Treatment of Domestic Wastewater with Simultaneous Electricity Generation in Microbial Fuel Cell under Continuous Operation

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In order to apply microbial fuel cell (MFC) process more practically in wastewater treatment, both power generation and removal of chemical oxygen demand (COD) were examined in an air-cathode MFC fed with domestic wastewater under continuous operation. At a hydraulic retention time (HRT) of 2.0 h, the air-cathode MFC was able to generate electricity from domestic wastewater with a maximum power density of $P = 103 \pm 2$ mW m^{-2} (5772 mW m^{-3}) and an average Coulomb efficiency (CE) of 18.4 %; meanwhile, to achieve an average COD removal up to 71 %. Increasing HRT from 2h to 10–30 h was found to be more effective for COD removal, however, instability in voltage output was also observed. An increased power generation of 173±4 mW m^{-2} (9648 mW m^{-3}) was obtained with the aid of NaCl addition at a mass fraction of $w = 2.4$ %, because of an elevated conductivity of the solution with accord internal resistance of 227 Ω.

Key words:
Microbial fuel cell (MFC), power generation, Coulomb efficiency (CE), hydraulic retention time (HRT), COD removal

Introduction

Smalley R. E., who won the 1996 Nobel Prize in chemistry, claimed: "Energy is the single most important challenge facing humanity today; for worldwide peace and prosperity it must be cheap and electricity will be the key." [1] Substantial consumption of energy in wastewater treatments is becoming burdensome to governments and nationwide economics, particularly for the case of those developing countries. In order to reduce the capital investment and operating costs of wastewater treatment plants, two aspects should be emphasized. One is to improve the overall performance for the existed processes, and the other is to explore some renewable technologies that can recover useful materials or energy from wastewater. Methane or hydrogen may be recycled from organic wastewater by anaerobic or fermentative biological processes, but it does not mean that alternative new methods to recover valuable energy from wastes are not needed. Recently, it has been found that organic substances present in organic wastewater can be used to directly generate electricity using bacteria as biocatalysts, at the same time with an achievement of wastewater treatment in a **m**icrobial **f**uel **c**ell (MFC),[2] and it is gradually becoming an increasingly popular method to make wastewater treatment processes more economical and sustainable.

Generally, a MFC has an anode chamber and a cathode chamber that are separated by ion-selected membrane (i. e. proton exchange membrane, PEM). Biological oxidation of organic matter in anode chamber will result in release of electrons and protons. Thereafter, electrons are transferred onto the surface of anode by anaerobic bacteria (e. g. *Shewanella putrefaciens,*[3] *Rhodoferax ferrireducens,*[4] *Clostridium butyricum*[5] and *Aeromonas hydrophila*[6]) and then conducted to cathode through external circuit. Meanwhile, protons arrive at cathode through PEM, followed by combining with electrons and oxygen (electron acceptor) to form water. Electrons are driven from the anode to the cathode at the function of potential difference between two electrodes as a result of currents in external circuits.

Recently, *Liu* and *Logan*[7] developed a new model of MFC, in which expensive PEM was omitted at the cathode. Such kind of MFC costs less and has a lower internal resistance than conventional two-chamber MFC. Several studies in this field are focusing on the defined substrates such as glucose,[7] acetate or butyrate[8] in a MFC at batch mode. However, the goal of a MFC system in wastewater treatment plant should include both electricity generation and organic pollutants removal. Accordingly, these given organic substrate cannot well represent the practically discharged wastewater, which may

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lead to a great discrimination in the system performance between pure substrates and wastewater. On the other hand, batch operation is impractical for large-scale wastewater treatment due to small treating capacity as well as the instability of the operation. Consequently, there is a need for MFC to be further studied using complex wastewater as substrates under continuous operation so as to make such novel technology accessible in a wastewater treatment plant for practice.

The scope of this study includes three aspects as follows: (1) to examine the electricity generation and chemical oxygen demand (COD) removal using an air-cathode MFC fed with domestic wastewater under continuous operation; (2) to study the performance of the MFC system at different hydraulic retention time (HRT); and (3) to investigate into the effect of NaCl mass fraction in wastewater on power output.

Materials and methods

MFC construction

Air-cathode MFC used in this study was similar to that used by *Liu* and *Logan*,[7] being composed of an anode and a cathode placed on the opposite sides of plastic cylindrical chamber, respectively. Toray 90 carbon paper (diameter of 4 cm and effective area of 13 cm^2, E-Tek) was used as anode, and the cathode was made of carbon cloth (the same size to the anode, E-Tek), containing platinum catalysts (0.15 mg cm^{-2}) without proton exchange membrane (PEM). The empty length of the chamber was 4 cm and the approximate effective volume of MFC was 52 mL. The anode and the cathode were connected with copper wire through a rheostat (0–1000 Ω) and all exposed metal surfaces were sealed with a nonconductive epoxy.

MFC incubation and operation

Anaerobic activated sludge had been proven to be the best candidate as inocula for starting up several MFCs successfully, according to the previous studies.[9] In this study, anaerobic activated sludge (MLSS of 3500 mg L^{-1}) was collected from the secondary clarifier of Wenchang Wastewater Treatment Plant in Harbin city, China, and then stocked in an anaerobic bottle of 1000 mL by adding glucose solution (COD of 1000 mg L^{-1}) once a week. MFC was directly inoculated with domestic wastewater (17mL, COD of 300 mg L^{-1}) and diluted anaerobic sludge (35 mL, MLSS of 500 mg L^{-1}). After successful inoculations, domestic wastewater was continuously fed into MFC using peristaltic pump to generate electricity. Power generation was monitored when stable voltage output was obtained. All the experiments and tests were conducted under the constant temperature (25 °C) and pressure (1.013 MPa) conditions.

Calculation and analytics

Measurements of voltage produced during experiments for long-term studies were recorded directly from potentiostat output every 60 s using a dual-channel voltage collection instrument (12 bit A/D conversion chips, US) connected with a personal computer via universal serial bus (USB, Intel) interface and calibrated with a digital multimeter (Agilent HP 34970, US) before each test. Voltage obtained was converted to power density normalized by the anode area and reactor volume according to

$$P = \frac{U\,I}{A} = \frac{U^2}{R\,A} \tag{1}$$

and

$$P = \frac{U\,I}{V} = \frac{U^2}{R\,V} \tag{2}$$

where U (V) is the voltage, I (mA) the current, R (Ω) the external resistance, A (m^2) the area of the anode chamber and V (m^3) the volume of the MFC reactor.

Coulomb efficiency (CE) was defined to be the relative experimental coulombs (C_{Ex}) to theoretical coulombs (C_{Th}) as

$$\mathrm{CE} = \frac{C_{\mathrm{Ex}}}{C_{\mathrm{Th}}} \cdot 100 \tag{3}$$

in which

$$C_{\mathrm{Ex}} = \frac{\int U(t)\mathrm{d}t}{R} = \frac{\sum_{i=1}^{T} U_i t_i}{R} \tag{4}$$

and

$$C_{\mathrm{Th}} = \frac{\gamma_{S_r} \cdot Q \cdot t}{M} \cdot \mathrm{b}F \tag{5}$$

where R (Ω) is the external resistance; γ_{S_r} (g L^{-1}) COD removal during the reaction period; Q (mL min^{-1}) the flow rate; t(s) the reaction time; M (32 g O_2/mol^{-1} O_2) the molar mass; b (4 mol e^- mol^{-1} O_2) the number of moles of electrons produced per mole of substrate; and F (96485 C mol^{-1} e^-) Faraday's constant.

The absolute value of the slope of regressive line between V and I can reflect the internal resistance according to

$$U = E - I \cdot R_{in} \quad (6)$$

where U (V) is the voltage; E (V) the electromotive force; I (mA) the current and R_{in} (Ω) the internal resistance.

Measurements for working potential of the anode and the cathode were performed by linking two electrodes respectively to reference electrode (Ag/AgCl, +195 mV *vs* standard hydrogen electrode, SHE), that was placed on the middle top of the reactor. Measurements for COD were performed according to the standard methods.[10] The morphologies of biofilm developed on the surface of the anode were observed using a scanning electron microscope (SEM) (Hitachi, S570; Japan). Sample was collected and fixed overnight in 2.5 % paraformaldehyde and 1.5 % glutaraldehyde in buffer (0.1 mol L^{-1} cacodylate, pH 7.5) at 4 °C, washed twice in buffer, dehydrated stepwise in a graded series of water/ethanol solutions (25, 50, 70, 85, 95, 100 %), and then dried (critical-point carbon dioxide). Samples were then sputter coated with Au/Pt before SEM observation.

Results and discussion

Startup of the MFC reactor

Following a lag time of about 130 h after incubation of the MFC reactor, using anaerobic sludge and domestic wastewater, the voltage started to increase gradually (data not shown). When the voltage decreased below 0.05 V, feeding fresh domestic wastewater with no extra sludge addition generated a voltage of about 0.247 V (external resistance of 500 Ω), and then followed by a gradual voltage decrease below 0.026 V within 14 h along with the consumption of organic matter in wastewater. Once domestic wastewater was dosed repeatedly, the voltage output showed the same variational trend without lag phase (Fig. 1). The SEM image of the biofilm on the anode surface revealed a homogeneous and grain-shape morphology (Fig. 2), suggesting the colonization of electron-transfer bacteria to the electrode. These indicated, that electricity was produced from organic pollutants in wastewater by microorganisms on the surface of the anode.

Continuous power generation

When the MFC reactor was again employed with domestic wastewater (γ_{COD} 298.65 mg L^{-1}) and operated under continuous mode at HRT of 2.0 h, a stable electricity generation was obtained with voltage of 0.346 V at external resistance of 1000 Ω as shown in Fig. 3. Thereafter, in order to examine power output from MFC, polarization curve was made by varying external resistance in the circuit. As a result, a maximum power density of 103±2 mW m^{-2} (5772 mW m^{-3}) was obtained at current

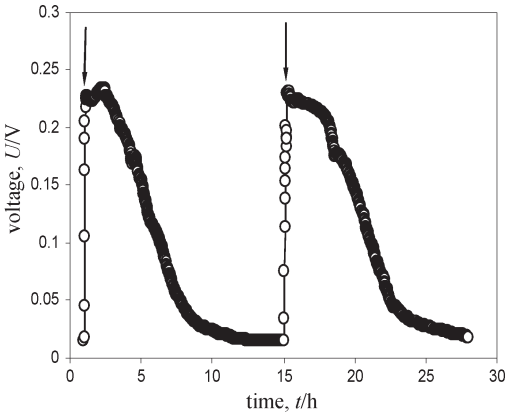

Fig. 1 – *Voltage generation in MFC fed with domestic wastewater (Arrowheads stands for wastewater replacement)*

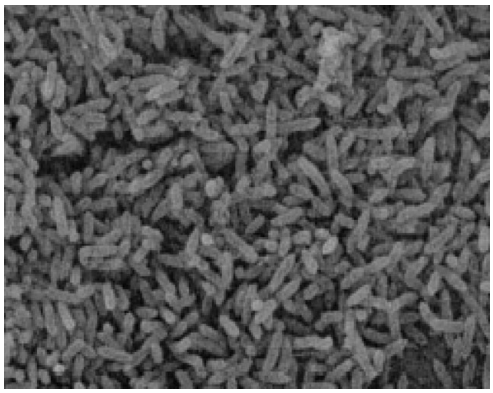

Fig. 2 – *SEM image of the surface of the anode following the growth of electron-transfer bacteria*

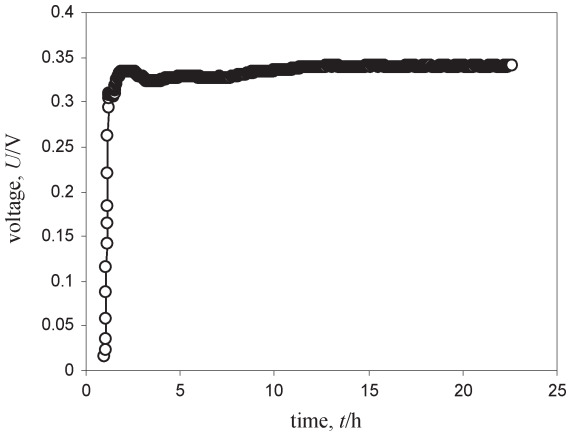

Fig. 3 – *Continuous electricity generation at HRT of 2.0h*

density of 0.042 mA cm^{-2} (Fig. 4). As the current density increased from 0 to 0.09 mA cm^{-2}, the working potential of the anode increased from –490 mV to –420 mV (vs Ag/AgCl electrode; by 14.3 %); and the cathode potential decreased from 118 mV to –395 mV (vs Ag/AgCl electrode; by 434.7 %), as indicated in Fig. 5, demonstrating that the limiting factor of voltage output was the cathode and not the anode.

During electricity generation from wastewater, removal of organic pollutants in term of COD was also obtained with an average removal efficiency of 70.4 ± 0.66 %. It could have two biological conversion routes for the elimination of COD in the air-cathode MFC. On the basis of Eqs. 3, 4 and 5, the calculated average CE value indicated that COD converted into coulombs by the electron-transfer bacteria accounted for 18.4 ± 0.81 % of the total removed COD. The other portion of COD that was not converted into power could be ascribed to the alternative respiration of organic matters by such microbial community as aerobic or anoxic bacteria. The most probable reason for this could be the design configuration of the air-cathode MFC, in which the cathode was directly open to air, allowing oxygen molecule diffusing from the cathode into the reactor.

Effect of hydraulic retention time on power output and COD removal

For a wastewater treatment process, HRT is usually one of the most significant parameter that affects the design and operation of treating facilities. In this study, HRT was demonstrated to influence the MFC reactor performance in both power generation and COD removal. When HRT of the system was maintained at 30 h, 15 h and 10 h, respectively, the MFC revealed an unstable voltage output. In comparison, a very stable voltage of 0.346 V could be obtained based on external resistance of 1000 Ω at HRT of 2.0 h, as shown in Fig. 6. However, COD removal showed an opposite variation over voltage with HRT. For example, when HRT was increased from 2.0 h to 30 h, COD was removed with an increased efficiency from 71 % to 91.5 % (Fig. 7). This suggested that the advanta-

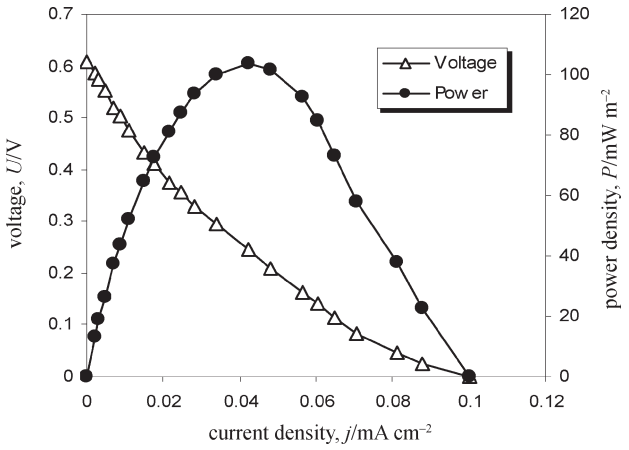

Fig. 4 – *Power and voltage output as function of current density*

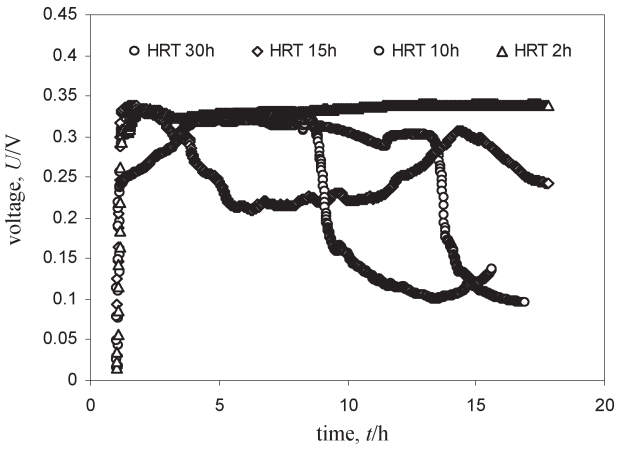

Fig. 6 – *Voltage output of the MFC under different HRT*

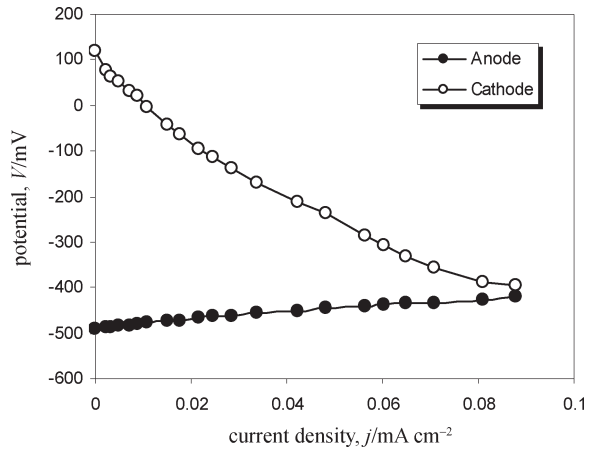

Fig. 5 – *Working potential as function of current density*

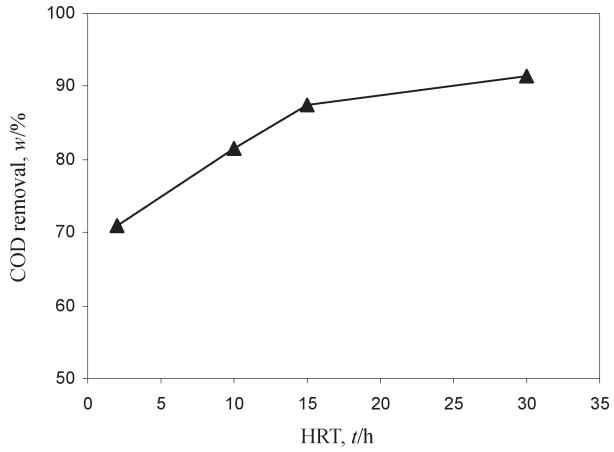

Fig. 7 – *COD removal as function of HRT*

geous growths of electron-transfer bacteria could be better selected by short HRT. Further studies were needed, in order to clarify how physiological-ecological competition for substrates between electron-transfer bacteria and other communities of bacteria affected electricity output in MFC.

Effect of inorganic salts on power generation

Adding inorganic salt of NaCl solution into the MFC reactor was observed to increase power generation. As noted in Fig. 8A, power output increased when NaCl mass fraction in domestic wastewater was increased (HRT 2.0 h). The maximum power density at NaCl mass fraction of 2.4 % could reach 173±4 mW m^{-2} (9648 mW m^{-3}), increasing by 67.5 % in contrast to that obtained in the absence of NaCl addition (103 mW m^{-2}). Such increase in power was possibly due to the decrease of internal resistance of the MFC. Fig. 8B demonstrated a difference in voltage with respect to current at different NaCl fraction. Based on Eq 6, V and I were plotted linearly to show the difference in internal resistance, resulting in 423 Ω (without NaCl), 296 Ω (NaCl 0.6 %), 259 Ω (NaCl 1.2 %), and 227 Ω (NaCl 2.4 %), respectively. Lower internal resistance could be obtained at high mass fraction of NaCl due to an increase of solution conductivity that enhanced proton flow rate from the anode to the cathode. The results obtained using domestic wastewater here is similar to that reported in an air-cathode MFC using pure medium (acetate) as the substrate.[11]

Applications of MFC technology for continuous wastewater treatment

Traditional activated sludge process (ASP) has been frequently and widely adopted as an effective way of domestic wastewater treatment. Despite effective removal of COD, substantial energy consumption due to aerating seems to be the most significant challenge facing ASP in the future. It is roughly estimated that a medium-scale wastewater treatment plant with a capacity of $3.0 \cdot 10^5$ m^3 d^{-1} will consume electricity energy up to $1.5 \cdot 10^5$ kWh with according operational cost of ¥350 million RMB (¥0.6 RMB per kWh), annually. In this sense, ASP by no means represents a sustainable process to treat wastewater. This study showed that domestic wastewater could be effectively treated with simultaneous electricity generation under continuous operation in an air-cathode MFC and provide us with a proof-of-concept demonstration of a novel pathway to make wastewater treatment more sustainable and economical.

At a HRT of 2 h, the maximum power density could reach 103 ± 2 mW m^{-2} and about 71 % of COD in domestic wastewater could be removed. CE of the system was observed to be relatively at low level (18.4 %), but organic pollutants present in domestic wastewater should be considered as a free source of fuels; hence, it was possible for MFC to be used for electricity generation in a wastewater treatment plant. Long HRT was found to be effective for COD removal, however, it led to an unstable voltage output. Thus, the balance between electricity production and wastewater treatment is needed to be taken into account, according to practical situations. The addition of electrolytes such as NaCl could increase power density up to 173±4 mW m^{-2}, indicating the substantial dependence of power generation on internal resistance. This means that MFC is much more available to generate electricity from industrial saline wastewater or domestic wastewater containing seawater (i. e. Hong Kong[12]), in which high concentration of salts is generally present. Nevertheless, it is possibly difficult to predict the real economics that the MFC may bring us,

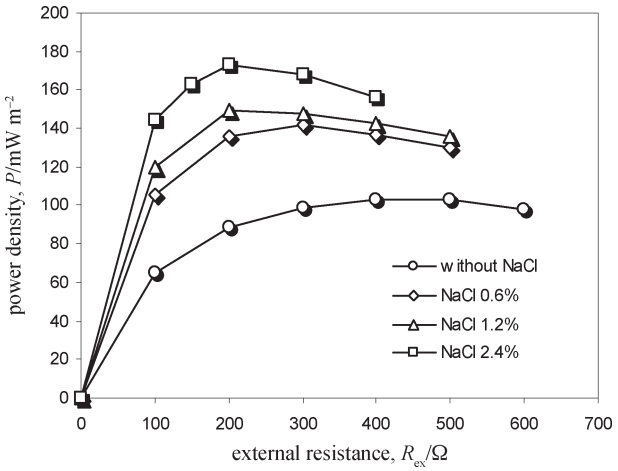

Fig. 8A – *Power generation at different NaCl concentration*

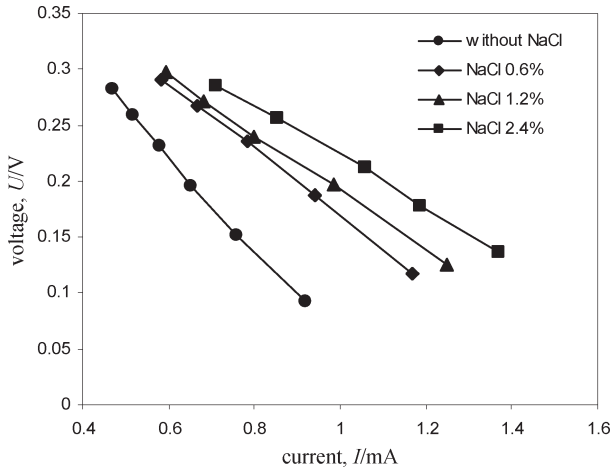

Fig. 8B – *Voltage as function of current at different NaCl mass fraction*

because the maximum power generation is commonly affected by a great many factors, for example, the design configuration, the organic matter oxidation rate, the electron transfer rate, the cathodic electron acceptor and operating conditions, and so forth, some of which have been known, and some of which are still under clarification. Consequently, much more efforts are required in this focus in order for MFC technology to be practically applied in wastewater treatment for more accessible electricity energy recovery from domestic wastewater in the coming days.

Conclusions

Using an air-cathode MFC, domestic wastewater could be continuously treated with COD removal of 71% coupled with a simultaneous electricity generation with the maximum power output of 103 ± 2 mW m^{-2} (5772 mW m^{-3}) and average CE of 18.4 % at HRT of 2.0 h. Longer HRT was more effective for removing COD, but it led to an unstable voltage output. Addition of inorganic salts, such as NaCl, could be used as electrolytes to enhance proton flux rate from the anode to the cathode to achieve lower internal resistance, therefore, resulting in an increase of power generation to 173 ± 4 mW m^{-2} (9648 mW m^{-3}, NaCl 2.5 %). This study suggested a completely new biological approach to treat domestic wastewater and recover energy from wastes.

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List of symbols

P – power density, mW m^{-2}
U – voltage, V
I – current, mA
A – area of the anode, m^2
R_{ex} – external resistance, Ω
R_{in} – internal resistance, Ω
C_{Ex} – experimental coulombs, C
C_{Th} – theoretical coulombs, C
γ_{Sr} – COD removal, mg L^{-1}
γ – mass concentration, mg L^{-1}
Q – flow rate, mL min^{-1}
t – reaction time, s
V – reactor volume, mL
F – Faraday's constant, 96485 C mol^{-1}
b – number of electrons produced per mole of substrate, 4 mol $e^-/molO_2$
M – molar mass, m_{O2}/n_{O2} g mol^{-1}
E – electromotive force of the cell, V
w – mass fraction, %

List of abbreviations

MFC – microbial fuel cell
COD – chemical oxygen demand
HRT – hydraulic retention time
CE – Coulomb efficiency
PEM – proton exchange membrane
MLSS – mixed liquid suspended sludge
SHE – standard hydrogen electrode
SEM – scanning electron microscope
ASP – activated sludge process

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