Ecological Engineering 112 (2018) 65–71

Contents lists available at ScienceDirect

Ecological Engineering

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

Degradation of nitrobenzene-containing wastewater by a microbial-fuel-cell-coupled constructed wetland

Tingyu Xie, Zhaoqian Jing*, Jing Hu, Peng Yuan, Yali Liu, Shiwei Cao

College of Civil Engineering, Nanjing Forestry University, Nanjing 210037, China

ARTICLE INFO

Keywords:
Microbial fuel cell
Constructed wetland
Nitrobenzene
Electricity generation
Power density

ABSTRACT

A single chamber membrane-less air cathode microbial fuel cell coupled constructed wetland (MFC-CW) was constructed to treat nitrobenzene-containing wastewater and generate electricity simultaneously. Three devices of blank control (CK), microbial fuel cell (MFC) and MFC-CW were investigated. The inherent relationship between substrate degradation and electricity generation were evaluated by the electronic characteristics. The maximum voltage of MFC-CW was obtained at the electrode spacing of 13 cm. The maximum power density of MFC and MFC-CW were 0.59 and 1.53 mW/m^2 respectively. The maximum nitrobenzene removal rate of 92.89% was attained in the MFC-CW when the concentration ratio of nitrobenzene to chemical oxygen demand (COD) was 1:16 with hydraulic retention time at 24 h. The COD removal rate was between 67.92% and 78.30%, and the MFC-CW was efficient for COD degradation.

1. Introduction

Microbial fuel cells have gained tremendous global interest over the last decades as a device that use bacteria to oxidize the organic and inorganic matters with bioelectricity production and wastewater treatment simultaneously (He et al., 2015). MFCs are an excellent mode of converting biomass spontaneously into electricity through the metabolic activity of the microorganisms (Pant et al., 2010). Electrons are liberated from substrates at anode, pass through an external load as electric current, and then combined with a cathodic electron acceptor (Rosenbaum et al., 2010).

MFCs can exploit a variety of soluble or dissolved complex organic waste/wastewater as substrate to fulfill renewable electricity generation along with simultaneous waste remediation (ElMekawy et al., 2015). A complex substrate composition helps in building a diverse and electrochemically active microbial community while a simple substrate is easier to degrade and improves the electricity generation of the system (Chae et al., 2009). As an innovative treatment of wastewater, MFCs can use both easily degradable organics and refractory organics as its fuels. Zhang et al. (2016) applied an anoxic/oxic MFC reactor to treat domestic wastewater and achieved the maximum power density of 2.04 W/m^3 with 91.7% COD and 98.2% ammonia nitrogen removals. Cheng et al. (2015) attempted to study the oxygen stimulation to bioanode for energy recovery from aniline in MFCs and obtained electrons recovery with efficient aniline removal.

A constructed wetland-containing system is operationally friendly, economically sustainable, treatment efficient, and suitable for wastewater treatment (Yu et al., 2012). Studies showed that the presence of the macrophytes increases microbial diversity and provides large surface areas for the development of biofilm (Button et al., 2015). A microbial fuel cell − coupled constructed wetland is a novel system that embeds the electrodes into the constructed wetland. MFC-CW is an emerging technology that realizes the conversion of solar energy to bioelectricity through the syntrophy between plants and electrochemically active bacteria (Lu et al., 2015). MFC-CW enhances indirect utilization of solar radiation to produce green electricity by integrating the rhizosphere with artificially introduced electrodes (Venkata Mohan et al., 2014). Photosynthesis leads to oxygen generation through the plant roots, which causes a redox potential increment and thus has a favorable effect on the MFCs performance (Villaseñor et al., 2013). Studies on a miniatured floating macrophyte ecosystem with water hyacinth and snails embedded with sediment fuel cells documented good electrogenic activity as well as treatment efficiency but was found to depend on the organic load and nature of wastewater (Chiranjeevi et al., 2013). Wu et al. (2015) tested a pilot-scale constructed wetland managed with a membraneless microbial fuel cell with the influent COD of 228 mg/L. Under batch flow mode, the removal rates of total nitrogen, ammonium nitrogen and total phosphorus appeared ranging between 95% and 99% while electricity generated from the CW-MFC. The maximum power density of 320.8 mW/m^3 and current density of 422.2 mA/m^3 were achieved in a research carried out by Srivastava et al. (2015), in which they integrated microbial fuel cell into

* Corresponding author.
E-mail address: zqjing@njfu.edu.cn (Z. Jing).

https://doi.org/10.1016/j.ecoleng.2017.12.018
Received 4 August 2017; Received in revised form 4 December 2017; Accepted 17 December 2017
0925-8574/

constructed wetland.

Nitrobenzene (NB) compounds are widely used in the production of pesticides, dyes, explosives, rubber and other chemicals. Nitrobenzene compounds have high toxicity and are bioaccumulative and stable in groundwater. Nitrobenzene is included in the list of 'priority pollutants' by the USEPA. Inappropriate treatment of nitrobenzene wastewater will seriously endanger environmental safety and human health. Treatments of nitrobenzene-containing wastewater including physical (Rajagopal and Kapoor, 2001), chemical (Arslan-Alaton and Ferry, 2002; Bhatkhande et al., 2003; Jia et al., 2007), biological (Chunli et al., 2008) and composite (Al et al., 2008) treatment methods have been investigated by researchers. Wang et al. (2011) investigated the conversion of NB to aniline, a less toxic product that can easily be mineralized, using a bioelectrochemical system with biocatalyzed cathode. When a voltage of 0.5 V was applied in the presence of glucose, 88.2 ± 0.60% of the supplied NB (0.5 mM) was transformed to aniline within 24 h. High nitrobenzene concentrations in constructed wetland could inhibit the activity of microorganisms, resulting in a low nitrobenzene removal efficiency (Kirui et al., 2016), which gave us a motivation to find a feasible treatment that integrates microbial fuel cells with a constructed wetland.

In this work, microbial fuel cell coupled constructed wetlands were established to investigate the degradation of nitrobenzene-containing wastewater. The electricity generation capabilities of the MFC-CW system under different initial substrate loading and electrode spacing were explored. The voltage output, power density and coulombic efficiency of the MFC-CW were employed to evaluate the bioelectricity production performance. The hydraulic retention time (HRT) and wastewater parameters were altered to analyze the nitrobenzene removal rate and the MFC properties.

2. Material and methods

2.1. MFC-CW system configuration

The structure of the MFC-CW system is shown in Fig. 1. The main structure was made of organic glass with internal diameter 30 cm and height 55 cm. Gravels with diameter of 5–12 mm were used as a packing layer. The graphite was used as cathode and anode after being polished and drilled. Graphite is competitive with low-surface catalyzed cathodes in terms of cost and power production (Freguia et al., 2007). The gravel and the alum sludge both provided alternative surfaces for the attachment and growth of bacteria (Zhao et al., 2013). The anode was embedded into the packing layer while the cathode was placed at the air-water interface. This placement made the anode zone relatively anaerobic and the cathode zone more aerobic (Yadav et al., 2012). A closed circuit was formed by connecting the electrodes to the external resistance with a copper wire. The water hyacinth was planted above the cathode in the MFC-CW system to ensure the cathode to get oxygen from both the atmosphere and the rhizosphere of the water hyacinth (Doherty et al., 2015). The arrangement of MFC was same as the MFC-CW except that no water hyacinth was planted. A control group (CK) with no electrodes or plant was also constructed to investigate the direct degradation of microorganisms.

2.2. Synthetic wastewater

A synthetic wastewater with glucose as carbon source was used during the process of the experiment. Analytically pure nitrobenzene was purchased from Shanghai Lingfeng Chemical Reagent co, Ltd., China. 5–80 mg/L nitrobenzene and 0.1–0.6 g/L glucose were added to make nitrobenzene synthetic wastewater. The composition of the synthetic wastewater are as follows: 0.31 g/L NH_4Cl, 0.13 g/L KCl, 4.10 g/L Na_2HPO_4, 2.54 g/L NaH_2PO_4, 3.13 g/L $NaHCO_3$ and 10 mL/L trace elements (Liu et al., 2008).

2.3. System start-up and operation

Activated sludge obtained from the oxidation ditch of Jiangning Development District Wastewater Treatment Plant (Nanjing, China) was used for inoculating the MFC-CW. The activated sludge was acclimated under anaerobic condition for 10 days. The sludge and glucose culture medium used as the inoculum for the MFC-CW were poured into the reactors. The systems were formally started when the output voltages reached the maximum and remained stable for a while. In the start-up stage, the influent was continuously pumped into the reactors from the bottom (Fang et al., 2016) to accelerate the enrichment of electrogenesis bacteria and the formation of biofilms.

2.4. Analysis and calculation

The nitrobenzene concentration was measured by reducing-azo photometric method using UV/VIS spectrometer (INESA Scientific Instrument Co., Ltd, China). When nitrobenzene was degraded by electrogenesis bacteria, some of them was not degraded completely and was converted into aniline, and therefore aniline had an effect on the measurement of nitrobenzene concentration using this method. The aniline concentration was measured by Naphthyl Ethylene Diamine Azo Photometry. After excluding the aniline in the effluent, the removal rate of NB was calculated using the formula shown in Eq. (1):

$$NBremovalrate(\%) = (NB_{in} - NB_{out})/NB_{in} \times 100\% \quad (1)$$

NB_{in} and NB_{out} represent the influent and effluent NB concentration (mg/L).

The COD concentration was determined according the Standard Methods (APHA et al., 2012) via potassium dichromate oxidation method and the removal rate of COD was calculated using the formula shown in Eq. (2):

$$COD \quad removal \quad rate(\%) = (COD_{in} - COD_{out})/COD_{in} \times 100\% \quad (2)$$

COD_{in} and COD_{out} represent the influent and effluent COD concentration (mg/L) respectively.

The MFC and the MFC-CW voltage was recorded every 10 min by the data acquisition module and the data output terminal was connected with the computer so that the data could be recorded and saved in real time. The data acquisition module was calibrated with a digital multimeter to ensure the accuracy of the voltage readings.

The power density (mW/m^2) and the current density (mA/m^2) were calculated by dividing the power and current with the effective surface area (m^2) of the anode. The electrical characteristics of the systems were assessed by the power density curve and the polarization curve.

The coulombic efficiency (CE) was an important indicator of electron recovery efficiency and was determined by the formula shown in Eq. (3):

$$CE = \frac{M_{O_2} \times I}{F \times q \times b \times \Delta COD} \quad (3)$$

M_{O_2} is the molar mass of O_2 (g O_2/mol O_2), which is 32. I is current (A). F is the Faraday constant (C/mol), which is 96,485. q is the influent flow rate (L/s) and b is the number of electrons gained from per mol substrate (mol e^-/mol O_2), which is 4. ΔCOD is the difference of COD between the influent and the effluent (mg/L).

The internal resistance (R_i) was calculated by the liner region of the polarization curve.

3. Results and discussion

3.1. Electrochemical characteristics

3.1.1. Effects of initial substrate loading on electricity generation

Glucose was used as the main carbon source to investigate the effects of initial substrate loading on electricity generation. Studies