Journal of Zhejiang University-SCIENCE B (Biomedicine & Biotechnology)
ISSN 1673-1581 (Print); ISSN 1862-1783 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Electricity generation and brewery wastewater treatment from sequential anode-cathode microbial fuel cell*

Qing WEN†1, Ying WU[1], Li-xin ZHAO[2], Qian SUN[1], Fan-ying KONG[1]

([1]*College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China*)

([2]*Mechanical Science and Engineering College, Daqing Petroleum Institute, Daqing 163318, China*)

†E-mail: wenqing_hrbeu@yahoo.com.cn

Received Sept. 2, 2009; Revision accepted Dec. 25, 2009; Crosschecked Jan. 4, 2010

Abstract: A sequential anode-cathode double-chamber microbial fuel cell (MFC), in which the effluent of anode chamber was used as a continuous feed for an aerated cathode chamber, was constructed in this experiment to investigate the performance of brewery wastewater treatment in conjugation with electricity generation. Carbon fiber was used as anode and plain carbon felt with biofilm as cathode. When hydraulic retention time (HRT) was 14.7 h, a relatively high chemical oxygen demand (COD) removal efficiency of 91.7%–95.7% was achieved under long-term stable operation. The MFC displayed an open circuit voltage of 0.434 V and a maximum power density of 830 mW/m^3 at an external resistance of 300 Ω. To estimate the electrochemical performance of the MFC, electrochemical measurements were carried out and showed that polarization resistance of anode was the major limiting factor in the MFC. Since a high COD removal efficiency was achieved, we conclude that the sequential anode-cathode MFC constructed with bio-cathode in this experiment could provide a new approach for brewery wastewater treatment.

Key words: Brewery wastewater, Chemical oxygen demand (COD) removal efficiency, Electrochemical impedance spectroscopy, Microbial fuel cell (MFC)

doi:10.1631/jzus.B0900272 **Document code:** A **CLC number:** X7; O69

1 Introduction

The brewery industry discharges large volumes of highly polluting effluents throughout the year (Braeken *et al*., 2004; Parawira *et al*., 2005). Traditional treatments, such as aerobic sequencing batch reactor and up-flow anaerobic sludge blanket reactor, require a high energy input and are thus costly. New approaches for wastewater treatment which not only reduce cost but also produce useful side-products have recently received increasing attention. The microbial fuel cell (MFC) technology offers a valuable alternative to energy generation as well as wastewater treatment.

MFC is a device to treat wastewater and produce electricity at the same time (Bennetto, 1984; Habermann and Pommer, 1991). A variety of readily degradable compounds such as glucose and acetate, and various types of wastewater such as domestic, starching and paper recycling plant wastewater, have operated successfully as substrate in MFC (Melhuish *et al*., 2006; Freguia *et al*., 2007; Kargi and Eker, 2007; Liu and Li, 2007; Min and Angelidaki, 2008; Venkata-Mohan *et al*., 2008). Most could achieve a considerable chemical oxygen demand (COD) removal efficiency accompanied with electricity generation. Among these studies, landfill leachate was treated using MFC at a hydraulic retention time (HRT) of 18.7 h, and biological oxygen demand (BOD) decreased from 630 to 269 mg/L with a low power density of 1.35 mW/m^2 (Greenman *et al*., 2009). A

* Project supported by the Heilongjiang Science and Technology Key Projects (No. GC07A305), the Fund of Harbin Engineering University (No. HEUFT08008), and the Daqing Science and Technology Key Projects (No. SGG2008-029), Heilongjiang, China

comparable result of 80% in COD removal efficiency was obtained by Liu *et al*. (2004) using domestic wastewater, accompanied with a maximum electrical power of 26 mW/m^2.

Currently, abiotic cathodes are the most commonly used cathodes in MFCs, which complete the circuit as electron acceptors, but do not perform direct wastewater treatment. Since concentrations of organic matters after anaerobic treatment in anode chamber are relatively high, deep aerobic treatment is expected to degrade wastewater further to achieve the wastewater discharge standard. It is noticeable that MFC is a combined system with anaerobic and aerobic characteristics. It can be regarded not only as an anaerobic treatment process in anode chamber, but also a complete unit with an aerobic treatment process in the cathode chamber. Consequently, a combination of anaerobic-aerobic process can be constructed using a double-chambered MFC, in which effluent of anode chamber could be used directly as the influent of the cathode chamber so as to be treated further under aerobic condition to improve wastewater treatment efficiency. Freguia *et al*. (2008) have constructed a sequential anode-cathode MFC to treat artificial wastewater, and reported that this configuration could improve cathodic oxygen reduction and effluent quality of MFCs.

In this experiment, brewery wastewater treatment using sequential anode-cathode MFC, in which the effluent of anode chamber was used as a continuous feed for an aerated cathode chamber, was studied. Degradation of organic matter of the MFC was investigated under long-term stable operation. Peak performance of the MFC was monitored by polarization curves. Electrochemical measurements, including Tafel plots and electrochemical impedance spectroscopy (EIS), were carried out to analyze the characteristics on polarization behavior of the electrodes and discharge resistances of the MFC.

2 Materials and methods

2.1 Microbial fuel cell construction

MFC was constructed by two plexiglas rectangular chambers (6 cm×5 cm×6 cm, each with a liquid working volume of 0.1 L) separated by a proton exchange membrane (PEM) (Nafion 117, Dupont Co., USA), which was pretreated according to the procedure reported by Yoshitake *et al*. (1996) to increase the porosity and stored in deionized water prior to use (Fig. 1). Anode was made of three parallel groups of carbon fibers, which were wound on two graphite rods (Φ8 mm, 5 cm long) to form 3-sheet structures (4 cm×3 cm); plain carbon felt (6 cm×6 cm, 3 mm thick) (Qijie Carbon Material Co., Shanghai, China) with biofilm was used as cathode. An aerator was inserted in the bottom of cathode chamber to supply air with an aquarium pump and provide mixing. Both anode and cathode chambers were constructed with a water inlet and outlet on each side, while six electrode tip jacks (forming a double line) with a diameter of 9 mm were set up on the top. Connections between two electrodes were made with copper wires through a rheostat (0.1–9999 Ω).

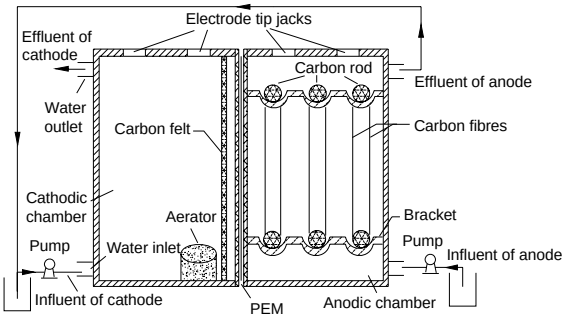

Fig. 1 Schematic diagram of sequential anode-cathode microbial fuel cell

2.2 Culture and operation

Anaerobically mixed sludge from Harbin brewery (Heilongjiang, China) was used as inoculum in the anode chamber of the MFC for electricity generation; aerobic sludge was collected from a sequencing batch reactor (SBR) (used to treat glucose artificial wastewater) in our lab. Then 20 ml of this aerobic sludge was injected into the cathode chamber as inoculum. Raw brewery wastewater was used as substrate of anode. The characteristics of brewery wastewater are listed in Table 1.

Table 1 Characteristics of brewery wastewater

Characteristic	pH	COD (mg/L)	NH_3-N (mg/L)	TN (mg/L)	SS (mg/L)
Value	6.5±0.4	1250±100	16±5	24±3	500±50

The MFC was operated in continuous flow at room temperature [(24±4) °C]. Raw brewery wastewater

was fed by a peristaltic pump (Longer BT100-1 J, China) to the anode chamber, of which the up-flow rate was 13.6 ml/h, corresponding to an HRT of 7.35 h. Effluent of anode was connected by a beaker, and then it was pumped into the cathode chamber with the same flow rate, which kept an HRT of 7.35 h. Thus the overall HRT of this system was 14.7 h.

2.3 Analytical methods

COD measurements were conducted using standard methods, the closed reflux method (Wei, 2002). Voltage (U) yielded from MFC for long time operation was recorded automatically by a computer at an interval of 3 min and converted to power density, according to P (W/m^3)=1000$U\times j\times A$/0.1 or P (W/m^2)=$U\times j$, where j is current density (A/m^2), which is calculated by $j=U/(R\times A)$ based on external resistance R (Ω) and projected surface area of cathode or anode A (m^2), 1000 is based on the unit change, and 0.1 denotes the volume of anolyte (L). A digital voltmeter was used against a saturated Ag/AgCl reference electrode to measure electrode potentials. Polarization curves were obtained by plotting potential and power density against current density at variable resistance points (9000 to 10 Ω) during stabilized MFC operation every one hour after each resistance load was changed.

To estimate the electrochemical performance of the MFC, electrochemical measurements, including Tafel plots and EIS, were performed with a potentiostat (CHI604B, Chenghua Instruments, Shanghai, China). Tafel plots were scanned at a rate of 0.1 mV/s, while EIS was measured at a frequency range of 0.01–10^5 Hz with amplitude of 0.005 V, which is shown in Nyquist plots (Barsoukov and Macdonald, 2005).

3 Results and discussion

3.1 Bioelectricity production during startup period of the MFC

Before anode inoculation, the cathode was pretreated in aerobic sludge for biofilm growth for one month (data not shown). Thereafter raw brewery wastewater was pumped continuously into anode, of which the effluent was used as substrate of cathode. Cell voltage was recorded by a computer, while electrode potentials were recorded every 12 h by a digital voltmeter against a saturated Ag/AgCl reference electrode. Following sequential connection of anode and cathode, an increase in performance of the MFC occurred (Fig. 2). After a transitory lag period, anode potential decreased sharply from −155 to −300 mV between Days 3 and 4, while cell voltage increased from 21 to 68 mV. Since the anode material has been used in previous experiment to treat brewery wastewater using a single-chambered MFC (Wen *et al*., 2009) for 5 months, it suggests that the activity of anaerobic biofilm at the anode maintained well and recovered fast. After 13 d of startup, the MFC performed a relatively stable voltage of about 60 mV at an external resistance of 100 Ω, accompanied with a power density of 0.36 W/m^3.

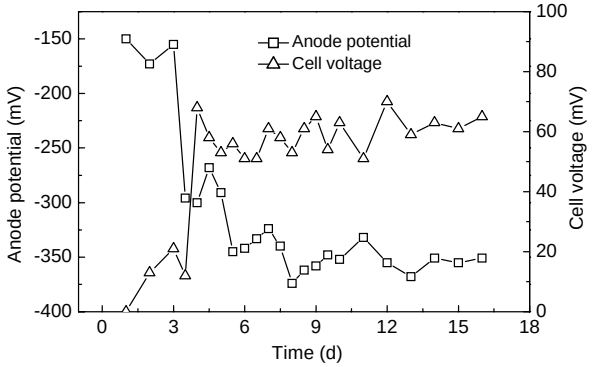

Fig. 2 Development of anode potential and cell voltage measured at 100 Ω during startup period

3.2 Wastewater treatment of the MFC during long-term stable operation

After a period of stable continuous operation, the wastewater treatment performance of the sequential anode-cathode MFC with direct air sparging was monitored at 100 Ω for a week. Both anode and cathode chambers were continuously monitored for substrate (as COD) removal to evaluate the potential of the MFC to act as an anaerobic-aerobic wastewater treatment unit (Table 2). Data showed that, as influent COD fluctuated between 1249 and 1359 mg/L corresponding to organic loading rates (OLRs) of 4.08–4.43 kg COD/(m^3·d), overall removal efficiencies of 91.7%–95.7% [3.87–4.24 kg COD/(m^3·d) for substrate degradation rates, SDRs] were achieved, while contributions of anode chamber were 45.6%–49.4% [1.86–2.12 kg COD/(m^3·d) for SDRs], which

Table 2 Wastewater treatment of the MFC during stable operation

Time (d)	Influent COD (mg/L)	Effluent COD of anode (mg/L)	Effluent COD of cathode (mg/L)	Removal efficiency of anode chamber (%)	Overall removal efficiency (%)
1	1299	657	107	49.4	91.7
2	1283	673	96	47.5	92.5
3	1283	705	63	45	95.1
4	1267	657	59	48.1	95.3
5	1305	695	62	46.7	94.9
6	1359	710	60	47.7	95.6
7	1249	680	54	45.6	95.7

account for about a half proportion. Wang *et al*. (2008) investigated the performance of an air-cathode MFC treating brewery wastewater at an HRT of 60 h, and found a COD removal of 79% was obtained when brewery wastewater concentration was 1333 mg COD/L. Compared with that, sequential anode-cathode MFC in this experiment can greatly improve the effluent quality at a much lower HRT. The sequential system in this study showed its potential for substrate removal in both anode and cathode, indicating that sequential anode-cathode MFC has a well capacity in brewery wastewater treatment.

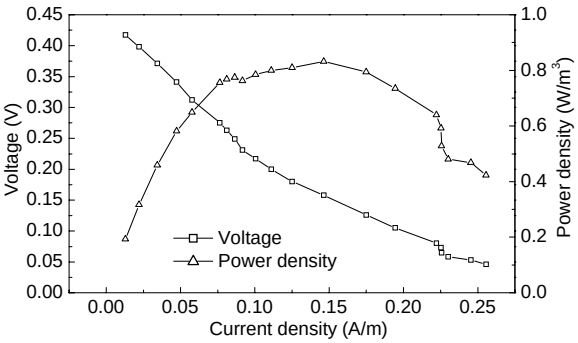

Fig. 3 Current and power generation details during MFC operation with the function of resistance

3.3 Electricity production determined by polarization curves

The feasibility of power generation in conjugation with the wastewater treatment was documented by measuring voltage and power output. Peak performance was determined by polarization curves obtained at different resistances (10–9000 Ω) when influent COD of anode was 1249 mg/L (Fig. 3). With an open circuit voltage of 0.434 V, a maximum power density of 830 mW/m^3 (23.1 mW/m^2 vs. cathodic area, 7.5 mW/m^2 vs. anodic area) was achieved at an external resistance of 300 Ω in this experiment. Data showed that the power output of the sequential anode-cathode MFC in this experiment was quite low, most likely due to a much higher internal resistance (300 Ω, the external resistance at the maximum power output), which is accordance with the result of Ieropoulos *et al*. (2008). Furthermore, it was said that excessive COD entering the cathode could eventually restrict oxygen supply to the cathodic biofilm and hence prevent electricity generation, which was caused by the growth of aerobic heterotrophs. Since the influent COD of cathode in this study was 650–710 mg/L, which can be considered relatively high, the inferior electrochemical performance of the MFC may be due to the excessive COD entering the cathode. In addition, the low cathodic open circuit potential of −0.034 V in this experiment also indicated a sign of incipient COD carry-over. Therefore, the performance of this sequential anode-cathode MFC can be further improved by optimization.

Although the electricity production was low, the MFC generated an effluent with consistently low COD of 60 mg/L around, as a stable and high organic removal efficiency (>90%) was achieved at an HRT of 14.7 h (7.35 h for both anode and cathode). The high COD removal was achieved because the cathode process acted as an additional aerobic polishing step following the standard anodic treatment. MFC anodes do not have the ability to thoroughly remove biodegradable COD as shown previously (Liu *et al*., 2004). By feeding the anode effluent to an aerobic cathode, heterotrophs growing on the cathode can use oxygen to hydrolyze and oxidize biodegradable COD. It can be concluded that sequential anode-cathode MFC could provide a new approach for brewery wastewater treatment, even the one that is much harder to be biodegraded. Moreover, since the raw brewery wastewater was directly used as substrate in this MFC,

of which the ion strength and buffer capacity were relatively low, the performance of the MFC could probably be improved by adding phosphate buffer solution (PBS), which will be our next study in the future.

3.4 Electrochemical evaluation

3.4.1 Polarization behavior of the electrodes

Since the power produced from the MFC was low, electrochemical measurements including polarization behavior of the electrodes (Tafel plots) and EIS were carried out to estimate the electrochemical performance of individual electrode and the cell. Electrode potentials were generated during the continuous operation using a potentiostat vs. a standard Ag/AgCl reference electrode. The MFC was first run at open circuit for 10 h to achieve a steady open circuit voltage and subsequently the MFC voltage was changed with the potentiostat at the scan rate of 0.1 mV/s (Fig. 4). After an initial lag period of overpotential, the Tafel lines became linear. Based on the Tafel equation, the *X*-axis intercept is the logarithm of the exchange current densities ($\ln j_0$), and thus the exchange current densities (j_0) of 0.1283 and 0.5499 A/m^2 were calculated for anode and cathode, respectively. Since j_0 represents the 'rate of exchange' between the reactant and product states at equilibrium, a higher value of j_0 means a faster reaction rate, following a lower activation energy barrier of forward reaction. Data showed that j_0 of cathode is more than four-fold of the one of anode, concluding that reaction at cathode was much faster than that at anode in the sequential anode-cathode MFC.

3.4.2 Discharge resistance analyzed by electrochemical impedance spectroscopy

EIS measurement was carried out to compare the characteristics of discharge resistances of the anode, cathode and cell under raw wastewater. The overall resistance was composed of polarization resistance of the electrode (including activation and diffusion resistances) and ohmic resistance (R_Ω), which contains the ohmic contributions of the electrodes, the anolyte and catholyte, and the membrane (Aswin *et al*., 2008). Fig. 5 shows that the discharge resistance of cathode is lower than that of anode, which is accordance with the result of Tafel plots.

R_Ω of the anode, cathode, and cell were 7.94, 1.93, and 28.3 Ω, accounting for only a small proportion of their respective overall discharge resistances

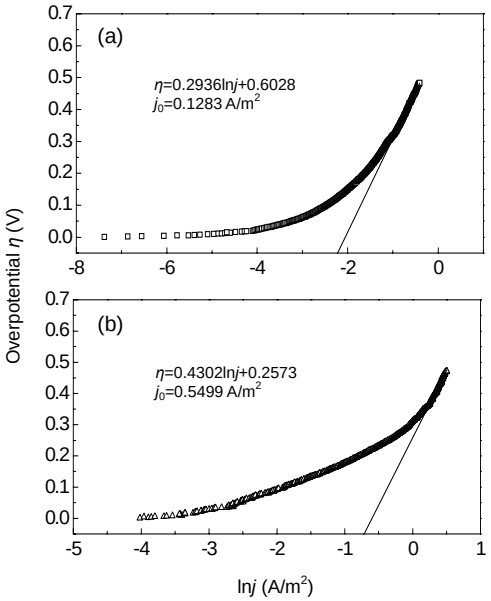

Fig. 4 Tafel plots estimated for j_0 of anode (a) and cathode (b)

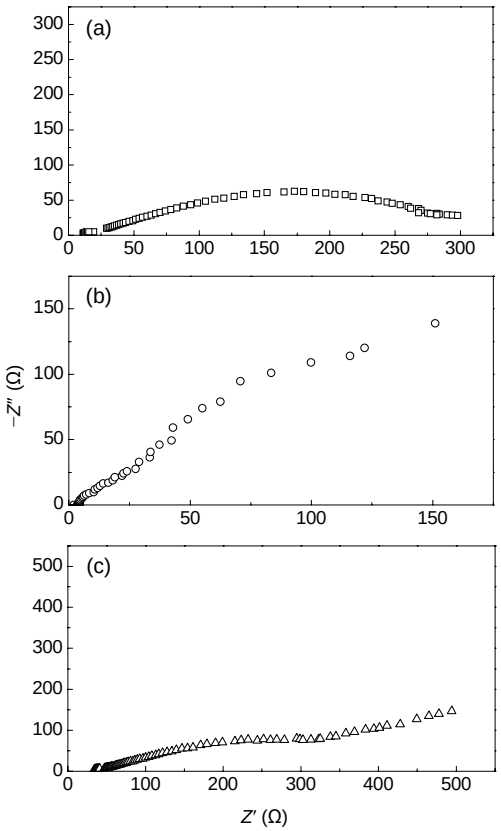

Fig. 5 Discharge resistances of anode (a), cathode (b), and cell (c) determined from EIS

(Ieropoulos *et al*., 2008). Hence, the most important limited factor of both anode and cathode was polarization resistance, which resulted in a high reaction resistance and finally caused an inferior electrochemical performance of the MFC. Moreover, the polarization resistance of anode was much higher than that of cathode, indicating that anode affected the performance of this sequential anode-cathode MFC much more than cathode.

Considering the analysis of electrochemical performance, it is thus concluded that the performance of the sequential anode-cathode MFC can be improved by increasing the kinetic reaction rate and mass transport rate, especially the rate at anode. To accelerate the reaction rate, there are many available methods, such as optimizing the reaction configuration (reducing the electrode space), using more effective electrode materials or catalysts, and improving solution conditions of both anode and cathode chambers (including pH, ion strength, temperature, etc.).

4 Conclusion

Performance of sequential anode-cathode MFC from raw brewery wastewater was investigated in this experiment. With an HRT of 14.7 h, a steady COD removal efficiency of 91.7%–95.7% [3.87–4.24 kg COD/(m^3·d) for SDR] was achieved at an external resistance of 100 Ω. Peak performance of electricity generation was determined by polarization curves, and an open circuit voltage of 0.434 V and a maximum power density of 830 mW/m^3 (23.1 mW/m^2 vs. cathodic area, 7.5 mW/m^2 vs. anodic area) were obtained at an external resistance of 300 Ω. Moreover, electrochemical measurements were carried out to evaluate the performance of individual electrode and cell. Results of Tafel plots and EIS showed that polarization resistance of anode was the major limited factor in the MFC. Since bio-cathode was used in the MFC, without any noble-metal catalysts, the cost of the whole system can be reduced. With a high COD removal efficiency, it is concluded that the sequential anode-cathode MFC constructed with bio-cathode in this experiment could provide a new approach for brewery wastewater treatment.

References

Aswin, K.M., Orianna, B., Kenneth, H.N., Florian, M., 2008. The use of electrochemical impedance spectroscopy (EIS) in the evaluation of the electrochemical properties of a microbial fuel cell. *Bioelectrochemisrty*, **72**(4):149-154.

Barsoukov, E., Macdonald, J.R., 2005. Impedance Spectroscopy Theory, Experiment and Applications, 2nd Ed. Wiley-Interscience, Hoboken, NJ, p.68-73. [doi:10.1002/0471716243]

Bennetto, H.P., 1984. Microbial Fuel Cells. Life Chemistry Reports Harwood Academic, London, p.363-453.

Braeken, L., van der Bruggen, B., Vandecasteele, C., 2004. Regeneration of brewery waste water using nanofiltration. *Water Res.*, **38**(13):3075-3082. [doi:10.1016/j.watres.2004.03.028]

Freguia, S., Rabaey, K., Yuan, Z., Keller, J., 2007. Non-catalyzed cathodic oxygen reduction at graphite granules in microbial fuel cells. *Electrochim. Acta*, **53**(2):598-603. [doi:10.1016/j.electacta.2007.07.037]

Freguia, S., Rabaey, K., Yuan, Z., Keller, J., 2008. Sequential anode-cathode configuration improves cathodic oxygen reduction and effluent quality of microbial fuel cells. *Water Res.*, **42**(6-7):1387-1396. [doi:10.1016/j.watres.2007.10.007]

Greenman, J., Gálvez, A., Giusti, L., Ieropoulos, I., 2009. Electricity from landfill leachate using microbial fuel cells: comparison with a biological aerated filter. *Enzyme Microb. Technol.*, **44**(2):112-119. [doi:10.1016/j.enzmictec.2008.09.012]

Habermann, W., Pommer, E.H., 1991. Biological fuel cells with sulphide storage capacity. *Appl. Microbiol. Biotechnol.*, **35**(1):128-133. [doi:10.1007/BF00180650]

Ieropoulos, I., Greenman, J., Melhuish, C., 2008. Microbial fuel cells based on carbon veil electrodes: stack configuration and scalability. *Int. J. Energy Res.*, **32**(13):1228-1240. [doi:10.1002/er.1419]

Kargi, F., Eker, S., 2007. Electricity generation with simultaneous wastewater treatment by a microbial fuel cell (MFC) with Cu and Cu-Au electrodes. *J. Chem. Technol. Biotechnol.*, **82**(7):658-662. [doi:10.1002/jctb.1723]

Liu, H., Ramnarayanan, R., Logan, B.E., 2004. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. *Environ. Sci. Technol.*, **38**(7):2281-2285. [doi:10.1021/es034923g]

Liu, Z.D., Li, H.R., 2007. Effects of bio- and abio-factors on electricity production in a mediatorless microbial fuel cell. *Biochem. Eng. J.*, **36**(3):209-214. [doi:10.1016/j.bej.2007.02.021]

Melhuish, C., Ieropoulos, I., Greenman, J., Horsfield, I., 2006. Energetically autonomous robots: food for thought. *Autonomous Robots*, **21**(3):187-198. [doi:10.1007/s10514-006-6574-5]

Min, B., Angelidaki, I., 2008. Innovative microbial fuel cell for electricity production from anaerobic reactors. *J. Power Sources*, **180**(1):641-647. [doi:10.1016/j.jpowsour.2008.01.076]

Parawira, W., Kudita, I., Nyandoroh, M.G., 2005. A study of industrial anaerobic treatment of opaque beer brewery wastewater in a tropical climate using a full-scale UASB reactor seeded with activated sludge. *Process Biochem.*, **40**(2):593-599. [doi:10.1016/j.procbio.2004.01.036]

Venkata-Mohan, S., Saravanan, R., Veer-Raghuvulu, S., Mohanakrishna, G., Sarma, P.N., 2008. Bioelectricity production from wastewater treatment in dual chambered microbial fuel cell (MFC) using selectively enriched mixed microflora: effect of catholyte. *Bioresour. Technol.*, **99**(3):596-603. [doi:10.1016/j.biortech.2006.12.026]

Wang, X., Feng, Y.J., Lee, H., 2008. Electricity production from beer brewery wastewater using single chamber microbial fuel cell. *Water Sci. Technol.*, **57**(7):1117-1121. [doi:10.2166/wst.2008.064]

Wei, F.S., 2002. Water and Wastewater Monitoring Analysis Method, 4th Ed. Publishing House of Environmental Science of China, Beijing, p.210-220.

Wen, Q., Wu, Y., Cao, D.X., Zhao, L.X., Sun, Q., 2009. Electricity Generation and modeling of microbial fuel cell from continuous beer brewery wastewater. *Bioresour. Technol.*, **100**(18):4171-4175. [doi:10.1016/j.biortech.2009.02.058]

Yoshitake, M., Tamura, M., Yoshida, N., 1996. Studies of perfluorinated ion exchange membrane for polymer electrolyte fuel cells. *Denki Kagaku*, **64**(6):727-736.