Bioresource Technology 182 (2015) 225–231

Contents lists available at ScienceDirect

Bioresource Technology

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

Enhancing waste activated sludge digestion and power production using hypochlorite as catholyte in clayware microbial fuel cell

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HIGHLIGHTS

- Sludge degradation of 81% achieved within 8 days in MFC with NaOCl catholyte.
- Sludge digestion and power production enhanced in MFC with NaOCl as catholyte.
- MFC using NaOCl as catholyte produced two times more power as compared to oxygen.
- Coulombic efficiency of 3.52% using O_2 increased to 13.83% with NaOCl as catholyte.
- Electrochemical analysis indicated faster reduction reaction with NaOCl catholyte.

ARTICLE INFO

Article history:
Received 1 January 2015
Received in revised form 31 January 2015
Accepted 2 February 2015
Available online 9 February 2015

Keywords:
Electrochemical analysis
Hypochlorite
Microbial fuel cell
Power density
Sludge digestion

ABSTRACT

Waste activated sludge was digested in anodic compartment of dual chambered clayware microbial fuel cell (MFC). Performance of MFC was evaluated using oxygen (MFC-1) and hypochlorite (MFC-2) as cathodic electron acceptors. Power production of 8.7 W/m^3 was achieved using hypochlorite as catholyte, which was two times higher than using oxygen (4.2 W/m^3). Total chemical oxygen demand of sludge was reduced by 65.4% and 84.7% in MFC-1 and MFC-2, respectively. Total and volatile suspended solids reductions were higher in MFC-2 (75.8% and 80.2%, respectively) as compared to MFC-1 (66.7% and 76.4%, respectively). Use of hypochlorite demonstrated 3.8 times higher Coulombic efficiency (13.8%) than oxygen. Voltammetric and impedance analysis revealed increase in reduction peak (from 8 to 24 mA) and decreased polarization resistance (from 42.6 to 26.5 Ω). Hypochlorite proved to be better cathodic electron acceptor, supporting rapid sludge digestion within 8 days of retention time and improved power production in MFC.

1. Introduction

Wastewater generated by domestic and industrial activities requires treatment before discharging into the environment. These wastewaters are generally treated by conventional aerobic treatment processes, generating considerable amount of sludge at the rate of 0.4–0.6 kg of sludge per kg of biochemical oxygen demand (BOD) removed. Handling and treatment of this generated sludge is a major problem in wastewater treatment plants due to its large volume and unavailability of sufficient land for disposal. Before disposal, this sludge requires further treatment for improving dewatering ability, reduction in oxygen demand and volume. It imposes nuisance to the environment and economic burden for safe sludge disposal. Currently, anaerobic digesters are being used for treatment of this sludge with intention of recovering methane, reducing volume of the sludge, and improvement in dewatering properties for further drying and disposal. However, the biogas generated needs purification and energy loss occurs while converting it into electrical energy.

Due to strict rules and regulations regarding sludge disposal, it has become crucial to abate the sludge volume in context to reduce the cost of operation, which amount to about 50% of total sewage treatment plant cost (He et al., 2013; Appels et al., 2008). This excess sludge generated can be effectively utilized as a renewable energy resource in bio-electrochemical processes. Recently, Guo et al. (2014) reviewed the different promising methods for efficient sludge utilization to reduce the dependency of non-renewable energy sources.

Microbial fuel cell (MFC) offers a novel waste to energy approach, which can be used to treat sludge in the anodic chamber (Liu et al., 2014). Dentel et al. (2004) first time used sludge for

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http://dx.doi.org/10.1016/j.biortech.2015.02.004
0960-8524/

harvesting electricity. Then onwards application of the MFC in energy recovery from sewage sludge has drawn wide interest among the MFC research community. MFC has the ability to convert organic matter present in the sludge directly into electricity. Total chemical oxygen demand (COD_T) reduction by 53% at alkaline condition of sludge was reported by Yuan et al. (2011). Due to high calorific value (about 10–20 MJ/kg dry sludge), waste activated sludge (WAS) can be used as a good organic source in MFCs (Lindquist, 2003). MFC can provide a solution for sludge volume reduction, organic matter stabilization, and improvement in its filtration ability for easy dewatering (Vajda et al., 2010).

Scott and Murano (2007) used sludge manure as a low-cost fuel for electricity generation in MFC without addition of any mediators. Similarly, sludge generated from primary and secondary clarifiers has been used successfully as substrate in the MFC for power production (Vologni et al., 2013). Addition of phosphate buffer to the primary sludge extended the current generation to 0.8 A/m^2 and simultaneously increased the power density to 0.18 W/m^2 (Vologni et al., 2013). The power density enhanced to 885 mW/m^2 by giving two-stage sludge treatment using pre-fermented supernatant of primary sludge in MFC (Choi and Ahn, 2014). Zhang et al. (2012) reported maximum power output of 13.2 ± 1.7 W/m^3 and Coulombic efficiency (CE) of 19.4% with COD_T removal of 40.8 ± 9% in MFC treating sewage sludge.

Although MFCs have achieved good sludge solids reduction, enhancing energy recovery is a key parameter to evaluate the suitability of MFC technology for the treatment of sludge on large scale. Performance of cathode is one of the key factors influencing the power output from MFC. Researchers have used chemical catholytes such as $K_3Fe(CN)_6$, $CuSO_4$, $FePO_4$ to enhance the performance of MFC using waste activated sludge in the previous studies (Jiang et al., 2009; Wang et al., 2012). However, these catholytes are not sustainable since byproducts generated from them are environmentally harmful and restricts their application for commercialization (Momoh and Naeyor, 2010a,b). Therefore, an alternative chemical catholyte is required to improve MFC's performance without damaging the environment. High redox potential (2.01V vs. SHE), inexpensive and environment friendly properties of NaOCl (Medeiros and Zoski, 1998) become an alternative to replace these chemical catholytes. Moreover, most of the studies in MFCs employed costly polymeric membrane that increases the cost and restricts its use for field application. Therefore, the main goal of this study was to evaluate performance of the low cost clayware separator MFC using NaOCl and oxygen as cathodic electron acceptor and waste activated sludge as feed in anodic chamber. The hypothesis was that MFC incorporated with chemical catholyte will help in achieving sludge digestion within relatively shorter solid retention time compared to conventional digesters.

2. Methods

2.1. MFC construction and operation

Two dual chamber MFCs were fabricated with clayware pots and WAS was used as substrate without any other inoculum. The WAS was collected from Bangur sewage treatment plant, Kolkata, India. The clayware pot with wall thickness of 5 mm was used as anodic chamber and wall of the pot worked as cation exchange membrane (CEM) separating anolyte and catholyte. Both anode and cathode were made with carbon felt (Zoltek Panex 35® Inc., St. Louis, MO, USA) material without any pretreatment. The projected surface area of each anode and cathode was 32 cm^2 and 140 cm^2, respectively. The net liquid volume of anodic and cathodic chambers of both clayware MFCs were 170 mL and 3 L, respectively. MFC-1 was operated using aerated tap water as catholyte and air was supplied by an aquarium pump (SOBO Aquarium air pump, China) at a constant rate of 3.5 mL/min; while sodium hypochlorite (NaOCl) solution of concentration 90 g/L (containing 4% w/v available chlorine) was used as cathodic electron acceptor in MFC-2. Both MFCs were operated in batch mode with a fresh feeding frequency of eight days for total duration of 65 days. The electrical contact between anode and cathode was established by concealed copper wires with an external resistance of 100 Ω. The temperature of catholyte was maintained at 30 ± 3 °C throughout the experimental duration by using an aquarium water heater.

2.2. Analyses and calculations

Sludge samples were collected from the anodic chamber to measure COD_T and soluble chemical oxygen demand (COD_S) in the beginning and at the end of each batch cycle. Both COD_T and COD_S were determined by closed reflux colorimetric method as described in Standard Methods (APHA, 1998). The parameters such as total dissolved solids (TDS), conductivity and pH were measured using water quality bench meter (Cyber Scan, pH 620, Eutech Instruments, Singapore). The sludge characteristics such as total solids (TS), total suspended solids (TSS), volatile suspended solids (VSS) were measured as per Standard Methods (APHA, 1998). The carbon (C), hydrogen (H), and nitrogen (N) contents in the raw sludge and sludge after treatment in MFCs were measured using CHN elemental analyzer (Perkin Elmer 2400, Series II, USA).

The operating voltage (OV) and current across the external resistor (R_{ext}) of 100 Ω was measured using data acquisition unit (Agilent Technologies, Penang, Malaysia). Open circuit voltage (OCV) during operation was measured after allowing the circuit to remain in open condition (no current flow) till the potential value stabilized. The individual electrode potential was measured using Ag/AgCl reference electrode (+197 mV vs. standard hydrogen electrode (SHE), Bioanalytical Systems Inc., West Lafayette, Indiana, USA). The CE is the fraction of effective electrons utilized for current production to the total electron theoretically available in substrate. CE of the MFC operated under batch mode over a time period of '*t*' was calculated as per Eq. (1) (Logan, 2008).

$$CE = \frac{8\int_0^t I dt}{F V_{an} \Delta COD} \quad (1)$$

where, I is electric current, A; 8 is a constant used for COD, based on molecular weight of O_2; F is Faraday's constant = 96,485 C/mol; V_{an} is the volume of anolyte, L; ΔCOD is the difference in the influent and effluent COD, g/L.

2.3. Electrochemical techniques

2.3.1. Polarization

The polarization and power density curves were plotted during the stable power generation phase of MFC operation against variable external resistances using resistance box (GEC05R Decade Resistance Box, Renown Systems, Kolkota, India) by varying external resistance from 40,000 Ω to 1 Ω. The volumetric power density (mW/m^3) normalized to the effective volume of anolyte was calculated by dividing the power with working volume of anodic chamber. The internal resistance of MFC was estimated using the maximum power point method from plot of power density curve (Jadhav et al., 2014a). Tafel plot analysis was used to understand the kinetics of electrode.

2.3.2. Cyclic voltammetry (CV) analysis

Cyclic voltammetry (CV) is an important means to study the mechanisms of electrode reactions and oxidation–reduction processes (Zhao et al., 2009). In the present study, whole cell system was used for voltammetric analysis consisting of carbon felt as