Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Unveiling optimal modes of operation for microbial fuel cell-aided dye bioremediation

Jun-Ming Hong[a], Yu-Feng Xia[a], Chuan-Chung Hsueh[b], Bor-Yann Chen[b,*]

[a] College of Chemical Engineering, HuaQiao University, Xiamen 361021, China
[b] Department of Chemical and Materials Engineering, National I-Lan University, I-Lan 26047, Taiwan

ARTICLE INFO

Article history:
Received 20 January 2016
Revised 13 July 2016
Accepted 8 August 2016
Available online xxx

Keywords:
Microbial fuel cell
Bioelectricity generation
Anaerobic processes
Optimization
Biodegradation
Biofilms

ABSTRACT

Through equivalent concepts of electrochemical resistances, this first-attempt study disclosed optimal operation mode(s) of microbial fuel cells (MFCs)-assisted dye decontamination. With supplementation of energy substrate(s) and textile dye(s), internal resistances could be significantly reduced for effective electron transfer (ET) to dye decolorization (DD) and bioelectricity generation (BG). The findings indicated that increases in nutrient substrates and azo dye- reactive blue 160 would favor DD in MFC systems. According to analyses for the best contacting patterns of reacting systems, a batch or plug-flow MFC system is the most appropriate mode of operation for DD. The also suggested that continuous flow-modes of operation seem to be relatively favorable for BG. Apparently, whether DD or BG is electron-transfer dominant in MFCs directly depended on reaction order(s) of nutrient substrate and dye concentrations.

1. Introduction

Azo dyes are the largest and most versatile class of textile dyes widely used in myriads of industries [1]. Due to recalcitrant characteristics of azo dyes, these compounds released to the environment seemed to be inevitably urgent to be treated. As known, bioremediation to environmental problems using indigenous microorganisms is considered as one of ecologically friendly and cost-effective methods for pollutant decontamination. Therefore, in-situ and on site dye bioremediation would be of great importance [2]. Recently, microbial fuel cells (MFCs) were considered as rapidly evolving methods for wastewater treatment (WWT) via simultaneous bioelectricity generation and dye decolorization (SBG&DD) [3]. In fact, several studies suggested to use different MFC-based alternatives for removal of azo dyes from simulated dye-laden wastewater [4–9]. Even these studies used MFCs to inspect reductive degradation of various azo dyes, optimal mode(s) of MFC operation to enhance the performance of dye degradation for practical applications still remained not clearly disclosed. Moreover, recent findings [10] revealed that decolorized metabolites (DM) could act as electron shuttles to improve bioelectricity generation and stimulate reductive decolorization. These all suggested that interactive biostimulation of DM and bioaugmentation of degrading bacteria for MFC operation would be more promising for WWT. In fact, there are several types of MFC configurations that have been proposed for MFC-oriented pollutant bioremediation. For example, double-chamber MFCs were mentioned as bioreactors with proton exchange membrane (PEM) to control release of exogenous redox reactions taking place in the anode and cathode. However, mass transfer resistance of PEM still significantly limited operation efficiency of MFCs. Thus, due to concentration gradients as driving forces in the chamber, single-chamber MFCs (SC-MFCs) provided technically feasible alternatives, in particular offering cost and operational savings among other advantages [11]. A typical SC-MFC basically contained an anaerobic biofilm anode and air-cathode to accelerate electron transfer (ET)-characteristics for power generation. Chen et al. [12] applied SC-MFCs for simultaneous power generation and dye decolorization, showing that increased LB substrate concentrations would augment the power-generating performance of MFC systems. Although some studies also showed operation efficiencies of different modes of MFC operations, conclusive remarks for optimal modes of MFCs still remained open to be disclosed. For example, Fang et al. [6] adopted wetland-simulated MFCs for dye-bearing WWT, revealing that increases of hydraulic retention time (HRT) would increase color removal efficiency of reactive red X-3B (ABRX3) and COD degradation. Using various modes of continuous flow MFCs for WWT, decreases in HRT essentially attenuated the degradation performance of organics [13]. As Ren et al. [14] mentioned, electron-transport performance of continuous flow modes of MFC operation seemed to be lower than batch mode of operation. This work quantitatively deciphered such mysteries behind MFC performance to suggest the

* Corresponding author. Fax: +886 3 9357025.
E-mail address: boryannchen@yahoo.com.tw, bychen@niu.edu.tw (B.-Y. Chen).

http://dx.doi.org/10.1016/j.jtice.2016.08.011
1876-1070/

most appropriate mode of MFC operation for pollutant degradation and power generation. To the best of our knowledge, this first-attempt study could provide a systematic and quantitative assessment, suggesting the most promising modes of MFC operation for optimal contaminant degradation (*e.g.*, dye decolorization).

2. Materials and methods

2.1. Single-chamber MFC construction and microbial cultures

Membrane-free air cathode single-chamber MFCs (SC-MFCs) inoculated with *Proteus hauseri* ZMd44 were constructed in cylindrical tubes made by polymethylmethacrylate (PMMA) (cell sizing ID = 54 mm, l = 95 mm) with the working volume of *ca.* 220 ml. Porous carbon cloth (CeTech^{TM}) (without waterproofing or catalyst) with a projected area of *ca.* 22.9 cm^2 (*i.e.*, $\pi \times 2.72^2$) on one side were used as anode electrodes. The air cathode was nearly identical to the anode in size and consisted of a polytetrafluorethylene (PTFE) diffusion layer (CeTech^{TM}) on the air-facing side. Note that using PTFE can prevent microbial propagation onto the cathode to utilize oxygen in air; thus, significantly augmenting power generating capabilities of MFCs. Acclimation of SC-MFCs using complete decolorization of RBu160 at 200 mg l^{-1} as selection pressure was carried out at ambient temperature for *ca.* 1 year to ensure stable performance of MFC operation.

2.2. Microorganisms and culture conditions

The model azo dye- reactive blue 160 (RBu160) (CAS number 71872-76-9, analytical grade, purchased from Everlight Chemical Ltd., Taipei, Taiwan) was used to color removal. Considering maintaining biodiversity of Taiwan for sustainable development, indigenous decolorizers *Proteus hauseri* ZMd44 isolated from Lanyang Plain and identified via 16S rRNA phylogenetic tree analysis were used for study [10]. A loopful of strain seed taken from all isolated colony on a LB-streak plate was precultured in 50 ml LB broth for 12 h overnight at 30 °C, 125 rpm using water bath shaker (SHINKWANG, SKW-12). Note that LB broth, Miller (Luria-Bertani) (per liter) contained 10.0 g Bacto tryptone, 5.0 g Bacto yeast extract, 10.0 g sodium chloride. Then, 1% (v/v) precultured broth was inoculated into 100 ml fresh LB broth for 12 h culture at 30 °C, 125 rpm. Cultures were then transferred into MFCs at ambient temperature to simulate practical-operation situations.

2.3. Experimental operations

As LB medium is not economically feasible for practical applications in wastewater treatment, nutrient medium for cell growth was selected to be 0.1 × (10%), 0.2 × (20%), 0.3 × (30%), and 0.4 × (40%) of LB medium (fixed sodium chloride at 10.0 g l^{-1}) to show which medium could be more cost-effective for bioelectricity production in MFC. Moreover, the LB medium was used as an energy source for initial enrichment and biofilm formation in MFC. For experiments, MFC was operated initially under batch-fed mode of operation for *ca.* 60 days (0.2×LB as fed substrate), the electrochemical biofilm stably formed onto anode for current generation in MFCs after approximately 20 days as the voltage of MFC increased sharply [10]. Compared to popularly used substrate- glucose, power generation using LB medium could maintain a longer period of time (*e.g., ca.* 2000 h for LB and > 480 h for 0.2× LB; data not shown) [15] and thus we selected 4 days (*i.e.*, 96 h) as the time interval for clear demonstration of operation performance with prior results [12]. To explore characteristics of SBG&DD, the batch-fed mode of MFC operation with impulse injection of dye-bearing or dye-free substrate was carried out. That is, 5.0 ml of 8.8× LB broth laden with appropriate concentrations of RBu160 (*e.g.*, 200, 400, 600, and 800 mg l^{-1}) was supplemented into MFCs for comparison. After injection, dye concentration, COD and cell voltage at different time were both measured. Continuous modes of operation were taken place as replacement strategy (as described in Fig. 4) to prevent well-mixed situation for ET resistance.

2.4. Analytical methods

The voltage difference between the anode and cathode of MFCs (under external resistance of 1000Ω) were continuously recorded every 5 min using a precise multimeter via a 8-channel data acquisition system (Jiehan 5020, Taiwan) via data storage of a personal computer. Dye concentrations were determined as described elsewhere [16]. COD was determined using rapid digestion spectrophotometric determination method (HACH, DR3900). The electrical current I (A) can be determined by the relationship of output voltage between anode and cathode U (V) ÷ external resistance R_{ex} (V). Electrochemical impedance spectroscopy (EIS) (HIOKI 3522-50, Japan) was used to evaluate internal resistance (R_{in}), diffusion resistance (R_{diff}), kinetic resistance (R_{kin}) and electrolyte resistance (R_{elec}) as illustrated elsewhere [13].

3. Results and discussion

3.1. MFC performance under different condition

Regarding simultaneous bioelectricity generation and dye decolorization (SBG&DD), as PTFE was used on the surface of air-facing side of cathode to prevent microbial propagation onto cathode to utilize oxygen, augmentation of power generating capabilities of MFCs was mainly due to reduction in anodic biofilm. In SC-MFC, azo dye (*i.e.*, RBu160) could act as electron acceptor without dispute. Therefore, DD alone (*i.e.*, open circuit control experiment) might be predominant by color removal of suspended cultures. That is, dye to synergistic interactions of BG and DD, DD taken place in MFC would not simply be considered as solely a bioelectrochemical reaction. However, combined interactions of electron transfer (ET) in external circuit between anode and cathode and dye decolorization in the chamber maximized stimulation of ET capabilities for SBG&DD. This suggested that MFC-assisted pollutant degradation is biologically feasible for system optimization. In addition, current-generating anode in MFCs could serve as a favorable electron acceptor to provide sufficient energy for cell viability/growth and metabolic functioning inside biofilm [17]. Here, this first-attempt study tended to quantitatively explore the most promising pattern of contacting and modes of MFC operation.

3.1.1. The effect of LB concentrations

As shown in Fig. 1, the performance of COD degradation and bioelectricity generation was apparently affected by substrate concentrations. A sharp rise of output voltage was observed when a new medium was supplemented to MFC. In addition, maximal output voltage nearly remained invariant, even different concentrations of nutrient substrate were provided. For 800 mg l^{-1} RBu160 supplemented, dye decolorization could be almost completed in 3 h. Therefore, time series profiles of COD removal were nearly in parallel with those of power generation, indicating that organic matter was oxidized to effectively generate electrons for current generation. Comparing each steps of substrate supplementation, COD removal efficiencies of MFCs using 0.1x, 0.2x, 0.3x and 0.4x LB medium as energy sources were obtained to be 38.17%, 39.46%, 56.03%, 61.41%, respectively. Meanwhile, average output voltages ($V_{avg} = \frac{1}{100}\int_{100n}^{100(n+1)} V(t)dt; n = 0, 1, 2, 3$) were gradually increased as more nutrient-enriched media were provided (*e.g.*, 66.62, 76.42, 87.75, 96.87 mV for 0.1x, 0.2x, 0.3x, 0.4x LB, respectively). Moreover, initial decolorization rate (IDR) gradually increased with

Please cite this article as: J.-M. Hong et al., Unveiling optimal modes of operation for microbial fuel cell-aided dye bioremediation, Journal of the Taiwan Institute of Chemical Engineers (2016), http://dx.doi.org/10.1016/j.jtice.2016.08.011