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# Simultaneous bioelectricity generation and biodegradability improvement of refinery wastewater using microbial fuel cell technology

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ABSTRACT

Wastewater contains abundant chemical bond energy that can be recovered by microbial fuel cell (MFC), so the aim of this study was to explore the feasibility of using MFC technology to dispose refinery wastewater and generate electricity simultaneously by recycling the chemical energy in wastewater. The energy recovery rate together with the wastewater treatment performance of MFCs with different structures was studied, respectively. Results indicate that both the single- and double-chambered MFC could be successfully started up to generate electricity, using refinery wastewater as fuel, the highest voltage output of two-chambered MFC was 305 mV, and the relevant maximum power density output was 310.08 $mW/m^3$. Meanwhile, the maximum coulombic efficiency of refinery wastewater was 3.0%. Refinery wastewater treatment efficiency of MFCs was higher than that of traditional anaerobic biological treatment process. The oil pollutant removal rate of double-chambered MFC could reach to as high as 83.60%. In refinery wastewater MFC, the petroleum pollutants could be degraded through microbial metabolism, generating plenty of phthalic acid esters and alcohols metabolites; the removal rate of aromatic hydrocarbons was higher than volatile phenol, and that of short-chain fatty hydrocarbon was higher than long-chain fatty hydrocarbon. In addition, when refinery wastewater was treated by MFC, toxic effects on living beings would be reduced obviously, resulting in the sufficient improvement of degradability.

*Keywords:* Refinery wastewater; Microbial fuel cell; Electricity generation; Microbial degradation rules; Biodegradability improvement

## 1. Introduction

Refinery wastewater generated from the production process of petroleum products was characterized by the concentrated organic pollutants toxic and refractory to the biodegradation, and the damage from which to ecological system and human health was serious [1]. So far, biochemical treatment is used primarily for the disposal of refinery wastewater [2].

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However, a huge amount of energy is needed by micro-organisms to aerobically breakdown the high energy organic pollutants in the biochemical treatment of wastewater, the application of which is limited in contemporary society which has serious energy shortage [3]. Actually, a huge quantity of chemical energy is stored in the chemical bonds of organics, contained in wastewater. Research indicates that the energy stored in the wastewater is about 14.7 kJ/g chemical oxygen demand (COD), that is, about $2.2 \times 10^{18}$ joules of energy per year in the global municipal wastewater, equivalent to burning 52 million tonne of oil in a modern power station [4,5]. Recovery utilization of chemical energy stored in wastewater simultaneously with wastewater treatment was really significant to renovate the traditional biochemical treatment process and solve global issues on energy shortages, together with environmental pollution [6].

Microbial fuel cell (MFC) is a promising method to integrate the advantages of simultaneously recovering energy and removing the organic pollutants from the wastewater [7]. MFC uses electricigens as cheap catalyzer to breakdown the organic and inorganic compounds in anolyte and directly transform the chemical energy into electricity, simultaneously [8]. Many studies about MFC treatment of municipal wastewaters have been carried out [9–11], but the study on using refinery wastewater as fuel was not reported. Therefore, the aim of this study is to explore the feasibility of using MFC technology to dispose refinery wastewater which is different from municipal wastewater and generate electricity simultaneously to recycle the chemical energy. Energy recovery rate together with wastewater treatment performance of MFCs was studied, respectively. Furthermore, petroleum pollutants microbial degradation rules and wastewater biodegradability changes in anode chamber of MFCs were analyzed.

## 2. Materials and methods

### 2.1. Wastewater and inoculum

Refinery wastewater used was obtained from the effluent of flotation process in Beijing Yanshan Refinery. Anolyte of MFC was made of refinery wastewater and growth medium with a certain proportion of 1:1 [12]. Before anolyte was injected into the anode chamber, $N_2$ was bubbled into anolyte for 30 min to maintain the anaerobic environment. MFC was inoculated by the activated sludge generated from the refinery wastewater treatment system in Dagang Petrochemical Company (China).

### 2.2. MFC constructions

Two types of MFCs were employed, single-chambered and double-chambered. The single-chambered MFC was made of polymethyl methacrylate and the active volume of cylinder-shaped reaction chamber was 113 mL (3 × 4 cm). In MFC, carbon cloth with (0.35 mg/cm$^2$, E-TEK) and without (E-TEK) platinum was used as cathode and anode, respectively, and the circuit was connected by a copper wire.

The double-chambered MFC was made of glass and the active volume of each cylinder-shaped chamber was 300 mL; the two chambers were separated by a nafion proton-exchange membrane which was pretreated in 5% hydrogen peroxide solution and 0.5 mol/L sulfuric acid solution (Fig. 1). In the anode chamber packed with graphite granules, a graphite rod was used as electrode and a rubber was used to maintain the anaerobic condition. In the cathode chamber, another graphite rod was used as electrode and Fe (III)-EDTA complex system [13], whose concentration was 20 mmol/L, was used as the catholyte.

Unless otherwise noted, the external resistance between anode and cathode was 1,000 Ω and MFCs were operated at 30˚C.

### 2.3. Calculations

The voltage output of the MFCs was recorded automatically with a data logger (e-corder, ED401, eDAQ Pty Ltd, Australia), and time interval was 1 min. The current density and power density were calculated with the formula given below:

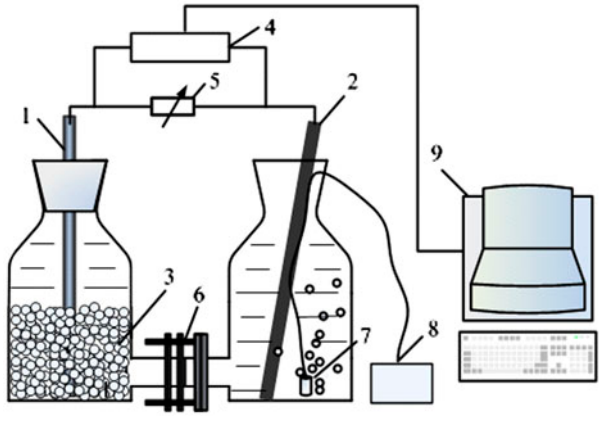


Fig. 1. Schematic diagram of double-chambered MFC.
Note: 1: anode; 2: cathode; 3: granule graphite; 4: data recorder; 5: resistance box; 6: PEM; 7: aerator; 8: oxygen pump; 9: computer.

$$I = U/(RV) \quad (1)$$

$$P = UI \quad (2)$$

where $I$ is the current density (mA/cm$^3$), $U$ is the voltage (mV), $R$ is the external resistance (Ω), $V$ is the working volume of the anode chamber (cm$^3$), and $P$ is the power density (mW/cm$^3$).

The coulombic efficiency of MFCs was calculated with formula (3).

$$E = M\sum_{i=1}^{n} u_i \times t_i / RF_i b_i \Delta S V \quad (3)$$

where $u_i$ is the voltage in $t_i$ (V), $R$ is the external resistance (Ω), $F_i$ is the faraday constant (96,485 C/mol), $b_i$ is the electron numbers of 1 mol COD ($4e^-$ mol/mol), $\Delta S$ is the change of COD concentration (mg/L), $V$ is the volume of substrate (L), an d$M$ is the molecular weight of oxygen (32 g/mol).

### 2.4. Analytics

#### 2.4.1. Conventional water quality analysis

The COD was measured by 5B-6 COD speed meter (LianHua Tech, Lanzhou, China), oil concentration was determined by infrared oil analyzer (MC-OIL420, Huaxia Kechuang, Inc., China) after carbon tetrachloride extraction, and pH was determined by the pH monitor (PHSJ-4, Leica Instrument, Inc., Shanghai, China).

#### 2.4.2. GC–MS analysis

The organic composition of refinery wastewater was analyzed by GC–MS. First, the wastewater samples extracted by guarantee reagent methylene chloride were injected into a GC–MS which consists of a commercial quadrupole mass spectrometer (SSQ-710C, Thermo-Finnigan, San Jose, California), connected to a Varian 3400 GC (Varian, Middleburg, the Netherlands). A septum-equipped temperature programmable injector was used together with a DB-5 HT capillary column (15 m × 0.25 mm × 0.1 μm, from J&W Scientific, Folsom, USA). The temperature program for the GC capillary column was 60℃, maintained for 10 min, and then lifted to 300℃ at a speed of 8℃ min$^{-1}$ and maintained for 20 min. Electron capture negative ionization with methane (scientific 5.5, AGA Stockholm, Sweden) as a reagent gas and an electron energy of 70 eV was used. Helium was used as the carrier gas, the ion source temperature was 200℃, and the transfer line temperature was set to 290℃. Selected ion monitoring mode (isotopes m/z 79 and 81) was used.

## 3. Results and discussion

### 3.1. Refinery wastewater properties

Refinery wastewater used in this study was obtained from the effluent of flotation process in Beijing Yanshan Refinery; its COD was 450 ± 50 mg/L, oil concentration was 50 ± 5 mg/L, and the pH value was 8.5 ± 0.5. In order to acquire more information of the refinery wastewater, GC–MS analysis was made and the results indicated that the wastewater influent of MFCs was conform to the general characteristics of refinery wastewater. The chief components of the wastewater were volatile phenol, aromatic hydrocarbon, and saturated hydrocarbon, etc. and there were no microbial metabolites, such as phthalic acid esters and alcohols. Among all the components of refinery wastewater, the relative amount of volatile phenol, aromatic hydrocarbon, and fatty hydrocarbon was 41.01%, 4.4%, and 54.59%, respectively.

### 3.2. Refinery wastewater MFC start-up and electricity generation performance

Three single-chambered and two double-chambered MFCs were constructed, respectively, and each of them had a control MFC with the circuit unconnected. As shown in Fig. 2, the highest start-up voltage of single-chambered and directly domesticated MFC 1-1 was 49.1 mV and the relative power density was just 8.036 mW/m$^3$. Then, it dropped slowly after the circuit was connected. After 5 d of continuous cultivation, the highest cell voltage output reached 134.9 mV and the maximum power density reached 60.660 mW/m$^3$, both are highest during the whole operation period of MFC 1-1. However, the peak voltage value could not maintain for long. Continuing to cultivate, the highest voltage output dropped slowly and could not be recovered. The reason of this phenomenon was that along the cultivation, the micro-organisms and secretions were attached onto the cathode carbon cloth and the cathode reaction was blocked.

Single-chambered MFC 1-2 was domesticated with 1 g/L glucose to shorten the start-up time until its voltage output was stable. As shown in Fig. 3, when refinery wastewater together with glucose was injected into MFC, the voltage output rose rapidly to 225 mV (power density was 168.750 mW/m$^3$) and could maintain stable operation for 30 h; the highest voltage

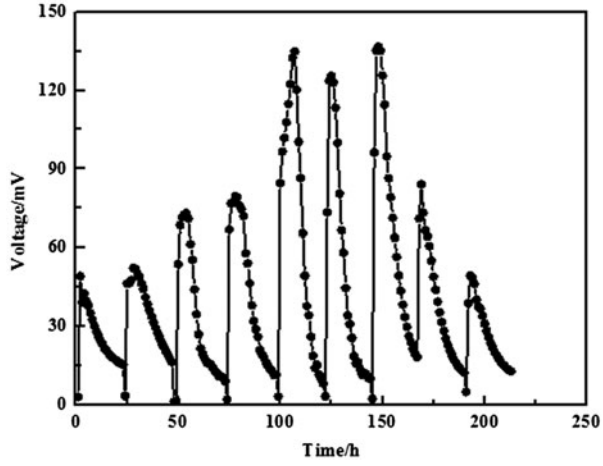


Fig. 2. Voltage generation by MFC 1-2 during start-up.

output was 252 mV during the culture cycle, and the relative power density was 211.680 mW/m$^3$. When the voltage output was dropped to less than 10 mV, anolyte was replaced. After 10 d of continuous cultivation (anolyte was replaced for five times), the addition of glucose was stopped, the maximum voltage output dropped to 80 mV, and the stable operation period was shortened to less than 10 h. Along with the increase in non-glucose anolyte replacing times, the voltage output change trend of MFC 1-2 was totally the same as directly domesticated MFC 1-1 (Fig. 2). The aim of using glucose as an adjuvant domestication substrate was to curtail the adaptive phase of microbes to refinery wastewater, and further shorten

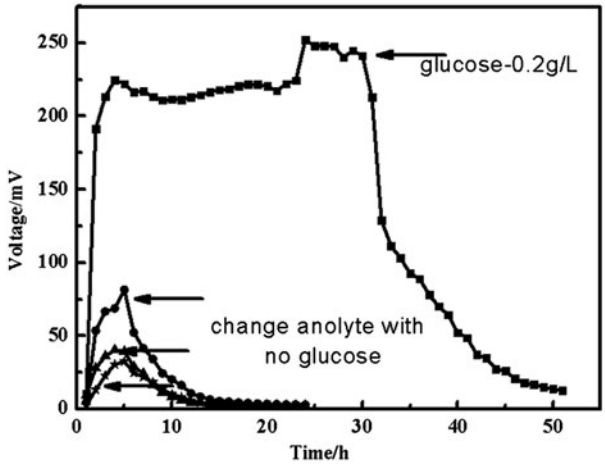


Fig. 3. Voltage generation by MFC 1-1 during start-up.
Note: ■: with glucose; ●: the first time anolyte replaced without glucose; ▲: the second time anolyte replaced without glucose; ▼: the third time anolyte replaced without glucose.

the start-up period of MFC. However, the voltage output change of MFC 1-2 indicated that the assumption was unserviceable. When glucose existed in anode, microbes would primarily use the glucose to generate electricity but not petroleum pollutants, because of its recalcitrance.

During the start-up period of double-chambered MFC 2-1, anolyte was replaced every 8 d, and when MFC turned into stable operation period, the culture cycle was changed to 5 d. As shown in Fig. 4, the starting voltage output of MFC 2-1 was as high as 270 mV (power density was 243.000 mW/m$^3$) and then dropped sustainably. With continuous anolyte replacement like other two single-chambered MFCs, the voltage output increased rapidly to the maximum and then dropped, although MFC 2-1 still had relatively high voltage output period (50 h). After 18 d of continuous cultivation, the maximum voltage output reached to 305 mV, and the maximum power density reached to 310.083 mW/m$^3$. It can be seen that the electricity generation performance of double-chambered MFC with refinery wastewater as fuel was obviously better than single-chambered MFC.

### 3.3. Energy recovery rate of MFCs

According to Eq. (3), coulombic efficiency of refinery wastewater MFC was between 2.5 and 3.0%, lower than that of domestic wastewater MFC (3.0–12.0% [14]). It means that when MFC technology was used to treat refinery wastewater, the energy recovery rate was low; only a trace amount of COD was consumed to generate electricity, while most of which was consumed by microbes to their proliferation. Therefore, a lot of works should be done to improve the energy recovery efficiency of refinery wastewater MFC

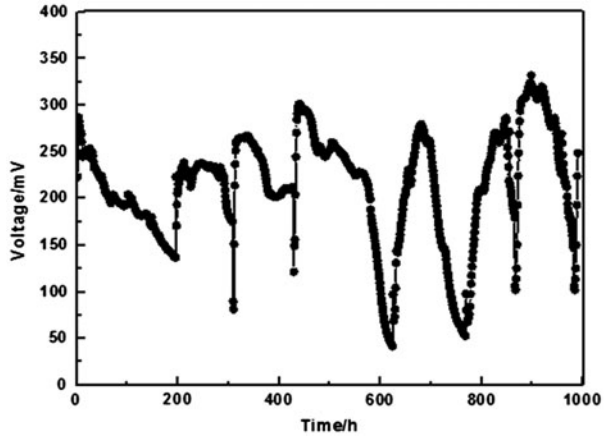


Fig. 4. Voltage generation by double-chambered MFC.

further. Actually, compared with acquire huge amount of electricity and energy recovery rate, simultaneous improved wastewater treatment and energy recovery performances were more significant when MFC technology was used to treat refinery wastewater. Besides, MFCs could also be used as the pre-treatment process of refinery wastewater to reduce wastewater toxic effects on living beings and improve its degradability, by providing wastewater with good quality for subsequent treatment processes and certifying that the effluent wastewater could comply with the discharge standards (described in more detail in Section 3.4).

In our research group, besides using MFC technology generating electricity, aerobic–anaerobic fermentation was also used to generate $CH_4$ to recover energy in refinery wastewater. The relative results indicated that with the middle and low organic loading rates of refinery wastewater, methane production rate was low, and the energy recovery efficiency was bad. So compared with acquire huge energy recovery rate, simultaneous recovery energy and improved wastewater degradability are more utility than using anaerobic biochemical treatment process to treat middle- and low-loads refinery wastewater.

### 3.4. Wastewater treatment efficiency and petroleum degradation rules

The COD concentration, oil concentration, and pH value of solution, influent, and effluent of MFC was detected, respectively, and the results are shown in Table 1. Oil degradation rates of MFC 1-1 and MFC 1-2 were 46.80 and 44.44%, respectively, which are basically the same. The relative COD removal rates were 31.92 and 30.38%, with little difference. Just as what was shown in Section 3.2, the running state of MFC domesticated with glucose was in accordance with direct-domesticated MFC without glucose. Oil degradation of single-chambered control MFC 1-3 was just 29.24% and COD removal rate was 16.92%, both of which are obviously lower than single-chambered experimental MFCs. This result evidenced that compared to traditional anaerobic treatment processes, the degradation of refinery wastewater could be facilitated by MFC technology. On the other hand, compared to single-chambered MFC, the petroleum pollutants removal rate of double-chambered MFC was 83.60%, twice as much as the degradation rate of single-chambered MFC. And at the same time, COD removal rate of this MFC could reach as high as 61.92%, the maximum among all the MFCs. This result was in accordance with the electricity generation performances of double-chambered MFC and single-chambered MFC.

As phosphate buffer solution solution existed in medium, the influent was neutral. After treated by MFCs, the pH values of effluents of single-chambered MFC were about 7.00, while that of double-chambered MFC were about 5.80, much lower as compared with the former. It indicated that the acidulating phenomenon of two-chambered MFC was more serious than the single-chambered MFC. The reason may be due to the proton-exchange membrane existed in double-chambered MFC, which could block the transfer of $H^+$ generated from the degradation of oil pollutants, leading to the accumulation of $H^+$ in the anode chamber [15].

GC/MS analysis was done for the influent and effluent of double-chambered MFC. Results indicated that when wastewater was treated by double-chambered MFC, the main composition of which was changed; metabolites such as acids, esters, and alcohols were detected in wastewater effluent and the relative percentage of petroleum pollutants decreased; the relative content of phenols decreased from 41.01 to 10.03%, and the relative content of aromatic hydrocarbon decreased from 4.4 to 0.54%. Meanwhile, the relative content of short-chain fatty hydrocarbon decreased from 36.37 to 7.96%, and the relative content of long-chain fatty hydrocarbon decreased from 18.22 to 8.84%. The relative content of metabolites was 72.63%. The removal rate of aromatic hydrocarbons was higher than that of volatile phenol (87.7% vs. 75.5%), and that of short-chain fatty hydrocarbon was higher than long-chain fatty hydrocarbon (78.1% vs. 51.1%).

Table 1
Water quality index of MFCs

| Wastewater | MFC | COD (mg/L) | COD degradation rate (%) | Oil content (mg/L) | Oil degradation rate (%) | pH |
|---|---|---|---|---|---|---|
| Influent | – | 260 | – | 17.1 | – | 7.10 |
| Effluent | 1-1 | 177 | 31.92 | 9.10 | 46.80 | 7.01 |
| Effluent | 1-2 | 181 | 30.38 | 9.50 | 44.44 | 7.01 |
| Effluent | 1-3 | 216 | 16.92 | 12.1 | 29.24 | 7.03 |
| Effluent | 2-1 | 99.0 | 61.92 | 2.80 | 83.60 | 5.80 |
| Effluent | 2-2 | 176 | 32.31 | 8.10 | 47.40 | 5.10 |

Refinery wastewater discharge standard was reduced to 50 mg/L in China, so the degradability of refinery wastewater must be improved in order to comply with new discharge standards. Results of GC–MS analysis of influent and effluent of MFC indicated that when refinery wastewater with poor degradability was treated by MFC, the relative contents of both volatile phenol and aromatic hydrocarbon, which had strong toxic effects on micro-organisms, were reduced significantly, even lower than the detected limits, and plenty of metabolites easy for the microbes to degrade, such as acids, esters, alcohols, and so on, were generated, which means that the toxicity of wastewater was reduced, resulting in the improvement of the degradability. It is evidenced that besides energy recovery and wastewater treatment, MFC technology could also be used as pre-treatment process of refinery wastewater to reduce the toxicity of wastewater and improve its degradability, which is significant to refinery wastewater process innovation under new and lower wastewater discharge standards.

## 4. Conclusions

Wastewater contains abundant chemical bond energy and can be recovered by MFC. Petroleum refinery wastewater treatment efficiency of MFC is obviously higher than that of traditional anaerobic biological treatment process; 83.60% of petroleum pollutants can be removed by double-chambered MFC. In MFC, organic pollutants could be degraded through microbial metabolism producing plenty of metabolites as intermediate products, which are easily biodegraded, and some energy is recovered as electricity simultaneously.

## Acknowledgments

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## References

[1] R.P. Cote, The effects of petroleum refinery liquid wastes on aquatic life, with special emphasis on the Canadian environment, National Research Council of Canada, NRC Associate Committee on Scientific Criteria for Environmental Quality, Ottawa, 1976, p. 77.
[2] R.G. Fan, F. Hao, Methods and technical characteristics for oil-refining wastewater treatment, Sciencepaper Online 5 (2010) 410–414.
[3] H.S. Guo, Situation and problems of treatment of refinery wastewater and countermeasure for them, Environ. Protection Chem. Ind. 30 (2010) 93–99.
[4] I. Shizas, D.M. Bagley, Experimental determination of energy content of unknown organics in municipal wastewater streams, J. Energy Eng. 130 (2004) 45–53.
[5] E.S. Heidrich, T.P. Curtis, J. Dolfing, Determination of the internal chemical energy of wastewater, Environ. Sci. Technol. 45 (2011) 827–832.
[6] X. Guo, Y.L. Zhan, S.H. Guo, G.X. Yan, S.X. Sun, L.J. Zhao, R.M. Geng, Start up and influence factors of microbial fuel cell with refinery wastewater as fuel, Chin. J. Environ. Eng. 6 (2013) 2100–2104.
[7] X. Guo, Y.L. Zhan, S.H. Guo, S.X. Sun, G.X. Yan, C.M. Chen, Study on start-up and performance of microbial fuel cell with refinery wastewater as fuel, J. Chem. Eng. Chin. Univ. 27 (2013) 159–163.
[8] B.E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Microbial fuel cells: Methodology and technology, Environ. Sci. Technol. 40 (2006) 5181–5192.
[9] D.C. Roland, D.K. Patrick, E.L. Bruce, A monetary comparison of energy recovered from microbial fuel cells and microbial electrolysis cells fed winery or domestic wastewaters, Int. J. Hydr. Energy 35 (2010) 8855–8861.
[10] Y. Jaecheul, S. Jiyun, P. Younghyun, C. Sunja, L. Taeho, Electricity generation and microbial community in a submerged-exchangeable microbial fuel cell system for low-strength domestic wastewater treatment, Bioresour. Technol. 117 (2012) 172–179.
[11] F. Zhang, Z. Ge, J. Grimaud, J. Hurst, Z. He, Long-term performance of liter-scale microbial fuel cells treating primary effluent installed in a municipal wastewater treatment facility, Environ. Sci. Technol. 47 (2013) 4941–4948.
[12] J.M. Morris, S. Jin, B. Crimi, A. Pruden, Microbial fuel cell in enhancing anaerobic biodegradation of diesel, Chem. Eng. J. 146 (2009) 161–167.
[13] L.F. Deng, S.G. Zhou, J.T. Zhang, L. Zhuang, N. Lu, L.X. Zhang, Sustainable electricity generation in microbial fuel cells using Fe(III)-EDTA as cathodic electron shuttle Fe(III)-EDTA, Environ. Sci. 30 (2009) 2142–2147.
[14] H. Liu, R. Ramnarayanan, B.E. Logan, Production of electricity during wastewater treatment using a single chamber microbial fuel cell, Environ. Sci. Technol. 38 (2004) 2281–2285.
[15] R.A. Rozendal, H.V.M. Hamelers, C.J.N. Buisman, Effects of membrane cation transport on pH and microbial fuel cell performance, Environ. Sci. Technol. 40 (2006) 5206–5211.