Bioresource Technology 157 (2014) 305–309

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Anode-biofilm electron transfer behavior and wastewater treatment under different operational modes of bioelectrochemical system

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HIGHLIGHTS

- Anode-biofilm ET rate differs greatly in different BES operational modes.
- Bioelectroactive species with different formal potentials function as ET mediators.
- The amount of available bioelectroactive species determines anode-biofilm ET rate.
- MEC is the only feasible BES operational mode for advanced wastewater treatment.

ARTICLE INFO

Article history:
Received 14 November 2013
Received in revised form 18 January 2014
Accepted 21 January 2014
Available online 6 February 2014

Keywords:
Electron transfer
Anode biofilm
Operational mode
Bioelectrochemical system
Wastewater treatment

ABSTRACT

Anode-biofilm electron transfer behavior was investigated during the advanced wastewater treatment process by three bioelectrochemical systems (BESs): microbial fuel cell (MFC), MFC operated under short circuit condition (MSC), and microbial electrolysis cell (MEC). Under different operational modes, current produced by the anode biofilm varied from 0.92, 4.15 to 8.21 mA in the sequence of MFC, MSC and MEC, respectively. The cyclic voltammetry test on the anode biofilm suggested that the current generation was achieved via various bioelectroactive species with formal potentials at −0.473, −0.402 and −0.345 V (vs. SCE). Gibbs free energy and charge transfer resistance data demonstrated that different amounts of available bioelectroactive species functioned in different BESs. The comparative investigation among MFC, MSC and MEC suggested that MEC was the only feasible operational mode for advanced wastewater treatment, because of its superior current generation capability.

1. Introduction

Microbial fuel cell (MFC) draws wide interest because of its capacity in terms of electricity generation. Based on the biocatalysis characteristic of MFC, many other similar bioelectrochemical systems (BESs) have also been developed for different applications (Liu et al., 2005; Cao et al., 2009; Choi et al., 2012). Wastewater treatment has been successfully realized and proposed to be a promising application in the BES field (Du et al., 2007; Zhu et al., 2013). During the wastewater treatment process, various factors including BES operational mode play important roles on the treatment efficiency (Lorenzo et al., 2010; Mohan and Srikanth, 2011; Erable et al., 2011). Changes in the BES operational mode significantly affect the bacterial kinetics and current generation, which further influence the wastewater removal efficiency (Erable et al., 2011).

In general, depending on the link status between the anode and cathode, there are three BES operational modes developed for wastewater treatment. MFC, whose anode and cathode are linked by an external resistance, is the most common BES operational mode. In MFC, wastewater treatment can be realized coupled with power generation (Liu et al., 2004; Choi et al., 2012). Another kind of BES operational mode is that the anode and cathode are short-circuited (without external resistance), which is denoted as MSC for short. This kind of BES has been utilized for the enhancement of swine wastewater treatment (Xu et al., 2011). In order to further improve the wastewater removal efficiency, microbial electrolysis cell (MEC) has also been employed (Wang, et al., 2013; Wen et al., 2013). Generally, wastewater treatment can be improved in the order of MFC, MSC and MEC, because of their current generation increases also in the same order. Current generation has been demonstrated to be a decisive variable for wastewater treatment. Moreover, the current is directly determined by the bioelectrochemical characteristic of biofilm attached on the anode. Therefore, a clear understanding of the anode biofilm characteristic

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http://dx.doi.org/10.1016/j.biortech.2014.01.088
0960-8524/

is important for the future application of BES in wastewater treatment.

In BES, current is generated from a continuous electron flow which is originally extracted from the anodic substrate by anode-respiring bacteria (ARB). Thus, the electron transfer (ET) rate largely relies on the electrochemical behavior of ARB (or ARB biofilm). Bioelectroactive species (e.g., outer membrane cytochromes, conductivity pili and extracellular excretions) play a crucial role on the ET between the ARB biofilm and the anode (Richter et al., 2009; Gorby et al., 2006; Newman and Kolter, 2000). Besides the biofilm itself (e.g., community, Torres et al., 2009), some abiotic factors can also influence the performance of bioelectroactive species during ET process (Qiao et al., 2008; Busalmen et al., 2008). For example, oxidative and reductive peaks in the cyclic voltammetry of the anode biofilm varied a lot as a function of pH (Qiao et al., 2008). In addition, Geobacter biofilm with various outer membrane cytochromes produced different currents under different electrode potentials (Fricke et al., 2008). Therefore, the ET behavior of the anode-biofilm is considered to be a helpful tool for understanding the fact that current generation differs greatly among MFC, MSC and MEC.

This study aims to investigate the anode-biofilm ET behavior during the wastewater treatment process under different BES operational modes. In addition, a comparative study of advanced treatment of non-degradable real wastewater by cathodic bioelectro-Fenton process (Feng et al., 2010a,b) was carried out among these modes. Current generation, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were recorded for investigating the anode-biofilm ET behavior. Total organic carbon (TOC) was determined to evaluate the feasibility of advanced wastewater treatment by different BESs.

2. Methods

2.1. Reactor configuration

Dual-chamber bioelectrochemical reactor consisting of two identical cylindrical chambers (100 mL for each) was employed in this study. The two chambers were separated by a cation exchange membrane (Zhejiang Qianqiu Group Co., Ltd., China). Graphite felt with a projected surface area of 23.7 cm^2 was used as the anode and cathode (about 3 cm distance between them).

2.2. Advanced wastewater treatment and electrochemical measurement of the anode biofilm

To obtain basically identical anode biofilms, five reactors were operated under the MFC mode with mixed sludge acquired from a coking wastewater treatment plant (Shaoguan Iron & Steel Group Co., Ltd., China). The anode medium contained 0.1 M phosphate buffer solution (PBS, pH 7.0), 0.39 g/L NH_4HCO_3, 10 mL/L mineral solution (Lovley and Phillips, 1988) and 10 mL/L vitamin solution (Lovley and Phillips, 1988). Acetate (30 mM) was added into the anode chamber as electron donor and replenished when it was depleted. The cathode solution contained 0.1 M PBS (pH, 7.0) and was bubbled with air at a rate of 200 mL/min. During the anode biofilm formation process, approximately the same magnitude of voltage was produced in the five reactors. When a stable voltage was produced for three continuous cycles, the five reactors were stopped and identical mixed anode biofilms were supposed to be obtained. One of the five reactors was randomly selected for power density measurement and the result revealed that the maximum power density was obtained under a 180 ohm external resistance.

Three of the four remaining reactors were employed for coking wastewater (CW, collected from the effluent of biological treatment unit, TOC = 28.3 mg/L) treatment by the cathodic bioelectro-Fenton process (Feng et al., 2010a,b). The solution in the cathode chamber was replaced with CW containing 0.1 M PBS (pH, 7.0) and 1 g γ-FeOOH (homemade according to Li et al., 2007). These reactors were operated under different modes, namely, MFC (180 ohm external resistance), MSC (short circuit, 0 V was supplied by an electrochemical workstation in the two-electrode mode) and MEC (0.3 V was supplied with an electrochemical workstation in the two-electrode mode). During the entire operation process, the catholyte pH was kept at 7.0. For investigating the anode characteristic in different BESs, representative anode potentials were recorded when MSC and MEC reached current peaks. The three reactors were continuously operated for 40 h because the cathodic TOC showed little change in the later period. Then, catholyte samples were taken for TOC measurement to determine the treatment efficiency.

In the meantime of CW treatment process, the last one of the five reactors was employed for the anode-biofilm CV measurements in the presence and absence of acetate, respectively. The CV of anodic planktonic bacteria was also conducted with a fresh graphite felt. In addition, this anode biofilm was also utilized for EIS measurement for investigating the charge transfer resistance (R_{ct}) in three BES conditions. It should be noted that some necessary control tests were also conducted and this entire study was repeated in a biochemical incubator at 30 °C.

2.3. Measurements and analysis

The voltage output in MFC was recorded by a data collector (AD8223, Analog Devices, USA), and the current generation in MSC and MEC was recorded by a electrochemical potentiostat (CHI 1000a, Chenhua Instrument, China). CV and EIS of the anode biofilm were performed using the CHI 660c electrochemical potentiostat (CHI 660c, Chenhua Instrument, China). The EIS measurements were recorded in the frequency range from 100 kHz to 10 mHz with a typical three-electrode mode, and the EIS result was fitted by ZSimpWin software to determine the R_{ct} and exchange current. All the potentials recorded in the following sections were reported *vs.* saturated calomel electrode (SCE). Wastewater sample was analyzed by a TOC analyzer (TOC-V CPN, Shimadzu, Japan).

2.4. Calculations

The current generation in MFC was calculated according to Ohm's law as previously described (Feng et al., 2010a,b).

The exchange current I_o (A) is given by Eq. (1) (Bard and Faulkner, 2001),

$$I_0 = \frac{R_g T}{nFR_{ct}} \tag{1}$$

where R_g is the gas constant, T(k) is the temperature, $n = 1$ is the number of electron transferring from one bioelectroactive species molecule to electrode, F is Faraday's constant, and R_{ct} (ohm) is the charge transfer resistance.

3. Results and discussion

3.1. Current generation by the anode biofilm under different BES operational modes

After the biofilm formation process, ARB were successfully attached onto the anode surface according to the scanning electron microscope images (data not shown). The current generation is a representative for reflecting the anode-biofilm ET behavior in dif-