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In-line deoxygenation for organic carbon detections in seawater using a marine microbial fuel cell-biosensor

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HIGHLIGHTS

- An electrochemical cell was developed to reductively remove oxygen from seawater.
- A MFC-biosensor could monitor assimilable organic carbon (AOC) in anoxic seawater.
- The combination of the above enabled online AOC monitoring in aerobic seawater.
- The reductive oxygen removal was specific to oxygen and caused no interference.
- Online AOC monitoring was reproducible and seems feasible for desalination plants.

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ABSTRACT

Assimilable organic carbon (AOC) is a key predictor for membrane biofouling in seawater desalination reverse osmosis (SWRO). Microbial fuel cells have been considered as biosensors for the detection of biodegradable organics. However, the presence of dissolved oxygen (DO) is known to completely suppress the signal production (i.e., current) of a typical MFC. This study describes AOC detection in normal oxygenated seawater by coupling an electrochemical cell for DO removal with a MFC-biosensor for AOC detection. The electrochemical deoxygenation for oxygen removal caused no interference in the AOC detection. A linear relationship (R^2 = 0.991) between the AOC concentration and current production from the MFC biosensor was achieved. The coupling of an electrochemical cell with a MFC-biosensor can be effectively used as an online, rapid and inexpensive measure of AOC concentrations and hence as an indicator for biofouling potential of seawater.

1. Introduction

Seawater reverse osmosis (SWRO) has been a widely applied technology for producing fresh water. One of the main challenges for successful operation in SWRO is membrane biofouling (Matin et al., 2010). Membrane biofouling involves the growth of microorganisms into a biofilm on the membrane surface, which leads to significant increase in cost of operation in SWRO treatment. Membrane flux decline, increase in pressure drops in the RO modules, increase in salt passage.

Controlling and identifying biofouling is rather challenging as it depends on various factors. There are numerous indirect measurement techniques to assess the fouling potential of feed-water. Traditional fouling potential of a membrane is measured using silt density index (SDI) and modified fouling index (MFI). These methods predict particulate fouling but are not predictive for bio/organic-fouling caused by organic adsorption or biological growth on the membrane surface. Specifically, soluble assimilable organic carbon (AOC) present in seawater is highly influential to the development of membrane biofouling (Chien et al., 2007). AOC is one of the main food sources for bacteria to proliferate and hence it is more appropriate to be used as an indicator of the relative biofouling potential of feed-water (Jeong et al., 2013). Other attempts at AOC tests such as biochemical oxygen demand BOD_5 (Bourgeois et al., 2001; Clesceri et al., 2005), modified bioassay (Lechevallier et al., 1993), optical fiber (Lin et al., 2006), bioluminescence (Weinrich et al., 2011) and flow-cytometric enumeration (Hammes and Egli, 2005) can be time consuming, need an appropriate reference organisms, and are costly with a long turn-around time for results. Hence, a critical need exists for a quick and reliable measurement of AOC in seawater.

Recent work from our research group has demonstrated that microbial fuel cell (MFC) based biosensors can detect low concentration of AOC under marine conditions in the absence of oxygen

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(Quek et al., 2014a,b). MFC-biosensor has been proven to be a convenient organic biosensor showing major advantages over many other types of biosensors given the mechanical and electronic simplicity, not only for its construction but also when signal acquisition and electronic requirements of the system are taken into consideration. MFC-biosensors have been shown to be convenient organic biosensors showing major advantages over other types of biosensors given the mechanical and electronic simplicity. Also the online signal acquisition and electronic requirements of the system are simple and rapid. In previous studies, MFC-biosensors for organic detection were developed for detecting organic substrates in anoxic waters such as wastewater (Di Lorenzo et al., 2009), groundwater (Tront et al., 2008) and anaerobic digestion liquid (Kaur et al., 2013). The use of MFC-biosensors for the detection of low concentration of AOC in marine environments is of industrial interest as it can be used in prediction and possible control strategies of bio-fouling SWRO plants. The current study focuses on the development of a MFC-biosensor for detecting low concentration of AOC under real world SWRO plant conditions, which includes the presence of oxygen, a known inhibitor of MFC sensors.

A typical MFC-biosensor consists of an anodic chamber (anaerobic) and a cathodic chamber separated by a cation exchange membrane. The active anodophilic bacteria oxidise organic carbon in the anodic chamber and generate electrons and protons. Electrons are then passed to the cathodic chamber through an external circuit and thus current is generated. However, the presence of dissolved oxygen (DO) in the anodic chamber can completely suppress the metabolic activity of electrochemically active anodophilic bacteria and hence the current productions (Liu et al., 2005; Ringeisen et al., 2007). This is quite understandable as the typical anodophilic bacteria such as *Geobacter* sp are strict anaerobes (Bond and Lovley, 2003; Lin et al., 2004). In order to obtain an accurate AOC measurement by MFC, it is mandatory to completely remove DO. It is also important to develop a DO removal method that does not interfere with the highly sensitive measurements of low concentrations of AOC measurement. Numerous physical and chemical approaches for fresh water deoxygenation have been developed, such as (a) physical methods (i.e., inert gas purging), which have inherent deficiencies of being bulky, costly and inflexible in operation (Tan et al., 2004), and (b) chemical reducing agents (i.e., hydrazine) (Moon et al., 2000), which are highly toxic and likely to modify organic species present. Therefore, these methods are not suitable for AOC analysis. The electrochemical deoxygenating method has been described as a possible method for deoxygenation of fresh water (Pedrotti et al., 1994; Tamminen et al., 1996; Vuorilehto et al., 1995). The advantages of this method are high efficiency (>99.5% DO removal) and low interference with the sample.

The aim of the current study is to develop an online low AOC detection system for oxygen-saturated seawater by combining a suitably designed electrochemical oxygen removal cell with a MFC-biosensor.

2. Methods

2.1. Marine-microbial fuel cell biosensor setup

A two-chamber MFC-biosensor physically separated by a cation exchange membrane (CMI-7000, Membrane international Inc.) filled with conductive graphite granules (EI Carb 1000, Graphites Sales Inc, Chagrin Falls, OH, USA) with internal anolyte and catholyte volumes of 100 mL was set up as described in Quek et al. (2014b). A potentiostat was connected to the biosensor was used to control the anodic potential (AP). The DO, pH, AP and cell potential were monitor continuously using LabView™ 7.1 software interface with a National Instrument™ data acquisition card (DAQ). The pH was monitored during batch and continuous operation of the MFC-biosensor and no detectable pH change was recorded from individual tests. This suggests that a pH controlling device as needed for MFC designed for electricity production (Cheng et al., 2008), will not be necessary for the real world usage of the described sensor. Marine sediment from Coogee Beach, Coogee, South Fremantle, Western Australia was used as inoculum for the biosensor. Filtered seawater obtained at the same location was used as anolyte and catholyte. Details operation and monitoring of the MFC-biosensor set up were described in our previous paper (Quek et al., 2014b).

2.2. Microbial fuel cell sensor operation

2.2.1. Operation and evaluation

The anodic chamber (as described in Section 2.1) of the MFC-biosensor was inoculated with 50 mL of the inoculum, prepared according to the procedure described in Quek et al. (2014a) and 50 mL of seawater containing 0.5 g L^{-1} yeast extract (YE). YE was added every two days. The cathodic chamber was filled with 100 mL of seawater and was replaced every 4–6 weeks. The MFC was operated in a fed-batch mode with both catholyte and anolyte continuously re-circulating at a flow rate of 5 mL/min via the cathodic and anodic compartments, respectively. Where different operation modes were used, this is specified in the results section. The biosensor-MFC was maintained at +250 mV (vs Ag/AgCl) throughout this study.

Approximately 5 days after start up, the MFC-biosensor gave responses to YE addition. The old anolyte was drained out and the anodic compartment was re-filled with fresh seawater. During batch mode, the anolyte was replaced every 3–5 days. As indicated in previous research (Cheng et al., 2014; Quek et al., 2014a), a short period (several minutes) of oxygen exposure has no effect on the sensitivity and performance of the MFC-biosensor of the MFC-biosensor operated at positive AP of +250 mV (vs Ag/AgCl).

2.2.2. Organic (YE) detection and analyses procedure

Specific concentrations of YE, which represented mixed AOC and were utilized by the marine anodophilic bacteria, were fed into the anolyte. The total COD of YE measurement was conducted according to the American Public Health Association (2005). A standard curve was drawn for different YE concentrations between 0 mg/L and 600 mg/L which resulted in a linear correlation with R^2 of 0.994 and a conversion factor of 0.64 mg COD/L per mg YE/L (data not shown).

2.2.3. Control and monitoring

The rate of electron flow from anode to cathode in microbial fuel cells is proportional to the rate of organic oxidation by the anodophilic bacterial biofilm. The electrons obtained from the organic oxidation are transferred to the anode and generate a current that is recorded by the potentiostat. To quantify the total electrons flown (charges transferred to the anode) the electron flow was integrated over the detection period. The cumulative charges were obtained by integrating the electrons transferred by the biofilm as current throughout the detection period (Cheng et al., 2014; Quek et al., 2014b,a).

The steady state was defined as no changes in current (±0.005 mA) over a period of 10 min. Recovery time was defined as the time required for the anodic potential (AP) to return to the initial level after the depletion of AOC. The signal (current peak) obtained from organic addition was calculated by subtracting the steady state value (due to maintenance respiration of the anodophilic bacteria) from the current value after the addition of AOC.