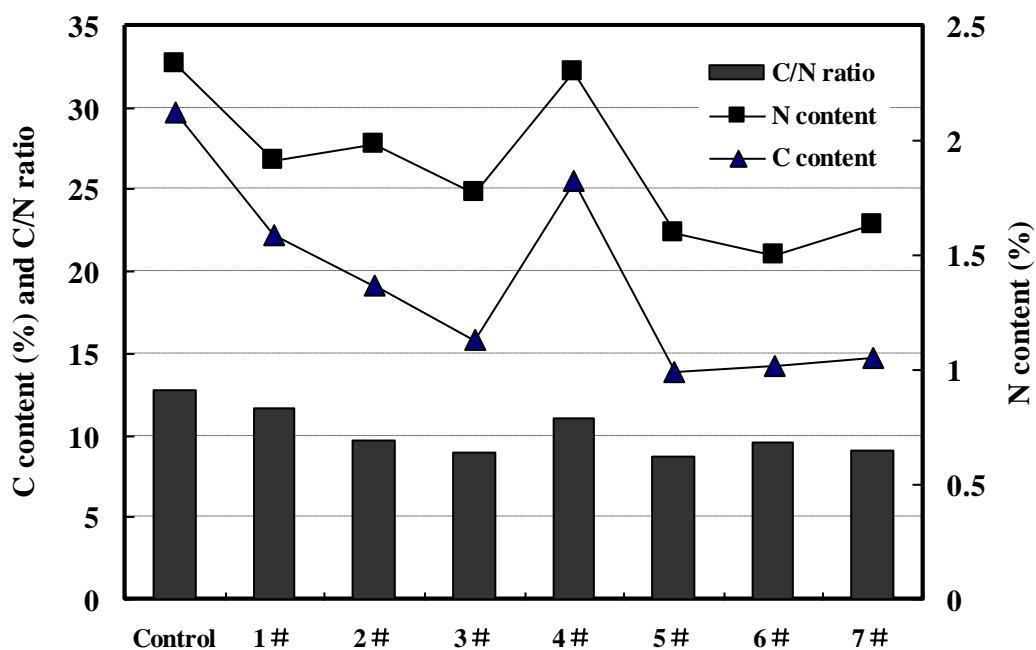


Figure 6. Degradation of organic component during composting the MFC process

Composting is also a process of microbial degradation of organic components so the concentrations of C and N and the C/N ratios varied among conditions of composting manure in the MFCs (Figure 6). The mass of C decreased in all the runs compared with the control in which the microbial community had been killed. Greater decreases were observed in runs 3, 5, 6, 7, which had greater water contents, which indicated the importance of water content in degradation of organic C. The least reduction in C was observed in run 4 which had no catalyst, a result that indicated that reactions within the MFC had enhanced biodegradation of organic carbon. Behavior of N was similar to that of C, except that the N content increased slightly in runs 2 with a moderate water content of

70% and run 7 with the least concentration of PBS. C/N ratio decreased in all runs with lesser values in runs 3 and 5 with greater water content, moderate concentrations of PBS in the presence of catalyst. The decrease of C/N ration during composting has been reported previously [18, 36, 37], which indicated greater reaction rate with lesser C/N ratios. Since oxidation of organic substrates can be enhanced when the electrons in anode area can be removed quickly to the cathode, reactions in the MFC, especially with catalyst in cathode played a more important role in affecting microbial degradation of organic component as compared to other factors such as water content, PBS concentration and electrode area.

3.6 Change of microbial community in the anode

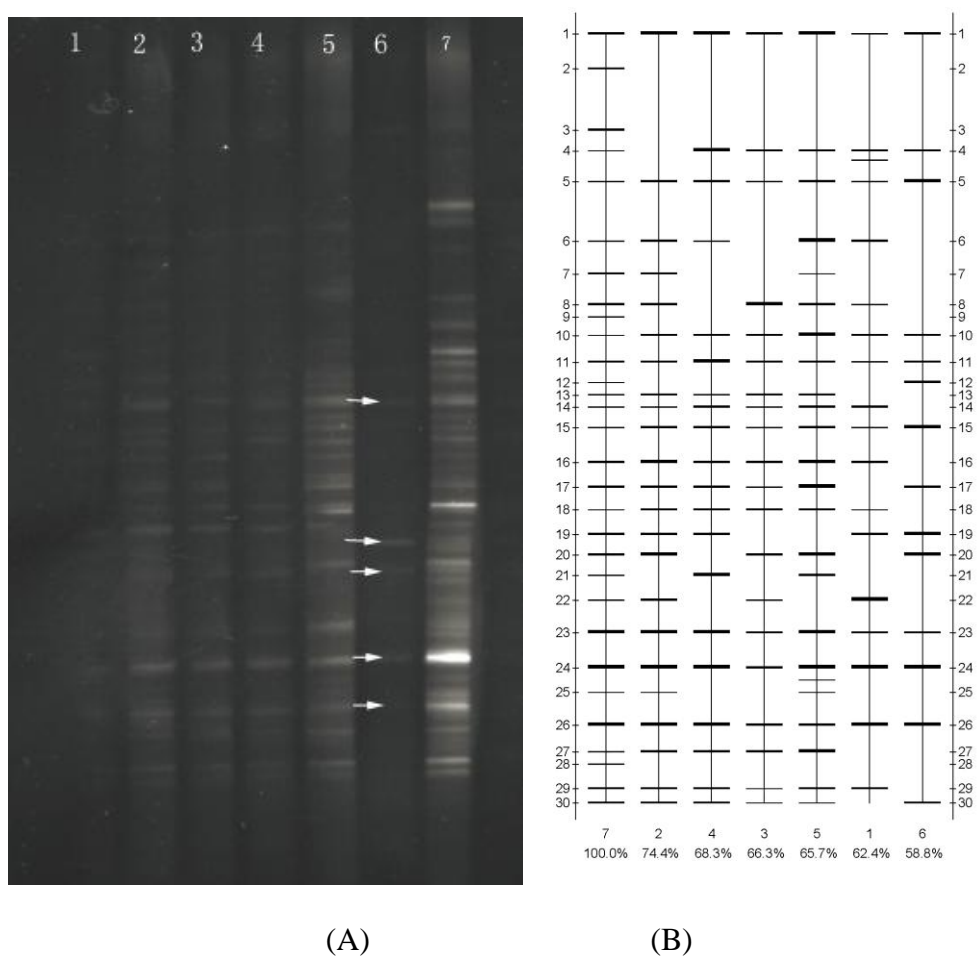


Figure 7. DGGE analysis of microbial community diversity during operation of the composting MFC process. (A) photo from DGGE analysis (B) bands simulation by quantity one.

The microbial community in the anode of composting MFC as determined by DGGE varied among conditions in the MFC (Figure 7). From the brightness of DGGE bands in Figure 7(A), there are more types of microbes in runs 5 and run 7, which had greater anode area and lesser concentrations of PBS, respectively. Diversities of the microbial communities were in decreasing order: 7>2>4>3>5>1>6. Since run 3 produced the greatest voltage and current density, it can be concluded

that production of electricity is not correlated with indexes of microbial diversity or total mass of the microbial community. The fewest number of bands were observed in lane 6 (Figure 7A), indicating that proliferation of the microbial community was inhibited by the greater PBS content in the compost substrate. The bands indicated by the arrow in the Figure might be from the electrogens. The lesser diversity of electrogeneous microbes has also been suggested by other researches [38, 39]. Some of the bands such as the second arrow did not appear in other lanes, which indicates that there are unique bacteria in the greater buffer salt condition. The growth of microbes other than electrogens in the anode might also inhibit proliferation of electrogens.

4. CONCLUSION

Generation of electric current can be affected by different influencing factors. Moisture content should be kept high for the practical application of composting MFC. Catalyst should be added in cathode and the value of maximum power density and output voltage may be low without catalyst. Proper concentration of PBS could promote conductivity of the system, which needs further study to get the suitable value according to different substrates and reaction conditions. Smaller electrode area was more efficient in current producing and resulted in shorter lag time. The MFC process can enhance the degradation of organic C at the same time. The microbial community change is not consistence with that electricity generation which suggested that electrogens and non-electrogens coexisted in the biofilm of MFC anode. Composting MFC could enhance solid waste degradation and generate electronic current at the same time, which will be a new development of MFC and can be applied in remote areas where water supply is insufficient but there are many organic wastes.

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