Bioresource Technology 129 (2013) 224–228

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Simultaneous anaerobic sulfide and nitrate removal coupled with electricity generation in Microbial Fuel Cell

Jing Cai [a], Ping Zheng [b,*], Jiqiang Zhang [b], Zuofu Xie [b], Wei Li [b], Peide Sun [a]

[a] College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China
[b] Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China

HIGHLIGHTS

- The MFC could remove sulfide and nitrate simultaneously from wastewater.
- The MFC generated electricity from anaerobic bioconversion of sulfide and nitrate.
- In the MFC, the electricity generation was coupled with the substrate conversion.

ARTICLE INFO

Article history:
Received 3 September 2012
Received in revised form 30 October 2012
Accepted 1 November 2012
Available online 10 November 2012

Keywords:
Microbial Fuel Cell
Graphite rod
Anaerobic sulfide and nitrite removal
Electricity generation
Substrate conversion

ABSTRACT

Two-chamber Microbial Fuel Cells (MFC) using graphite rods as electrodes were operated for simultaneous anaerobic sulfide and nitrate removal coupled with electricity generation. The MFC showed good ability to remove substrates. When the influent sulfide and nitrate concentrations were 780 mg/L and 135.49 mg/L, respectively, the removal percentages of sulfide and nitrate were higher than 90% and the main end products were nitrogen and sulfate. The MFC also showed good ability to generate electricity, and the voltage went up with the rise of influent substrate concentrations. When the external resistance was 1000 Ω, its highest steady voltage was 71 mV. Based on the linear relationship between the electrons released by substrates and accepted by electrode, it was concluded that the electricity generation was coupled with the substrate conversion in the MFC.

1. Introduction

A number of industries generate sulfide-containing waste streams, such as petrochemical plants, tanneries, viscose rayon factories etc. (Mahmood et al., 2007a). Various toxicological effects of sulfide on human health have been described elsewhere. Large volumes of wastewaters containing nitrogenous compounds are produced from industry, agriculture and housing settlements. Nitrate or nitrite can induce multidimensional hazards, such as the eutrophication of water bodies (Zheng et al., 2004). Untreated discharge of these wastewaters to the environment can lead to serious environmental problems. Hence, its removal from wastewaters is required from an environmental standpoint (Pikaar et al., 2011).

As alternatives for oxygen, nitrate can be used to control sulfide generation during treatment of S-containing wastewaters (Cirne et al., 2008). Compared to oxygen, nitrate has the advantage of being highly soluble. This means that its use does not require applying an external gas flow and, consequently, there will be less stripping of gaseous sulfide. For such reasons, the simultaneous anaerobic sulfide and nitrate removal process has been recently developed.

Microbial Fuel Cells (MFC) provide a new approach for wastewater treatment, and especially generate electricity from conversion of organic and inorganic matter (Logan et al., 2006). According to literature review, the sulfide removal and nitrate/nitrite removal have been studied separately in MFC (Rabaey et al., 2006; Sun et al., 2009; Clauwaert et al., 2007; Puig et al., 2011). Theoretically, they can also be removed simultaneously in MFC (Eq. (1)):

$$5HS^- + 2NO_3^- \rightarrow 5S^0 + N_2 + 6H_2O + 7e^- \Delta G_m^0 = -1264\ \text{KJ per reaction}\ E^0 = 1.87\ \text{V} \quad (1)$$

So far, however, few studies have been reported about the simultaneous sulfide and nitrate removal in MFC. Lee et al. (2012) investigated the interactions between denitrifying sulfide

* Corresponding author. Address: Department of Environmental Engineering, Zhejiang University, 866 Yuhangtang Road, Hangzhou, Zhejiang Province, China. Tel./fax: +86 571 888982819.
E-mail address: pzheng@zju.edu.cn (P. Zheng).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.11.008

removal (DSR) process and the MFC process, and confirmed that the MFC was able to remove sulfide and nitrate simultaneously using single culture *Pseudomonas* sp. C27. In the experiment of Lee et al., however, sulfide and nitrate were both put in the anode chamber, and the mechanism of electricity generation was not elucidated.

The objective of this study is to investigate the feasibility of simultaneous sulfide and nitrate removal from wastewater with activated sludge as biocatalyst, to investigate the performance of electricity generation from the anaerobic bioconversion of sulfide and nitrate and to investigate the coupling of electricity generation and substrate conversion. Since graphite rods were the most widely used electrodes (Wei et al., 2011), a two-chamber Microbial Fuel Cells (MFC) were constructed using graphite rods as electrodes.

2. Methods

2.1. Inoculum and enrichment of microbial communities

Inoculum was collected from the anaerobic methanogenic reactor operated at Dengta wastewater treatment plant (WWTP) located in Hangzhou City of China. Its total solids (TS) and volatile suspended solids (VSS) were 95.03 g/L and 68.68 g/L respectively, with VSS/TS ratio of 0.72. The simultaneous anaerobic sulfide and nitrate removal reactor was operated under lithoautotrophic conditions where sulfide was used as electron donor and nitrate was employed as electron acceptor. For initial 1 month, the reactor was fed with synthetic wastewater in order to acclimatize the bacteria to the new substrates and to enrich the sludge.

2.2. Synthetic wastewater

The MFC was fed with synthetic influent containing $NaHCO_3$, $MgCl_2$, KH_2PO_4 (1 g/L each), $(NH_4)_2SO_4$ (0.24 g/L) and trace element solution (1 mL/L). The composition of trace element solution used was according to Mahmood et al. (2007b). The nitrate and sulfide were added in the form of potassium nitrate (KNO_3) and sodium sulfide ($Na_2S{\cdot}9H_2O$), respectively, with their concentrations varying according to the type of experiment conducted.

2.3. Anaerobic sulfide oxidizing (ASO) MFC

The MFC consisted of an anode chamber and a cathode chamber, both of which had a total volume of 350 mL (300 mL net volume) (Fig. 1). They were connected by a cation exchange membrane (CEM) (Ultrax CMI-7000 Membrane International, USA). The electrodes were both graphite rods (6 cm × 1 cm, 18.80 cm^2 net superficial area), which were placed at the centers of each chamber and were parallel to the CEM. The external resistance was 1000 Ω. Activated sludge (100 mL) was inoculated in anode chamber, and the solution in anodic chambers was circulated by a peristaltic pump. The cathode medium was a mixture of 50 mM PBS buffer (pH 7.0) and 100 mg/L potassium permanganate ($KMnO_4$), which was circulated recycled over the cathode compartment using a 2.5 L external buffer vessel by peristaltic pumps.

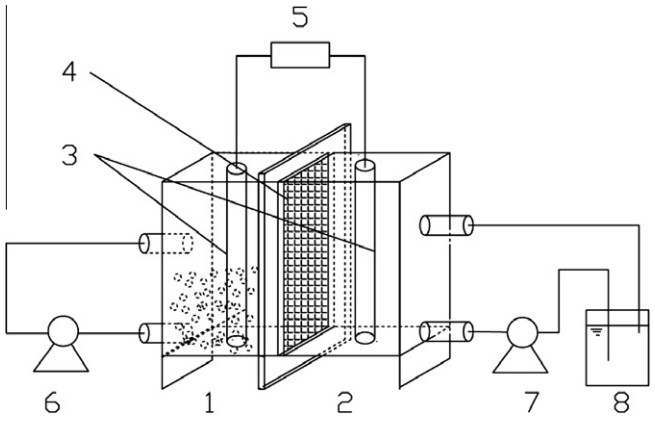

Fig. 1. Schematic diagram of MFC. 1. Anode chamber; 2. Cathode chamber; 3. Electrode; 4. Cation exchange membrane; 5. External resistor; 6.Recycle pump for anode chamber; 7. Recycle pump for cathode chamber 8. External buffer vessel.

2.4. MFC operation

The synthetic wastewater was fed to the anode chamber of the MFC every day. Sulfide was added to a final concentration of 60 mg/L after the anodic chamber was sparged with N_2 for 5 min to remove O_2 in solution. The concentration of nitrate was increased according to stoichiometry of the chemical reaction (S/N molar ratio was 5:2). The MFC was operated under the circumstances until the effluent quality became stable. Then the influent substrate concentrations were increased to the next level. In the experiment, five sulfide concentrations were studied, which were 60 mg/L, 300 mg/L, 540 mg/L, 780 mg/L and 1020 mg/L, respectively.

The effluent substrate concentrations were analyzed in the twenty-second hour after the injection of the influent solution.

2.5. Analytical procedures

Influent and effluent nitrate-nitrogen, pH and sulfide were analyzed during the operation of MFC. Nitrate-nitrogen (NO_3^--N) was analyzed through ultraviolet spectrophotometric screening method (APHA, 1998) on daily basis using spectrophotometer (Unico UV-2102 PC and 722S, China). The sulfide was determined by iodometric method and sulfate was measured through turbimetric method (APHA, 1998). The pH was determined following standard method (APHA, 1998). A three-point calibration of pH meter was performed on daily basis. Total solids (TS) concentration was determined according to gravimetric method at 103 °C (APHA, 1998) and volatile solids were analyzed through gravimetric method at 550 °C (APHA, 1998).

3. Results and discussion

3.1. Substrate removal in the MFC

When the influent sulfide concentration was gradually elevated from 60 mg/L to 1020 mg/L, the sulfide removal percentage remained higher than 99.5%, and its effluent concentration was less than 2.10 mg/L (Fig. 2). The effluent sulfate concentration went up with the rise of influent sulfide concentration, which was increased from 15.06 mg/L to 550.23 mg/L. However, when influent sulfide concentration reached to 1020 mg/L, the effluent sulfate concentration fell to 356.62 mg/L.

As the influent nitrate concentration was elevated from 12.12 mg/L to 51.34 mg/L, the effluent nitrate was not detected, and nitrate removal percentage reached 100%. When influent nitrate concentration was further elevated from 95.54 mg/L to 177.15 mg/L, the concentrations of nitrate and nitrite in the effluent gradually rose from 3.34 mg/L and 0.18 mg/L to 36.18 mg/L and 1.57 mg/L, respectively and nitrate removal percentage went down to 79.73%.

The MFC showed good ability to remove sulfide and nitrate simultaneously. The removal percentages of sulfide and nitrate were higher than 90% when influent sulfide and nitrate concentrations were 780 mg/L and 135.49 mg/L, respectively. It was observed that the sulfate conversion fluctuated largely. About