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Microbial fuel cell biosensor for rapid assessment of assimilable organic carbon under marine conditions

Soon Bee Quek*, Liang Cheng [1], Ralf Cord-Ruwisch [1]

School of Engineering and Information Technology, Murdoch University, 90, South Street, Perth, WA 6150, Australia

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ABSTRACT

The development of an assimilable organic carbon (AOC) detecting marine microbial fuel cell (MFC) biosensor inoculated with microorganisms from marine sediment was successful within 36 days. This established marine MFC was tested as an AOC biosensor and reproducible microbiologically produced electrical signals in response to defined acetate concentration were achieved. The dependency of the biosensor sensitivity on the potential of the electron-accepting electrode (anode) was investigated. A linear correlation ($R^2 > 0.98$) between electrochemical signals (change in anodic potential and peak current) and acetate concentration ranging from 0 to 150 μM (0–3600 μg/L of AOC) was achieved. However, the present biosensor indicated a different–linear relation at somewhat elevated acetate concentration ranging from 150 to 450 μM (3600–10,800 μg/L of AOC). This high concentration of acetate addition could be measured by coulombic measurement (cumulative charges) with a linear correlation. For the acetate concentration detected in this study, the sensor recovery time could be controlled within 100 min.

1. Introduction

Biofouling of reverse osmosis (RO) membranes used for seawater desalination is one of the most serious problems in seawater desalination. It causes significant decline of flux, requires frequent cleaning, and leads to elevated energy requirement. As a result, membranes are frequently replaced (Abdul-Azis et al., 2001). At present, the industry is subject to biofouling occurring without being able to monitor or predict the tendency of intake ocean water that causes biofouling.

A good biofouling monitoring/prediction system is necessary and crucial for the development and optimization of efficient anti-biofouling strategies. The information acquired from the biofouling monitoring system should be ideally on-line, and automatic (Klahre and Flemming, 2000). Current biofouling monitoring systems are acting as early warning tools by measurement of intake water quality, including total direct cell counts (TDC) (Jeong et al., 2012), silt density index (SDI) (Alhadidi et al., 2011; Hammes and Egli, 2005) and the biofilm formation rate (BFR) (Van der Kooij, 1992) prior to RO. Another patent (Ho et al., 2004) introduced methods for monitoring and controlling biofouling in membrane

* *Corresponding author*. Tel.: +61 8 9360 2804.
E-mail addresses: s.quek@murdoch.edu.au (S.B. Quek), L.Cheng@murdoch.edu.au (L. Cheng), R.Cord-Ruwisch@murdoch.edu.au (R. Cord-Ruwisch).
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separation systems using fluorogenic agents, which react with bacteria to give fluorescence signal. By using fluorometers to measure the amount of fluorescence signal in the feed stream, the retentate and permeate, changes in the fluorescence signal can represent the extent of biofouling (Lee and Kim, 2011). These methods are time-consuming (may take an hour to several days), offline and typically manual laboratory testing, and therefore they are not suitable for early detection of biofouling potential of feed water.

As the biofouling of the membranes is commonly due to bacterial growth, which is supported by organics in feed water (seawater), biofouling can also be predicted by monitoring low levels of organic substrates in feed water that can serve as a bacterial food source termed "assimilable organic carbon" (AOC) (Hambsch and Werner, 2000). Therefore, AOC monitoring in the feed water of RO plants is a suitable method for the prediction of its biofouling potential.

Methods for determining AOC exist in the freshwater and drinking water industry as biochemical oxygen demand (BOD) measurement. The BOD is a measure of the quantity of oxygen consumed by microorganisms to oxidize the organic matter in a sample of water during a period of 5 or 7 day incubation at 20 °C (BOD) (Bourgeois et al., 2001; Greenberg et al., 1992). The method is not suitable for rapid or online testing. In recent year, biosensors have demonstrated great potential to be an alternative to the conventional analytical method for BOD measurement. The main advantages of biosensors are the potential for rapid or online results, the portability and miniaturization (Rodriguez-Mozaz et al., 2006). Various BOD biosensors have been reported based on different mechanisms including monitoring dissolved oxygen (Jia et al., 2003; Trosok et al., 2001; Wen et al., 2008), measuring intensity of luminescence of luminescent bacteria (Borisov and Wolfbeis, 2008; Hambsch and Werner, 2000; Van der Kooij, 1992), and photocatalysis of sample (Elman et al., 2008).

With the discovery of microbes to transfer electrons to an electrode, not only can electricity be made from organic substances (Cheng et al., 2008) but also can the current be used to sense the presence of organic substances. A biosensor based on the microbial fuel cell (MFC) principle, a device that converts chemical energy to electrical energy, has been reported (Liu et al., 2011). In general, microorganisms grown on the surface of an anode electrode oxidize organic matter in the solution under anaerobic condition and transfer electrons to the anode electrode, which eventually pass through an external circuit to a cathode electrode. The flow of electrons through the circuit is proportional to the amount of organic material oxidized and can be quantified as a current. The anode chamber of an MFC needs to be kept anaerobic as the presence of dissolved oxygen can completely suppress the metabolic activity of electrochemically active bacteria and hence the current production (Liu et al., 2005). This is due to the dissolved oxygen being the preferred electron acceptor in a typical MFC.

Biosensors based on the principal of MFCs have been applied for fast BOD detection. As the current is already a measured signal, MFC biosensors do not need a transducer to translate the signal to an electrical signal, which is commonly required by other biosensors based on photocatalysis or luminescence detection (Peixoto et al., 2011). The MFC-based sensors have long-term stability (Gil et al., 2003; Kim et al., 2003) and can be used for continuous on-line water quality monitoring (Chang et al., 2004). However, as reported by previous research works, the measuring time (i.e. response time and sensor recovery time) varies significantly from 1 h up to several hours (Chang et al., 2004; Kang et al., 2003; Kim et al., 2003).

To date, the available methods of the MFC based biosensors could not detect very low AOC (less than 32 mg O_2/L as BOD_5 equivalent to 12 mg/L of AOC) levels (Modin and Wilén, 2012; Peixoto et al., 2011) and have not been demonstrated to be applicable under marine condition. The aim of the present study is to explore whether a marine biosensor based on MFC can be developed and gives reproducible and rapid signals to low levels of AOC in seawater (~100 μmol/L (~1200 μg/L of AOC) of dissolved organic carbon or less than 5 mg/L BOD) such that the foundation of a biofouling sensing technology for seawater reverse osmosis (SWRO) plants is established.

2. Materials and methods

2.1. Marine-microbial fuel cell biosensor

2.1.1. Bacterial inoculum and growth medium

The biofilm for the biosensor in the anodic compartment originated from marine sediment at Coogee Beach, Coogee, South Fremantle, Western Australia. The sediment was mixed with real seawater (obtained from the same location) with a weight ratio of 1–5 followed by continuously stirring for 24 h. After settling for 2 h the supernatant with OD_{600} value of about 0.2 was collected and used as inoculum for the marine anodophilic biofilm. Seawater (salt concentration of approximately 35,000 ppm) obtained at the same location was used as anolyte. In RO plants, suspended solids that are present in the feed-water will be removed by ultra-filtration. Therefore, this study utilized real seawater with no suspended solids (OD_{600} < 0.01) to demonstrate the applicability of this method in industry.

For the first 36 days yeast extract solution was periodically added (ca. every 7–10 days) to the anolyte (50 mgL^{-1} final concentration) as bacterial growth supplement. In the cathodic compartment, the catholyte contained 100 mM potassium ferricyanide ($K_3Fe(CN)_6$, Sigma–Aldrich, Inc., purity ca. 99%) and 150 mM sodium chloride. The catholyte was renewed periodically to maintain a stable cathodic potential.

2.1.2. Microbial fuel cell sensor set up

A two-chamber MFC (made of transparent Perspex) was used in the present study. The compartments of the fuel cell (anode and cathode) having equal dimension of (14 cm × 12 cm × 1.88 cm) were physically separated by a cation selective membrane (CMI-6000, Membrane International INC.) with a size of 168 cm^2. Both chambers were filled with conductive graphite granules (EI Carb 1000, Graphites Sales, Inc., Chagrin Falls, OH, USA), about 2–6 mm in diameter. A variable resistor box was used to set a specific desired external resistance manually. To facilitate electrical connections, the graphite granules were attached to graphite rods