

Parameters Influencing Power Generation in Eco-friendly Microbial Fuel Cells

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Abstract: Pulp and papermaking industries generate high volumes of carbohydrate-rich effluents. Microbial fuel cell (MFC) technology is based on organic materials' consumption and efficient power production. Using a classical two-chamber lab-scale MFC design with an external resistance of 2000 Ω , we investigated the effects of anode chamber biofilm adaptation (ACBA) and cathode chamber redox solutions (CCRS) on the operation efficiency of MFC when treating wastewater. In ACBA studies, biofilm growth activation showed an increase in the power density to 20.48, 35.18, and 36.98 mW/m^2 when the acetate feeding concentrations were 3, 6, and 12 g/L, respectively. Improvement by biofilm adhesion on granular activated carbon (GAC) was examined by scanning electron microscopy (SEM). The obtained power density increased to 25.47, 33.42, and 40.39 mW/m^2 when the GAC particles concentrations were 0, 50, and 100 g/L, respectively. The generated power densities were 51.26 and 40.39 mW/m^2 as well as the obtained voltages were 0.41 and 0.72 V when the electrode area increased from 16 to 64 cm^2 , respectively. Using the MFC optimized parameters, CCRS studies carried out using five different cathodic redox solutions. The results revealed that the use of manganese dioxide dissolved in hydrochloric acid generated the maximum power density of 112.6 mW/m^2 , current density of 0.094 A/m^2 , and voltage of 1.20 V with a successful organic removal efficiency of 86.0% after 264 h of operation.

Keywords: microbial fuel cell; bioenergy; biofilm; power density; effluent

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1 Introduction

Environmental protection and clean energy production are two issues of great importance to sustainable society. Renewable energy and water resources are two major sectors that influence our life. Pulp refining generally includes different processes that discharge wastewater containing polysaccharides, lignin, and other extracts. Cellulose, a polymer of glucose (C_6 -sugar) with both crystalline and amorphous regions. Hemicellulose, an amorphous polymer of xylose (C_5 -sugar), C_6 sugars, and a variety of side-chains, is an important structural polysaccharide. Lignin is an amorphous co-polymer of phenyl-propene units formed via a random radical co-polymerization of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol^[1-3]. Many renewable energy technologies are being continuously studied as a result of the increasing energy crisis. It is well-known that bacterial strains can break down organic substrates anaerobically and produce power. The increasing demand for energy has reinvigorated research interest in the development of microbial fuel cells (MFCs). Previous studies have demonstrated that MFCs can generate power from organic wastes, such as wastewater^[4-6], sediments^[7], enzymes^[8], and even rhizodeposits^[9]. Botanist M. C. Potter first conceived the idea of MFC operation using *E.coli* strain in 1931. The operation efficiency of MFCs is affected by the anode-cathode design, microbial strain, degraded chemical substances, ion-exchange membrane, and other operational parameters^[10-12].

MFCs have been used as biosensors for measurement of biochemical oxygen demand and detection of toxic compounds, such as heavy metals and anthropogenic chemicals, in both freshwater and wastewater. MFCs have gained significant interest in recent years as it considered as innovative and eco-friendly form of bioenergy that can produce sustainable power from liquid wastes. MFC operation depends on the biochemical reactions, where the anaerobic microbes can act as a catalyst without undesired carbon emission. Research studies have demonstrated that

any biodegradable compounds could be transformed into power^[13]. During MFC operation, anode generates electrons via organic compounds oxidation that transfer into cathode that acts as an electron acceptor. Anaerobic wastewater treatment is substantially less energy-intensive than aerobic treatment; however, it is time-consuming because of the inherently slow growth rate of anaerobic microbes. Hence, there is little interest for applying anaerobic processes to dilute wastewater such as domestic wastewater^[14]. Typical MFC consists of anodic chamber and cathodic chamber separated by proton exchange membrane (PEM). The role of PEM, or occasionally a salt bridge, is to allow protons to move across to the cathode, while obstructing diffusion of oxygen into the anode, as shown in Fig.1.

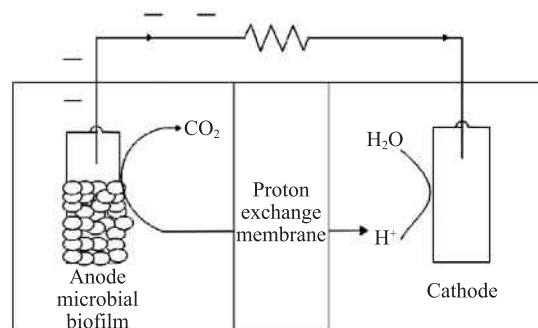


Fig.1 Typical structure of MFC

Power generation from MFCs is still less than that desirable for applicable power generation. In spite of advanced researches on MFC improvements in reactor design to increase power output, but still the cost would be excessive for real-time applications. Several attempts have been done for MFC application using synthetic and raw wastewater such as paper recycling wastewater, brewery wastewater, beer brewery wastewater, chocolate industry wastewater, domestic wastewater, food processing wastewater, meat processing wastewater, protein-rich wastewater, starch processing wastewater, and swine wastewater for waste treatment and power production^[15].

The objective of this study is to investigate the bioelectrochemical changes of lab-scale MFC and modify the parameters that influence its performance to get the maximum current and power density output

as well as organics removal efficiency represented in chemical oxygen demand (COD). The studied parameters include anode chamber biofilm adaptation (ACBA) and cathode chamber redox solution (CCRS) studies. Modification of these parameters enhances selection generation and electron transfer mechanisms. The ACBA studies focused on the anode bioreactor, the operation of which depends on the anaerobic biofilm used and the nature of the oxidized organic compounds since the biochemical reaction takes place. The CCRS studies focused on the cathode chamber, since the electrons are transferred into the cathode to generate power. Our aim is to the use of MFC for simultaneous achievement of desirable power generation and effective organic removal.

2 Materials and methods

2.1 MFC operation and instrumentation

Our lab-scale MFC design consists of two chambers with dimensions (length, width, height) of 10, 10, 15 cm for each chamber, separated by cationic exchange membrane, external resistance (R_{ex}) of 2000 Ω , carbon cloth as cathode and anode electrodes, as shown in Fig. 2. The anode chamber filled with 500 mL of anaerobic biofilm and 1000 mL of synthetic wastewater (COD about 2000 mg/L). Anaerobic biofilm was collected from the anaerobic reactor of Sun Paper Co., Ltd., Shandong province, China. Anaerobic biofilm was activated using basic nutrient media composed of 5 g/L glucose, 5 g/L peptone, 1.5 g/L beef extract, and 1.5 g/L yeast extract at 30°C incubated temperature. Five cathodic redox solutions were used: 0.2% potassium



Fig.2 Lab-scale MFC set-up with different cathodic redox solutions

permanganate, 50 mmol/L of both $K_3[Fe(CN)_6]$ - K_2HPO_4 , 3% H_2O_2 , 0.2% manganese dioxide dissolved in sulfuric acid, and 0.2% manganese dioxide dissolved in hydrochloric acid. Electrochemical voltages were measured with the aid of an online computer voltage digital data acquisition collector, MPS-010602 multi-function signal acquisition card, Beijing QICHUANG MOFEI Electronic Technology Co., Ltd. This device can measure voltages every minute for five MFCs simultaneously. COD was analyzed using a Lianhua Tech Ltd. COD rapid determination apparatus, 5B-6, 610 nm. Beijing Boyikang Laboratory Instrument Co. Ltd. freeze drier, FD-1D-5 was used for freeze-dried anaerobic biofilm preparation for SEM studies. SEM studies were carried out using a Japan Hitachi Nake High-Tech Enterprise SEM, S-3400N. Bi-distilled water was prepared using Beijing ASTK Technology Development Co., Ltd. water distillation plant, CSR-1-20II.

2.2 Electrical calculations

The power density (power/area, W/m^2) is calculated as:

$$\text{Power density} = \frac{V^2}{A \cdot R_{ex}}$$

The current density is calculated as:

$$\text{Current density} = \frac{V}{A \cdot R_{ex}}$$

Where, V is the voltage output (V), R_{ex} is the external resistance used (Ω), and A is the electrode area (m^2).

3 Results and discussion

A classical lab-scale MFC system consists of two electrodes: an anode for substrate oxidation and a cathode for oxygen reduction separated by a proton exchange membrane throughout study. The operating efficiency of the MFCs was evaluated in terms of both current output and organic removal by focusing on ACBA and CCRS studies.

3.1 ACBA studies

The ACBA studies are related to the anode chamber of the MFC, where electrons and protons are

produced from organic oxidation by the anaerobic biofilm bacteria attached to the anode electrode. The anaerobic biofilm microbes are electrogenic organisms. The electrochemical activity is characterized by direct electron transfer or transport (DET) and mediated electron transfer or transport (MET) mechanisms between the biofilm and the electrode. These mechanisms are the key principles of MFC operation^[16]. The ACBA parameters studied include growth activation by acetate feeding, biofilm growth on granular activated carbon (GAC), SEM examination of biofilm, and electrode area.

The MFC was operated using anaerobic biofilm inoculation collected from the anaerobic reactor of a paper mill in batch mode with a chemically defined medium such as glucose to generate energy at the anode chamber, potassium ferricyanide as a cathodic redox solution at the cathode chamber with R_{ex} of 2000 Ω , and electrode area of 64 cm². The voltages output were continuously recorded each minute using a data logger. The MFC was operated for more than two months to ensure anaerobic biofilm activation under pH value ≥ 5.5 , temperature 30°C and dissolved oxygen (DO) ≤ 0.7 mg/L with continuous adding of 50 mL/L of glucose solution 5 g/L and other growth factors every three days. Subsequently, we analyzed the effect of ACBA studies on the electrochemical data output.

As ACBA studies are based on biofilm, it is important to improve the physiological conditions to achieve efficient operational sustainability. The effect of acetate as a carbon source on the anaerobic biofilm in the anode chamber of the MFC was studied by varying the loading rate of acetate feeding concentrations. The results indicated a significant increase in both the obtained voltage and the power density output with the increase in the acetate feeding concentrations from 3 to 6 g/L. However, there were no significant changes when the acetate feeding concentrations increased from 6 to 12 g/L. The obtained voltages were 0.51, 0.67, and 0.69 V, the power densities were 20.48, 35.18, and 36.98 mW/m² and the achieved current densities were 0.040, 0.052, and 0.054 A/m², when the acetate feeding

concentrations were 3, 6, and 12 g/L, respectively as shown in Fig.3.

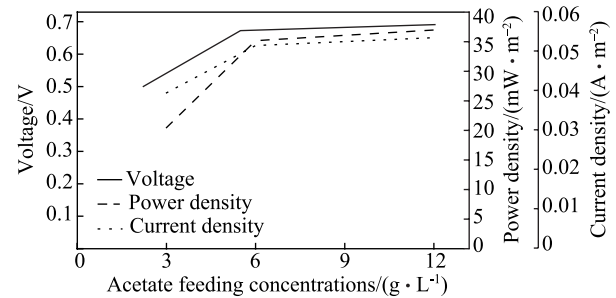


Fig.3 Effect of acetate feeding concentrations on the power output of MFC

The efficiency of the MFC was also studied by growing the anaerobic biofilm on GAC particles. Our results showed higher power generation in the case of GAC-MFC compared to the conventional MFC. As a result of the improved biofilm obtained using GAC particles, the DET and the MET electron transfer mechanisms increased to produce a positive effect on the GAC-MFC power generation. This could also be attributed to the growth of biofilm on the GAC particles, and good adhesion between the microbial biofilm cells and the GAC particles, which significantly increases the electron transport rate from the biofilm covering the electrode in the anode chamber to the cathode chamber, resulting in high current and power density output. As shown in Fig.4, a significant increase in both voltage and power density was obtained by increasing the concentration of GAC particles. The obtained voltages were 0.65 and 0.72 V at GAC particle concentrations of 50 and 100 g/L, respectively, which was higher than that obtained without GAC particles (0.57 V). The generated power densities were 33.42

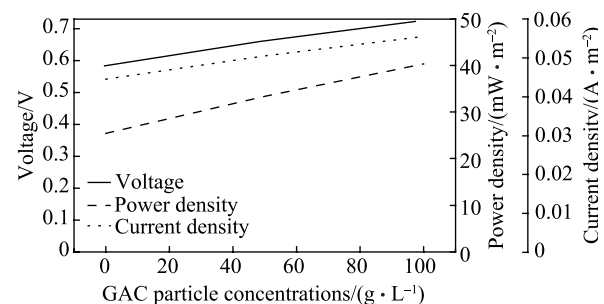


Fig.4 Effect of GAC particle concentrations on the power output of MFC

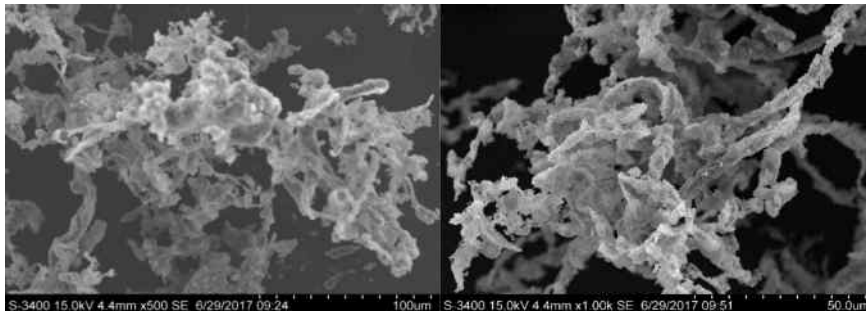


Fig.5 SEM images of the normal anaerobic biofilm

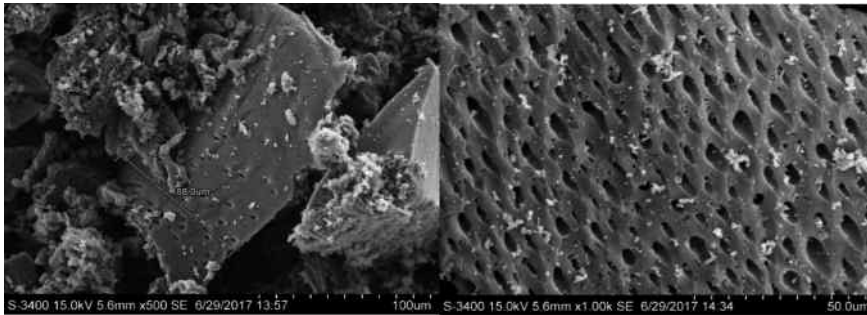


Fig.6 SEM images of the anaerobic biofilm on GAC particles

and 40.39 mW/m² at GAC particle concentrations of 50 and 100 g/L, respectively, which was higher than that obtained without GAC particles (25.47 mW/m²). The generated current densities were 0.051 and 0.056 A/m² at GAC particle concentrations of 50 and 100 g/L, respectively, which was higher than that obtained without GAC particles (0.045 A/m²)^[17].

The SEM examination of the studied anaerobic biofilm is considered an important part of the study, as the operation of the MFC depends on electron transfer mechanisms. The SEM was operated at two different magnification powers ($\times 500$ and $\times 1000$) for studying the anaerobic biofilms of both conventional MFC and GAC-MFC. From the SEM examination, we found that the studied anaerobic biofilm was mainly composed of filamentous mixed-culture biofilm species by which the electrons are transferred to the anode by electron transport systems as shown in Fig.5. In the GAC-MFC, we observed good adhesion between the microbial biofilm and the GAC particles, which increases the DET and the MET electron transfer to the anode electrode surface as shown in Fig.6. As a result, the GAC-MFC exhibited higher current and power density output than the conventional MFC^[18].

The effect of electrode area on the efficiency of the GAC-MFC was studied. An increase in the electrode area resulted in an increase in the obtained voltage and decrease in both current and power density output. As shown in Fig.7, the obtained voltages were 0.41 and 0.72 V at electrode areas of 16 and 64 cm², respectively. While the generated power densities were 51.26 and 40.39 mW/m² and the generated current densities were 0.127 and 0.056 A/m² at electrode areas of 16 and 64 cm², respectively. An increase in the electrode area resulted in an increase in the DET mechanism, and hence, the obtained voltage increased. However, the

generated power and current densities decreased because of reverse correlation with area^[19].

3.2 CCRS studies

The importance of CCRS as an electron acceptor and oxygen reduction inside the cathode chamber is equal to that of electrons transport and substrate oxidation inside the anode chamber^[20-23]. In GAC-MFC lab-scale classical system with acetate feeding concentration of 6 g/L, GAC partial concentration of 100 g/L, and electrode area of 64 cm², cathodic redox solutions of potassium permanganate, potassium ferricnide, hydrogen peroxide, manganese dioxide dissolved in sulfuric acid, and manganese dioxide dissolved in

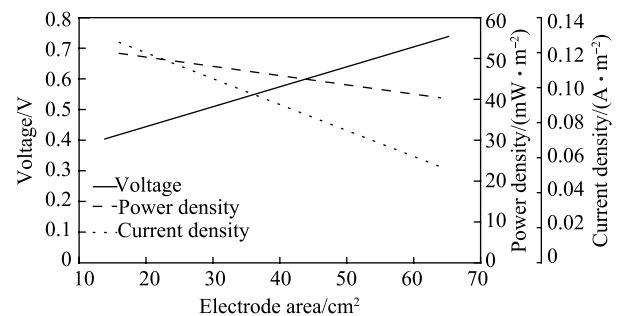


Fig.7 Effect of electrode area on the power output of GAC-MFC

hydrochloric acid were studied for their efficacy in attracting electrons and protons produced by the anode chamber for maximum power generation during the MFC operation.

The CCRSs were supplied into the cathode chamber by soaking over the carbon cloth electrode to prevent drying. The generated power densities were 35.07, 40.39, 45.01, 71.70, 112.62 mW/m^2 and current densities were 0.052, 0.056, 0.059, 0.075, 0.094 A/m^2 when potassium permanganate, potassium ferricyanide, hydrogen peroxide, manganese dioxide dissolved in sulfuric acid, and manganese dioxide dissolved in hydrochloric acid, respectively were used as the CCRS. As shown in Fig.8, the use of potassium permanganate generated the lowest current output, while the use of manganese dioxide dissolved in hydrochloric acid generated the maximum current output^[24-25].

The performance of the GAC-MFC was also examined using the optimized operation parameters in terms of bioelectrochemical changes that include organic removal and current harvesting efficiencies along with the hydraulic retention time (HRT). HRT can be defined as the contact time between the biofilm and the substrate required for optimal organic removal and maximum power generation. As a result of slow anaerobic microbial growth during the operation, the generated voltage, power density, and organic removal efficiencies were gradually increased^[26]. At acetate feeding concentration of 6 g/L, GAC particle concentration of 100 g/L, electrode area of 64 cm^2 ,

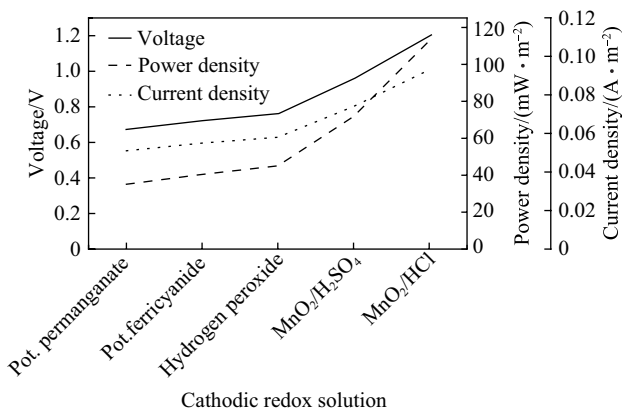


Fig.8 Effect of different CCRS on the power output of GAC-MFC

and manganese dioxide dissolved in hydrochloric acid as the CCRS in the GAC-MFC, the changes in the organic load concentrations and the electrical output as a function of time were observed daily for 264 h of operation. The results represented a significant forward correlation between the COD removal and the current intensity output with the HRT. As shown in Fig.9, the COD removal efficiency reached 86.0% after 264 h of operation. The maximum output voltage, power density, and current density were 1.20 V, 112.6 mW/m^2 , and 0.094 A/m^2 , respectively after 264 h of operation.

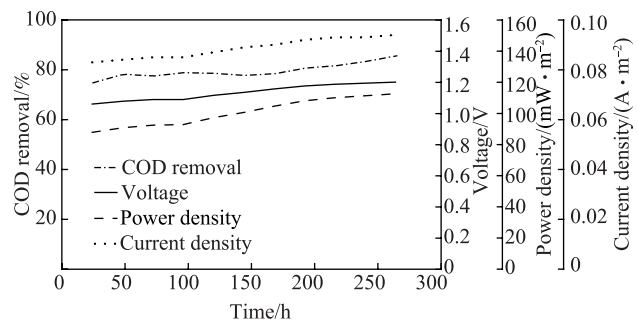


Fig.9 Variation in the bioelectrochemical data during GAC-MFC operation

4 Conclusions

The operation of MFC depends on the electron transfer mechanisms that affected by anode, cathode, and proton exchange membrane for effective power generation with high organic removal rate. It mainly depends on three fundamental branches of science: microbiology, biochemistry, and electrochemistry. According to the ACBA studies, it can be concluded that acetate loading of 6 g/L, biofilm growth on GAC [GAC-MFC], and electrode area of 64 cm^2 are required to enhance the electron transfer mechanism inside the MFC-anode chamber. Our CCRS studies revealed that manganese dioxide dissolved in hydrochloric acid is the best cathodic redox solution for electron transfer and for oxygen reduction compared to the other CCRSs. The development of MFC concerning our results can enhance its performance to achieve greater power generation and excellent COD removal rate.

Acknowledgments

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References

- [1] Allen R M, Bennetto H P. Microbial fuel cells: electricity production from carbohydrates[J]. Appl. Biochem. Biotechnol., 1993, 39(40): 27-40.
- [2] Farrukh A, Mays N A, Brian P, et al. A review of cellulosic microbial fuel cells: performance and challenges[J]. Biomass & Bioenergy, 2013, 56: 179-188.
- [3] Logan B E. Generating electricity from wastewater treatment plants[J]. Water Environment Research, 2005, 77(3): 209.
- [4] Lithgow A M, Romero L, Sanchez I C, et al. Interception of electron-transport chain in bacteria with hydrophilic redox mediators[J]. J. Chem. Res., 1986, 5: 178-179.
- [5] Liang F, Feng W, Su Z, et al. Effect of Electrode on the Treatment of OCC Wastewater Using a Microbial Fuel Cell[J]. Transaction of China Pulp and Paper, 2016, 31(2):24-28.
- [6] Liang F, Feng W, Su Z, et al. Research on OCC Wastewater Treatment and Power Generation Using a Microbial Fuel Cell[J]. China Pulp & Paper, 2016, 35(2):8-13.
- [7] Arends Jan B A, Evelyne Blondeel, Steve R Tennison, et al. Suitability of granular carbon as an anode material for sediment microbial fuel cells[J]. Journal of Soils and Sediments, 2012, 12(7): 1197-1206.
- [8] Song Y, Penmatsa V, Wang C. Recent development of miniaturized enzymatic biofuel cell[C]//Energy Harvesting and Storage: Materials, Devices, and Applications, Proceedings of SPIE 8035, 2011, DOI:10.1117/12.885569.
- [9] Timmers Ruud A, Strik David P B T B, Arampatzoglou Cristina, et al. Rhizosphere anode model explains high oxygen levels during operation of a *Glyceria maxima* PMFC[J]. Bioresource Technology, 2012, 108: 60-67.
- [10] Kothapalli Ananta. Sediment microbial fuel cell as sustainable power resource[D]. Wisconsin: University of Wisconsin-Milwaukee, 2013.
- [11] Gil G C, Chang I S, Kim B H, et al. Operational parameters affecting the performance of a mediator-less microbial fuel cell[J]. Biosens. Bioelectron., 2003, 18: 327-334.
- [12] Nykova N, Muller T G, Gyllenberg M, et al. Quantitative analyses of anaerobic wastewater treatment processes: identifiability and parameter estimation[J]. Biotechnology and Bioengineering, 2002, 78(1): 89-103.
- [13] Logan B E, Regan J M. Feature article: microbial fuel cells-challenges and applications[J]. Environ. Sci. Technol., 2006, 40(17): 5172-5180.
- [14] Hadi Yazdi, Liliana Alzate-Gaviria, Zhiyong Jason Ren. Pluggable microbial fuel cell stacks for septic wastewater treatment and electricity production[J]. Bioresource Technology, 2015, 180: 258-263.
- [15] Vinicius Fabiano Passos, Sidney Aquino Neto, Adalgisa Rodrigues de Andrade, et al. Energy generation in a Microbial Fuel Cell using anaerobic sludge from a wastewater treatment plant[J]. Sci. Agric., 2016, 73(5):424-428.
- [16] Zhuwei Du, Haoran Li, Tingyue Gu. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy[J]. Biotechnology Advances, 2007, 25: 464-482.
- [17] Hao Ren, Soonjae Pyo, Jae-Ik Lee, et al. A high power density miniaturized microbial fuel cell having carbon nanotube anodes[J]. Journal of Power Sources, 2015, 273: 823-830.
- [18] Jiang D, Li B. Granular activated carbon single-chamber microbial fuel cells(GAC-SCMFCs): A design suitable for large-scale wastewater treatment processes[J]. Biochemical Engineering Journal, 2009, 47(1): 31-37.
- [19] Ghangrekar M M, Shind V B. Performance of membrane-less microbial fuel cell treating wastewater and effect of electrode distance and area on electricity production[J]. Bioresource Technology, 2007, 98: 2879-2885.
- [20] Minghua Zhou, Hongyu Wang, Daniel J Hassett, et al. Recent advances in microbial fuel cells(MFCs) and microbial electrolysis cells(MECs) for wastewater treatment, bioenergy and bioproducts[J]. J. Chem. Technol. Biotechnol., 2013, 88: 508-518.
- [21] Babauta Jerome T, Nguyen Hung Duc, Ozlem Istanbulu, et al. Microscale gradients of oxygen, hydrogen peroxide, and pH in freshwater cathodic biofilms[J]. Chem Sus Chem, 2013, 6(7): 1252-1261.
- [22] Karra Udayarka, Guoxian Huang, Ridvan Umaz, et al. Stability characterization and modeling of robust distributed benthic microbial fuel cell(DBMFC) system[J]. Bioresource Technology, 2013, 144: 477-484.
- [23] Shima Fasahat. Microbial fuel cells and their applications in electricity generating and wastewater treatment[J]. International Scholarly and Scientific Research & Innovation, 2017, 11(3):203-207.
- [24] Li X, Hu B, Suib S, et al. Manganese dioxide as a new cathode catalyst in microbial fuel cells[J]. Journal of Power Sources, 2010, 195(9): 2586-2591.
- [25] Suib S L. Porous manganese oxide octahedral molecular sieves and octahedral layered materials[J]. Accounts of Chemical Research, 2008, 41(4): 479-487.
- [26] Rozendal R, Hamelers H, Rabaey K, et al. Towards practical implementation of bioelectrochemical wastewater treatment[J]. Trends in Biotechnology, 2008, 26(8): 450-459. PBM