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Bio-electrolytic sensor for rapid monitoring of volatile fatty acids in anaerobic digestion process

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ABSTRACT

This study presents an innovative biosensor that was developed on the basis of a microbial electrolysis cell for fast and reliable measurement of volatile fatty acids (VFA) during anaerobic digestion (AD) process. The bio-electrolytic sensor was first tested with synthetic wastewater containing varying concentrations of VFA. A linear correlation (R^2 = 0.99) between current densities (0.03 ± 0.01 to 2.43 ± 0.12 A/m^2) and VFA concentrations (5–100 mM) was found. The sensor performance was then investigated under different affecting parameters such as the external voltage, VFA composition ratio, and ionic strength. Linear relationship between the current density and VFA concentrations was always observed. Furthermore, the bio-electrolytic sensor proved ability to handle interruptions such as the presence of complex organic matter, anode exposure to oxygen and low pH. Finally, the sensor was applied to monitor VFA concentrations in a lab-scale AD reactor for a month. The VFA measurements from the sensor correlated well with those from GC analysis which proved the accuracy of the system. Since hydrogen was produced in the cathode as byproduct during monitoring, the system could be energy self-sufficient. Considering the high accuracy, short response time, long-term stability and additional benefit of H_2 production, this bio-electrolytic sensor could be a simple and cost-effective method for VFA monitoring during AD and other anaerobic processes.

1. Introduction

Biogas, an alternative to fossil fuels, is becoming a promising source of renewable energy worldwide. In Europe, there are more than 14,500 biogas plants by 2014 with total installed capacity of 7857 MWel (Dahlin et al., 2015). However, process instability caused by clogging, foaming and ammonia inhibition is often encountered in anaerobic digestion (AD), which may cause serious economic losses and prevent this technology from being widely applied. To prevent such problem and to ensure the biogas unit a long life-span, monitoring of the AD process is crucial. Parameters like volatile fatty acid (VFA) concentrations, pH, biogas yield, biogas composition and alkalinity are commonly used as indicators of the complex biochemical process (Li et al., 2014). Among those indicators, it is widely acknowledged that the concentration of VFAs in the digester is prone to be a more meaningful indicator of the process status (Falk et al., 2015). Several off-line methods for VFA monitoring such as titration method (Purser et al., 2014), GC (Boe et al., 2007), high performance liquid chromatography (HPLC) and mid-infrared spectroscopy (Falk et al., 2015) have been developed. However, these methods are time consuming, inaccurate, expensive and typically tested manually. There are also a few online VFA monitoring systems based on the aforementioned methods (Boe and Angelidaki, 2012). Nevertheless, those systems often require complex equipment and careful maintenance, or need difficult sample preparation, which prevents their widely application. Therefore, development of an efficient, accurate and cost-effective VFA sensing system is crucial for the application of AD technology.

In recent years, bioelectrochemical systems (BESs) have demonstrated great potential to be alternatives for water quality measurement. In particular, microbial fuel cell, a typical BES, has been applied as biosensors for monitoring biochemical oxygen demand (BOD) (Zhang and Angelidaki, 2011), dissolved oxygen (DO) (Zhang and Angelidaki, 2012), microbial activity (Zhang and Angelidaki, 2011), toxic components (Shen et al., 2013; Jiang et al., 2015), and even VFA concentrations (Kaur et al., 2013). BES-based biosensors have attracted great attention due to the cost-effectiveness, rapidity, sustainability and portability of the detection method. The first demonstration of VFAs quantitative measurement in a MFC was presented by Kaur et al. (2013). They further

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modified the anode by the immobilization of bacteria to ensure the sensor's stability and repeatability (Kaur et al., 2014). However, the detection range is quite limited for real application which is less than 80 mg/L and it would still function as a sensor of total organic matter instead of VFAs with real wastewater. To solve these problems, a VFA biosensor based on the principle of a microbial desalination cell (MDC) was proposed by our group which could detect a wide range of VFAs and eliminate the effect of sample matrix and complex organic matter (Jin et al., 2016). Nevertheless, there are several challenges still ahead on the filed application. For instance, the response time of the sensor, which is 5 h, needs to be further shortened. Moreover, the reported sensor was comprised of three chambers and two pieces of membrane which may add the capital costs during the practical application. Thus, more simplified sensor architecture is required.

In this study, an innovative biosensor based on a microbial electrolysis cell (MEC) was developed to monitor VFA concentrations during AD process. The bio-electrolytic sensor was constituted of only two chambers and the synthetic wastewater was dosed into the cathode chamber. An external voltage was supplied to accelerate the transportation of VFAs from the cathode to anode through an anion exchange membrane (AEM). To the best of our knowledge, MEC has never been applied as VFA sensor. MEC is a completely different bioelectrochemical system compared to MDC. It could not only inherit the advantages of MDC for VFA monitoring (e.g., good sensitivity), but may also have its own merits over MDC sensor. Firstly, with the assistant of external power supply, the migration and microbial oxidation of carboxylic acids could be accelerated and thereby shortening the response time. Secondly, the configuration of MEC which was only comprised of two chambers and one piece of membrane is much simpler than that of MDC. Thus the construction costs could be greatly reduced. Thirdly, H_2 could be produced at the cathode during the monitoring activity, which may partly compensate the energy used for powering the sensor and potentially store the electricity (e.g., excess from wind mill). The aim of the present study is to provide proof-of-concept evidence that the bio-electrolytic sensor can be an alternative to the traditional complex and time-consuming analytical methods for the real-time detection of VFA concentrations in anaerobic process. With this purpose, the current response of bio-electrolytic sensor to various VFA concentrations in the artificial wastewater (mimicking AD effluent) was tested in terms of response time, detection range, sensitivity and operational stability. The effect of external voltage, VFA composition, and ionic strength on the performance of the sensor was investigated. The interference such as the presence of complex organic matter, anode exposure to oxygen and the effect of low pH on the system performance was explored. Finally, effluent from a lab-scale AD reactor fed with manure and industrial food-wastes was detected by the bio-electrolytic sensor for 30 days to verify the sensor's reliability. The application of the bio-electrolytic sensor might have the potential to supply an efficient way to control AD process and bring economic benefit.

2. Material and methods

2.1. Biosensor setup and operation

Two double-chamber reactors constructed of nonconductive polycarbonate plates were used in this study. The dimensions of the anode and cathode chambers were the same (8 × 8 × 4 cm) for both reactors. Anion exchange membrane (AEM) (AMI 7001, Membrane international, NJ, 9 × 9 cm) was used to separate the two chambers. Prior to use, membranes were soaked overnight in 50 M NaCl solution, and then stored in distilled water until placed in the cell. The reactors were tightened by rubber gaskets and screws to avoid leakage. The anode electrode was made of carbon brush (5.0 cm in diameter, 5.0 cm in length, Mill-Rose, USA) and was attached with biofilm since it was obtained from an existing microbial electrochemical system (Jin et al., 2016). The cathode electrode was a titanium woven wire mesh (4 × 5 cm, 0.15 mm aperture, William Gregor Limited, London) coated with 0.5 mg/cm^2 Pt. Rubber tubes were inserted for medium refill and gas collection. A power supply (HQ PS3003, Helmholt Elektronik A/S, Denmark) was used to provide an additional voltage to the circuit. The positive lead of the power source was connected to the anode electrode, and the negative lead was connected to a 10 Ω resistance connecting the cathode electrode in the circuit (Fig. 1).

The anode electrode was initially placed in a conventional MFC reactor to consume the absorbed substrate for several days until the current density decreased below 0.1 A/m^2. Then the electrode was transferred to the bio-electrolytic sensor reactor. During the experiment, the anode chamber was filled with approximately 220 mL of buffer solution (pH = 7.22 ± 0.17) containing 50 mM phosphate buffer (Na_2HPO_4, 4.33 g/L; and NaH_2PO_4, 2.03 g/L) and nutrient solution (NH_4Cl, 0.31 g/L; KCl, 0.13 g/L; 12.5 mL mineral solution and 12.5 mL vitamin solution) (Kvesitadze et al., 2012). The cathode was filled with 220 mL of synthetic wastewater as “artificial AD effluent”, which was prepared with the same buffer solution containing varying concentrations of sodium acetate, sodium propionate and sodium butyrate (total VFAs ranges from 0 to 120 mM). To mimic real AD effluent, we set the concentration ratio of acetate, propionate and butyrate in “artificial AD effluent” at 5:1:1 which corresponds well to what is often measured in biogas plants (Hollinshead et al., 2014). In one set of tests, we tested the sensor with voltages at 0.3, 0.5, 0.8 and 1.0 V to elucidate the effect of external voltage on the current generation. Then the effect of VFA composition on the system was studied at three different concentration ratios (acetate: propionate: butyrate were 5: 1: 1 (R_1), 10: 10: 1 (R_2), and 20: 5: 1 (R_3)). Subsequently the performance of the system was evaluated under different ionic strength by adding 0, 20, 40, and 80 mM NaCl to the artificial AD effluent. The extra ionic strength of artificial AD effluent with addition of NaCl was expressed as ΔI with respect to the base ionic strength of sample without addition of NaCl. Both chambers were purged with N_2 for 15 min to maintain anaerobic conditions prior to each batch run. Mixing was ensured in the anode by a magnetic stirrer. A gas bag was connected with the cathode to collect the produced hydrogen. All chemicals were of reagent grade. All experiments were carried out in duplicate at least and at room temperature (22 ± 2 °C).

2.2. Electrochemical analyses and calculations

Conductivity and pH were measured by a CDM 83 conductivity meter (Radiometer) and a PHM 210 pH meter (Radiometer), respectively. VFAs were measured using a GC with FID detection (Agilent 6890) (Kaparaju et al., 2009). Hydrogen was analyzed by a GC-TCD fitted with a 4.5 m × 3 mm s-m stainless column packed with Molsieve SA (10/80). Voltage readings were taken every 10 min using a digital multimeter (Model 2700, Keithley Instruments, Inc.; Cleveland, OH, USA). Current density was calculated as $i = I/A$, where I (A) is the current calculated according to Ohm's law and A (m^2) is the project surface area of the cathode. The amount of energy supplied to the sensor by the power source (W_E) and the energy efficiency (η_E) relative to the electricity input were calculated as below:

$$W_E = \sum_{1}^{n} (IE\Delta t)$$