The Influence of Sulfate and Nitrate on Electricity Generation in Single-Chamber Microbial Fuel Cells

Chontisa Sukkasem[1,2], Hong Liu[1],

[1] Department of Biological and Ecological Engineering, Oregon State University, USA;
[2] Department of Food Science and Technology, Faculty of Technology and Community Development, Thaksin University, Phattalung Campus, Phattalung, 93110, Thailand
Oral speaker phone: +66-84-212-1788; Fax: +66-74-69-3996; e-mail: chontisa.s@gmail.com

Many waste streams, such as wastewater from rubber latex industries, pharmaceutical industries, and stainless industries, contain both high concentration of nitrate and sulfate. The objective of this study was to investigate the influence of sulfate and nitrate on electricity generation in single-chamber air cathode microbial fuel cells (MFCs). For artificial wastewater containing only sulfate, over 80% of sulfate converted to the element form at the end of batch. Power generation was not significantly affected by the presence of sulfate initially, but over 30% of reduction was observed after 1 month operation. For artificial wastewater supplemented with both sulfate and nitrate, the rates of denitrification and sulfate conversion both increased significantly. These results indicate that there is potential for using MFC technology to treat waste streams containing high concentrations of nitrate and sulfate.

Keywords: Microbial fuel cell, Nitrate, Sulfate, Wastewater treatment

Introduction

Using various wastewaters to generate electricity in microbial fuel cell (MFC) has been high attention recently [1], [2], [3], [4], [5], [6]. Many wastewaters contain various organic compounds (i.e. carbohydrate, protein, fat) as a sole of electrons and various inorganic compounds (i.e. sulfate and nitrate) as a sole of electron acceptor. Some of wastewater contain both high concentration of sulfate and nitrate such as wastewater from rubber latex industries, pharmaceutical industries and stainless industries. Previously, many researches separately studied the effect of sulfate and nitrate in MFC [7], [8], [9], [10], [11], [12], [13], [14], [15], [16]. For nitrate effect on MFC, It was revealed that over 84-90% of 8.0 mM nitrate was removed in 8 hours without an interruption on the maximum voltage output. However, the Coulombic efficiency was greatly affected by the nitrate concentration due to the competition between the electricity generation and denitrification processes [16]. For sulfate effect on MFC performance, Rabaey *et al.* [13] examined electricity generation from sulfide in two-chamber MFCs and it was found that sulfide was removed mainly through the oxidation of sulfide to sulfur on the anode surface.

A few researches reported the relationship between sulfate and nitrate in wastewater. Whitmire *et al.* [17] presented the relation between sulfate and nitrate in the freshwater wetland sediment that nitrate was removed as the first order, besides, both compounds were removed rapidly. The objective of this study was to investigate the influence of sulfate and nitrate on electricity generation in single-chamber air cathode MFCs.

Materials and Methods

MFC construction

Single chamber air cathode MFCs were constructed as described previously [18]. The MFC consists of an anode (2 cm^2 projected surface area) and cathode (7 cm^2 surface area) placed in a plastic (Plexiglas) cylindrical chamber with an electrode spacing of 2 cm. [5], [19]. The anode electrode was made of carbon cloth (without wet proofing; E-TEK, USA). The cathode was made of carbon cloth containing 0.5 mg/cm2 of Pt (10% of Pt/C catalyst, 30% wet-proofing; E-TEK, USA). The electrode was then dried at room temperature for 24 h before used.

MFC inoculation and operation

The MFCs were inoculated with active microorganisms from the anode of an MFC, which was initially inoculated with domestic wastewater and has been operated in semi continuous mode using acetate as a carbon source for over a year [5]. The artificial wastewater contained 70mM sodium acetate, 100mM phosphate buffer pH 7.0, 0.35mM

sulfate and nutrients as described previously [5]. The MFCs were started up by using 1000 Ω fixed external resistance to keep high electron on anode biofilm for awhile. Then, electricity was generated in the first batch and the solution was changed when the voltage started decreased similar to a previous report [2]. The system was considered to be operating under steady conditions when the voltage output was reproducible after refilling the reactor with medium at least two times. The start up normally takes about 4-5 days.

A series of experiments were designed to study the influence of sulfate and nitrate on MFC performance. Initially, the MFC was operated with basic artificial wastewater. Afterward, the set of tests was conducted by feeding the medium which contained sulfate supplemented (SS), and mixed sulfate and nitrate supplemented (MSNS) into the MFC. Those artificial wastewaters were prepared by supplemented with sodium sulfate (Na_2SO_4) and potassium nitrate (KNO_3) to obtain the final sulfate and nitrate concentration of 5.56 mM and 8.0 mM, respectively. All tests were conducted in temperature-controlled chamber or incubator.

Analysis and calculations

Cell voltage across external resistor was recorded using a multimeter with a data acquisition system (2700, Keithly). Current density and Coulombic efficiency (CE) were calculated according to the procedures reported previously [5]. Sulfate and sulfide were measured using turbidimetric method [20], and methylene blue method of Pachmayr [21], respectively. Nitrate concentration was measured using Ultraviolet Spectrophotometric Screening Method [20]. Moreover, the energy-dispersive X-ray spectroscopy (EDX) method [22] was used for determined sulfur element compound on electrode surface.

Results and Discussion

For artificial wastewater supplemented with only sulfate, over 80% of sulfate converted to the element form at the end of batch (Figure 1) which proved by EDX method that shown the sulfur element on anode surface was higher amount than on cathode surface and on the control one (Figure 2). Zhang *et al.* [23] reviewed that sulfate oxidizing bacteria (SOB) oxidized HS^- to S^0, which can be stored as intracellular globules and subsequently to SO_4^{2-}. The S^0, accumulated as end product in biological oxidation reactor (at anode surface) which O_2 was the electron acceptor (at cathode surface). The present of sulfate did not affected on the power generation initially but over 30% reduction of power density was observed after a month operation (Figure 4).

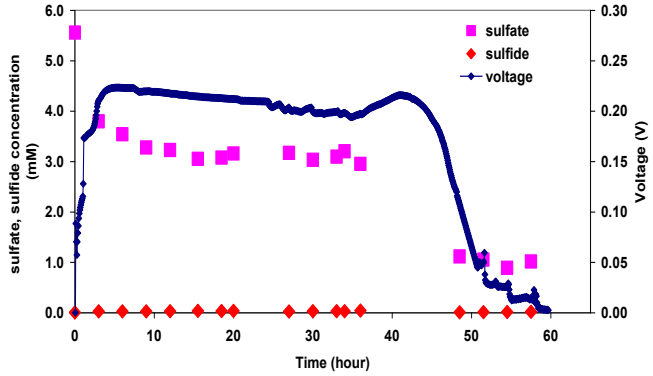

Figure 1 Effect of sulfate on voltage generation (270 Ω) and sulfate conversion

For artificial wastewater supplemented with both sulfate and nitrate, the rate of denitrification and sulfate conversion both increase significantly. Over 85% of nitrate and about 50% of sulfate were rapidly removed concomitant with a bulk of bubbles at first 6 hours. Afterward, the other half of sulfate concentration acted as the main effect until the end of batch (Figure 4). The artificial wastewater without sulfate and nitrate supplemented obtained the highest Coulombic efficiency in MFC comparing with SS, NS, and MSNS mediums (Figure 5). However, the positive effect of MSNS on the MFC performance was found that the Coulombic efficiency, and sulfate and nitrate removal rates were significantly increased from SS or NS mediums 6-7%, 1.2 mMh^{-1}, and 0.73 mMh^{-1}, respectively. It indicated that sulfate and nitrate promoted each other to maintain the MFC performance. It possibly due to the bacteria using elemental sulfur as energy source synchronize with sulfide oxidation and using nitrate as electron accepter to transform to nitrogen gas [24]. These results indicate that there is potential for using MFC technology to treat waste streams containing high concentrations of sulfate andnitrate.

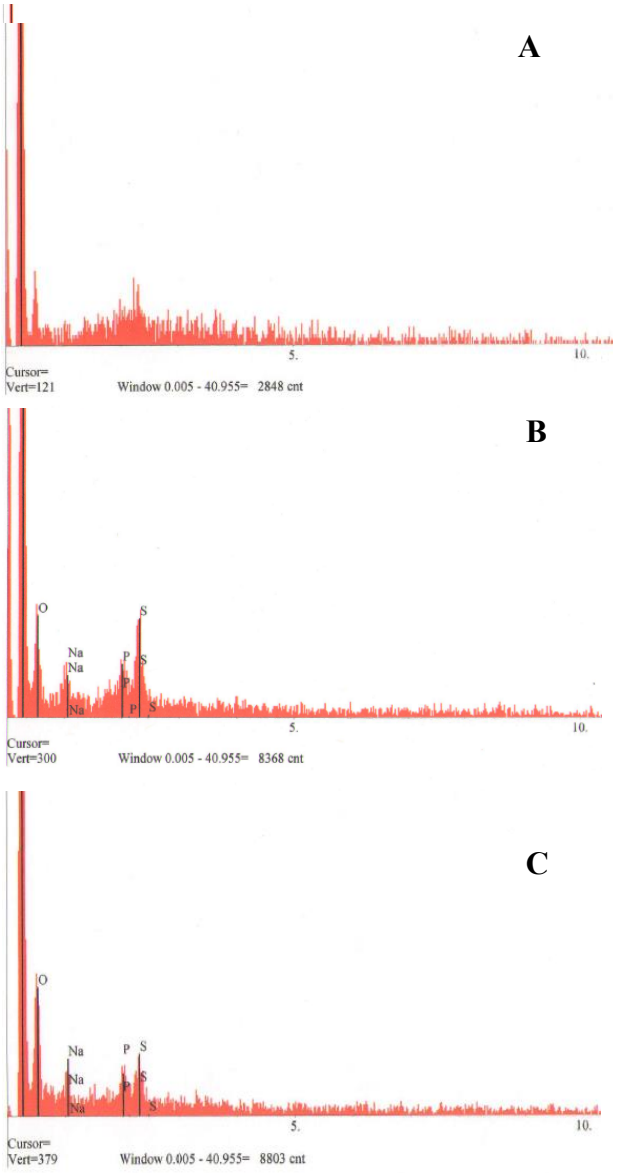

Figure 2 Sulfur element determination by EDX method on electrode surface: Control (both anode and cathode) (A), anode (B) and cathode (C)

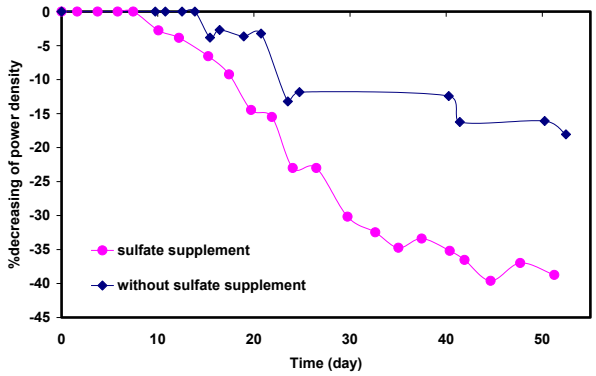

Figure 3 Percentage decreasing of power density at 270 Ω

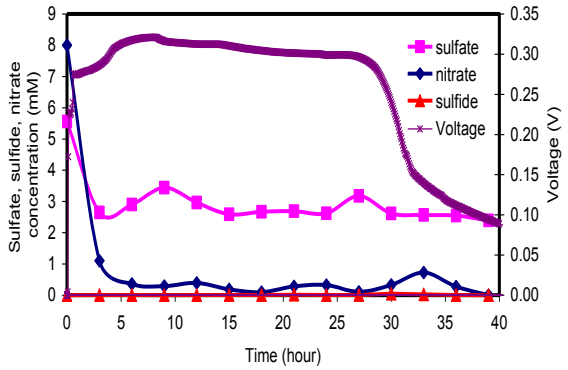

Figure 4 Effect of mixed 5.56mM sulfate and 8.0mM nitrate on MFC performance at 270 Ω.

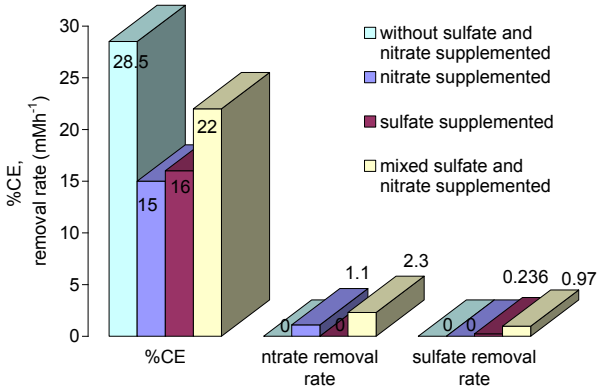

Figure 5 The influence of sulfate and nitrate on the single chamber MFC performance

Note: Some data was modified from Sukkasem *et al.* [16]

Conclusion

For artificial wastewater containing only sulfate, over 80% of sulfate converted to the element form at the end of batch. Power generation was not significantly affected by the presence of sulfate initially, but over 30% of reduction was observed after 1 month operation. For artificial wastewater supplemented with both sulfate and nitrate, the rates of denitrification and sulfate conversion both increased significantly. These results indicate that there is potential for using MFC technology to treat waste streams containing high concentrations of nitrate and sulfate.

Acknowledgement

This research was supported by Agricultural Research Foundation of Oregon State. Chontisa Sukkasem would like to thank The Commission on Higher Education, Ministry of Education, Thailand, for the financial support during her study at Oregon State University and thanks for Dr. Piyarat Boonsawang, Department of Industrial Biotechnology, Faculty of Agro-Industry, Prince of Songkla University, Thailand for the education supports.

References

1. Power, C.A., Richardson, R.E. and Scott, N.R. 2007. Microbial fuel cell operation and use with anaerobic digestion for power production from daily manure. American Society of Agricultural and Biological Engineers 074144.
2. Logan, B.E., and Regan, J.M. 2006 Electricity-producing bacterial communities in microbial fuel cells. TRENDS in Microbiology 14: 12.
3. Yokoyama, H.,Ohmori, H., Ishida, M., Waki, M. and Tanaka, Y. 2006. Treatment of cow-waste slurry by a microbial fuel cell and the properties of the treated slurry as a liquid manure. Animal Science Journal 77: 634-638.
4. Logan, B.E. 2005. Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. Water Research 39: 4673-4682.
5. Liu, H., Ramnarayanan R. And Logan, B.E. 2004. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environmental Science and Technology. 38: 2281-2285.
6. Kim, M., Youn, S.M., Shin, S.H., Jang, J.G., Han, S.H., Hyun, S.M., Gadd, G.G. and Kim, H.J. 2003. Pratical field application of a novel BOD monitoring system. Journal of Environmental Monitoring 5: 640-643.
7. Gregory, KB., Bond, D.R. and Lovley, DR. 2004. Graphite electrode as electron donors for anaerobic respiration. Environmental Microbiology 6(6): 596-604.
8. Goel, R.K. and Flora, J.R.V. 2005. Sequential nitrification and denitrification in a divided cell. Environmental Engineering Science 22: 440.
9. Park, H.I., Kim, D.K., Choi,, Y.J. and Pak, D. 2005. Nitrate reduction using an electrode as direct electron donor in a biofilm electrode reactor. Process Biochemistry 40: 3383–3388.
10. Tender, L.M., Reimer, C.E., Stecher, H.A., Holmes, L.M., Bond, D.R., Lowy, D.A., Pilobello, K., *et al.* 2002. Harnessing microbially generated power on the seafloor. Natural Biotechnology. 20: 821-825.
11. Holmes, D.E., Bond, D.R., and Lovley, D.R. 2004a. Electron transfer by *Desulfobulbus propionicus* to Fe(III) and graphite electrodes. Applied and Environmental Microbiology 70(2): 1234-1237.
12. Holmes, D.E., Bond, D.R., O'Neil, R.A., Reimers, C.E., Tender, L.R., and Lovley, D.R. 2004b. Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments. Microbial Ecology 48: 178-190.
13. Rabaey, K., Sompel, K.V.D., Maignien, L., Boon, N., Aelterman, P., Clauwaert, P., Schamphelaire, L.D., *et al.* 2006. Microbial fuel cell for sulfide removal. Environmental Science and Technology 40: 5218-5224.
14. Reimers, C.E., Gurguis, P., Stecher III, H.A., Tender, L.M., Ryckelynck, N., Whaling, P. 2006. Microbial fuel cell energy from an ocean cold seep. Geobiology 4: 123-136.
15. Reimers, C.E., Tender, L.M. Fertig, S., Wang, W. 2001. Harvesting energy from the marine sediment-water interface. Environmental Science and Technology. 35: 192-195.
16. Sukkasem, C., Xu, S., Park, S., Boonsawang, P. and Liu, H. 2008. Effect of nitrate on the performance of single chamber air cathode microbial fuel cells. Water Research 42(19) 4743-4750
17. Whitmire, S.L., and Hamilton, S. 2005. Rapid removal of sulfate and nitratein freshwater wetland sediments. Journal of Environmental Quality 34: 2062-2071.
18. Liu, H., Cheng, S., and Logan, B.E. 2005. Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. Environmental Science and Technology. 39: 5488-5493.

19. Liu, H., and Logan, B.E. 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environmental Science and Technology. 38: 4040-4046.
20. APHA, AWA, WPCF. 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed.; American Public Health Association, Washington DC.
21. Trüper, H.G. and Schlegel, H.G. 1964. Sulphur metabolism in *Thiorhodaceae I.* Quantitative measurements and growing cells of *Chromatium okenii*. Antonic van Leeuwenhock 30: 225-238.
22. Zadora, G., Bro'zek-Mucha, Z. 2003. SEM–EDX—a useful tool for forensic examinations. Materials Chemistry and Physics 81: 345–348.
23. Zhang, L., Schryver, P.D., Gusseme, B.D., Muynck, W.D., Boon, N., and Verstraete, W. 2008. Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. Water Research 42: 1-12.
24. Moon, H., Chang, I.S. and Kim, B.H. 2006. Continuous electricity production from artificial wastewater using a mediator-less microbial fuel cell. Bioresource Technology 97(4): 621-627.