Bioresource Technology 156 (2014) 14–19

Contents lists available at ScienceDirect

Bioresource Technology

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

Sulfate and organic carbon removal by microbial fuel cell with sulfate-reducing bacteria and sulfide-oxidising bacteria anodic biofilm

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HIGHLIGHTS

- Microbial fuel cell with SRB + SOB anodic biofilm treats sulfate + lactate wastewater.
- Tested MFC efficiently converted sulfate to elemental sulfur.
- Electrochemical analyses showed that sulfide is dominating species for performance.
- Form sulfide diffused to SOB cell for conversion to sulfur and excess electrons.
- Short diffusional distance of sulfide ions between cells enhances MFC performance.

ARTICLE INFO

Article history:
Received 18 November 2013
Received in revised form 28 December 2013
Accepted 30 December 2013
Available online 10 January 2014

Keywords:
Sulfate
Sulfide
Microbial fuel cell
Diffusion

ABSTRACT

Biological sulfur removal can be achieved by reducing sulfate to sulfide with sulfate-reducing bacteria (SRB) and then oxidising sulfide to elemental sulfur (S^0) with sulfide oxidising bacteria (SOB) for recovery. In sulfate–carbon wastewaters lacking electron acceptor for sulfide, excess sulfide will be produced and accumulated in the reactor. This study applied the microbial fuel cell (MFC) cultivated with the SRB + SOB anodic biofilm for treating the sulfate + organic carbon wastewaters. Excess sulfate ions were efficiently converted to sulfide by SRB cells in the biofilm, while the formed sulfide was diffused to the neighboring SOB cells to be irreversibly converted to S^0 with produced electrons being transferred to the anode. The cell–cell sulfide transport principally determined the electron flux of the MFC. Short diffusional distance of sulfide ions between cells significantly reduced the polarization resistances, hence enhancing performance of the MFC.

1. Introduction

Industrial effluents from sugar, alcohol, pharmaceutical products and monosodium glutamate can contain high levels of sulfate. The sulfate-redusing bacteria (SRB) can convert sulfate to sulfide in anaerobic environment (Silva et al., 2012). To remove sulfide from water, the use of sulfide-oxidising bacteria (SOB) was proved feasible (Wang et al., 2010). SRB are heterotrophic bacteria that consume organic compounds as carbon and energy sources. Conversely, SOB are commonly autotrophic so inorganic electron acceptors such as nitrate are needed for sulfide oxidising. The biological reactor with both SRB and SOB can achieve simultaneous removal of sulfide, nitrate and organic compounds (in term of chemical oxygen demand, COD) (Xu et al., 2013, 2014; Chen et al., 2013; Show et al., 2013; Lee et al., 2012a,b).

In wastewaters lacking nitrate or other electron acceptors, simultaneous removal of sulfide and organic compounds is not achievable; while addition of electron acceptors is not a cost-effective and environmental friendly option. Microbial fuel cells (MFC) can generate electricity from degradation of organic and inorganic substrates in wastewater and in sludges (Jiang et al., 2009). A few studies explored the removal of sulfide using MFC (Habermann and Pommer, 1991; Cooney et al., 1998; Wang et al., 2001; Tender et al., 2002; Ryckelunck et al., 2005; Zhang et al., 2009a,b; Nielsen et al., 2009; Rabaey et al., 2006; Sun et al., 2009, 2010; Chou et al., 2013; Lee et al., 2013). Zhang et al. (2008) proposed the use of SRB and SOB to remove sulfate from waters with MFC. Zhao et al. (2008, 2009) produced electricity from MFC with sulfate removal. Ghangrekar et al. (2010) noted that low COD/SO_4^{2-} ratio would yield poor MFC performance. Rabaey et al. (2006) noted that their microbial fuel cell (MFC) could convert the dissolved sulfide to S^0.

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0960-8524/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.12.129

Sulfate is an electron acceptor hence cannot be directly removed by MFC. Lee et al. (2012a) utilized SRB to convert sulfate to sulfide, then MFC further oxidised sulfide to S^0. Restated, the use of SRB + SOB MFC can remove sulfide and sulfate simultaneously with electricity production. This MFC study is a subsequent report to Lee et al. (2012a) to convert sulfate to S^0 with an SRB + SOB anodic biofilm and with anode as the electron acceptor. In particular, the electrochemical analysis was conducted to unveil the mechanisms noted for the behaviors of the studied SRB + SOB MFC.

2. Methods

2.1. Inoculation and medium

Activated sludge was collected from a bakery factory in Taoyuan County. The sludge was filtered using coarse screen and incubated anaerobic to enrich sulfate reducing consortium for one month in a medium of composition as follows: Na_2SO_4, 1.15 gl^{-1}; sodium citrate, 5.0 gl^{-1}; NH_4Cl, 1.0 gl^{-1}; K_2HPO_4, 0.5 gl^{-1}; sodium lactate, 5.0 gl^{-1}; $Fe(NH_4)_2(SO_4)_2$, 1.0 gl^{-1}; Wolf's vitamin solution, 1 ml; Wolf's mineral solution, 1 ml. The pH of the medium was adjust to 7.5 by 1 M HCl or 1 M NaOH. The Wolf's vitamin solution has the following composition (gl^{-1}): biotin, 0.2; folic acid, 0.2; pyridoxine HCl, 1.0; riboflavin, 0.5; thiamin, 0.5; nicotinic acid, 0,5; pantothenic acid, 0.5; B-12, 0.01; p-aminobenzoic acid, 0.5; thioctic acid, 0.5. The Wolf's mineral solution contained (gl^{-1}): NTA, 1.5; $MgSO_4$, 3.0; $MnSO_4$ H_2O, 0.5; NaCl, 1.0; $FeSO_4$ $7H_2O$, 0.1; $CaCl_2$ $2H_2O$, 0.1; $CoCl_2$ $6H_2O$ 0.1; $ZnCl_2$, 0.13; $CuSO_4$ $5H_2O$, 0.01; $AlK(SO_4)_2$ $12H_2O$, 0.01; H_3BO_3, 0.01; Na_2MoO_4, 0.025; $NiCl_2$ $6H_2O$ 0.024; Na_2WO $2H_2O$, 0.025.

Before inoculation, the enriched sulfate-reducing bacteria consortia were incubated in the same medium as in medium mentioned above for more than 3 days, then the enriched sulfate-reducing bacterial consortia were fed into the MFC anodic chamber for cultivation with syntheses sulfate-laden wastewater, which composition is as follows: Na_2SO_4, 1.15 gl^{-1}; NH_4Cl, 1.0 gl^{-1}; K_2HPO_4, 0.5 gl^{-1}; sodium lactate, 5.0 gl^{-1}; Wolf's vitamin solution, 1 ml; Wolf's mineral solution, 1 ml. The pH of the medium was adjusted to 7.5 by 1 M HCl or 1 M NaOH. For brevity sake, the syntheses sulfate-laden wastewater will be called "fresh media" in the following discussion relative to the "old media", which has been operated in the MFC for 3 days (18 cycles) and contained some metabolite excreted by the biological consortium.

2.2. MFC design

Dual MFC comprising anode and cathode cylindrical chambers (inside diameter 5 cm; length 4 cm each) were connected to a cation exchange membrane (CEM) (Ultrex CMI-7000; Membrane (International, Inc., Glen Rock, NJ, USA). Red rubber stoppers were placed in the sampling holes through which samples were taken and medium was replaced. Anode was made of carbon felt (C0S3002; CeTech Co., Taichung, Taiwan). Cathode was made of carbon cloth (W0S1002; CeTech Co., Taichung, Taiwan). The sizes of the carbon cloth in both experiments were 3 cm × 3 cm. Before inoculation, all the electrodes were first immersed in 1 M NaOH then in 1 M HCl for one-hour each to remove microbial residues on the electrodes surface.

The MFC reactor was started up by directly inoculated 10 ml pre-cultured SRB into 100 ml MFC reactor fed with 90 ml artificial waste water containing lactate and sulfate. Dual carbon felt electrodes are placed in the same anodic chamber to compare the difference of electrochemical performance in the same reactor. Ferricyanide solution is often used in cathodic medium in bench-scale MFC test to substitute the oxygen as cathodic electron acceptor due to low overpotential. 50 mM ferricyanide was used in this experiment and phosphate buffer was added to regulate the pH change in the cathode. The composition of this cathodic solution is as follows: NaH_2PO_4 H_2O, 17.77 gl^{-1}; Na_2HPO_4, 32.33 gl^{-1}; $K_3Fe(CN)_6$, 16.46 gl^{-1} at pH 6.9. At the end of each cycle when the cell voltage was dropped to lower than 100 mV, fresh medium was replenished to the anodic cell to start a new cycle.

2.3. Electrochemical analysis

The voltage of each MFC was recorded every 180 s using a data acquisition system developed by Advantech Co., Taipei, Taiwan. During measurements, the bioanode and another new anode were placed in the anodic chamber while the former was referred to as "biotic" and the latter as "abiotic" tests. The voltage of the MFC refers to the voltage difference across the external resistance. Precision resistors of 1000 ohms were used as external resistance in this experiment. All electrochemical tests were conducted using a potentiostat (CH Instruments Electrochemical Workstation model CHI611), including linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemcial impedance spectroscopy (EIS). And the power supply system used in this experiment was LPS 505N from MOTECH programmable DC power supply. For potentialstats, to control the anode potential, the working electrode of potentialstats was connected with the anode. The reference electrode was connected with the Ag/AgCl reference electrode, which placed on the sample hole at above side of anodic chamber. For power supply, voltage was added to the MFC system by connecting the positive lead of the power supply on the anode and the negative lead of the power supply on the reference electrode in the anode chamber. LSV experiments were carried out at a scan rate of 1 mV s^{-1} from the open-circuit cell voltage (OCV), where zero current is passed across the circuit ($I = 0$), to the short-circuit cell voltage, where current is at a maximum. From the V–I curve obtained using LSV, polarization curve and power density curve could be calculated.

In CV measurement the working electrode potential is ramped linearly versus time and the working electrode's potential ramp is inverted upon reaching a set potential (Liu et al., 2011).

In EIS a sinusoidal signal with small amplitude is superimposed onto the applied potential of the working electrode. The frequency of the sinusoidal signal is from 100 kHz to 5 mHz. The plots of measured electrode impedance can be obtained to show detailed information about the electrochemical system. EIS can be used to measure the ohmic and internal resistance of an MFC. In this

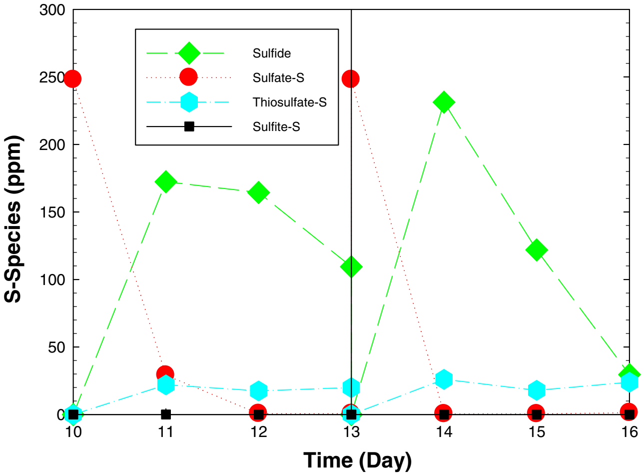

Fig. 1. Metabolite distributions.