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Flat microliter membrane-based microbial fuel cell as "on-line sticker sensor" for self-supported *in situ* monitoring of wastewater shocks

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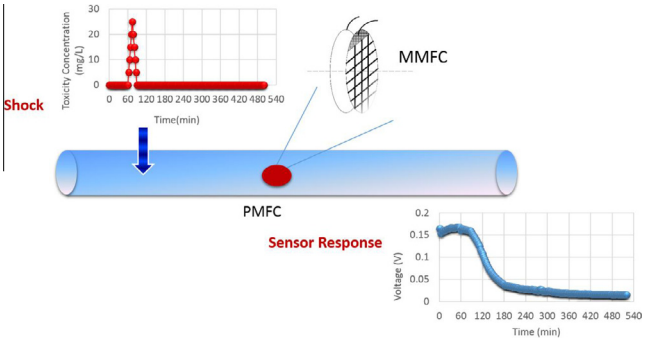
HIGHLIGHTS

- Flat microliter MMFC was developed as "on line sticker sensor".
- Hydrophilic and microporous membrane shortened the acclimation duration.
- MMFC sensors responded well to Cr^{6+} and Ni^{2+} shocks in wastewater.
- OCP of MMFC sensors well reflected shock types and concentrations.
- The voltage of the MMFC was clearly correlated with shock concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel flat membrane-based microbial fuel cell (MMFC) sensors were developed by compacting two filter membranes coated with carbon ink. High micro-porosity and hydrophilicity of membranes offered the distinct advantages of short acclimation period (couple hours), simple compact configuration with microliter size, and high sensitivity and stability. MMFC sensors were examined at two toxic shocks (chromium and nickel) in a batch-mode test chamber, and rapidly responded to shock types and concentrations. The variation of voltage output was correlated with open circuit potential (OCP). Filter membranes facilitated bacterial attachment and shortened acclimation. The MMFC sensors showed good reusability and recovered several days after toxic shocks. The robustness of MMFC sensors was validated through 1-month tests. The stability of sensor signals was examined with coefficient of variance (CV) statistical analysis. The flat microliter MMFC has a great potential as "on-line sticker sensor" for real time *in situ* monitoring of wastewater quality.

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1. Introduction

Wastewater treatment plants (WWTPs) have been designed and operated based on the average concentrations of contaminants. Short-term and long-term shocks (e.g. organic compounds and heavy metals) in wastewater disturb the stability of WWTPs. Real-time wastewater shock sensors are critical to provide effective precaution strategies and minimize shock impacts. Diverse biosensors (e.g. biological oxygen demand, ammonia, and heavy metal) have been developed to monitor the contaminants in wastewater. However, the biosensor performance is directly depended on the coated enzymes and microorganisms, which have inherent problems, such as short lifetime (Okochi et al., 2004;

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Curtis et al., 2009; Woznica et al., 2010), long respond time (Jiang, 2008), narrow specificity for chemicals (Curtis et al., 2009; Ikebukuro et al., 1996; Neufeld et al., 2006; Okochi et al., 2004), and the need for external power sources (Ikebukuro et al., 1996; König et al., 1998; Kumlanghan et al., 2008).

A novel bioelectrochemical device, microbial fuel cell (MFC), has been studied to convert wastewater to electricity by electrogenic bacteria (Liu et al., 2005; Oh and Logan, 2005; Pant et al., 2012; Li et al., 2014b). MFC possesses three unique features as wastewater sensors. First, wastewater shocks can cause immediate jump or drop of the voltage output of MFCs, which can be used as the real-time shock indicator. Second, with the electricity generated from wastewater to support its operation, MFCs are self-sustainable without external power supply. Third, MFCs utilize the microorganisms and organic substrates in wastewater without the need of coating external enzymes and bacteria, which simplifies its setup and prolongs the lifetime. MFC sensors have been developed for biological oxygen demand (BOD) (Chang et al., 2005), chemical oxygen demand (COD) (Wang et al., 2014), organic substances (Kumlanghan et al., 2007), and toxins (Liu et al., 2014) in wastewater. However, existing MFC sensors still utilize traditional MFC configurations (e.g. tubular bioreactor, single chamber, and cube shape) (Chang et al., 2005; Wang et al., 2014; Kumlanghan et al., 2007; Liu et al., 2014), which poses difficulties for real-time shock monitoring. These MFC sensors have the volume of 20–150 mL with inlets and outlets (Chang et al., 2005; Wang et al., 2014; Kumlanghan et al., 2007; Liu et al., 2014), which are the operational systems by themselves, and make it difficult for direct installation on wastewater facilities. In addition, the voltage output of MFC sensors is closely associated with open circuit potential (OCP) and inner resistance (R_{in}) (Logan et al., 2006), and keeping stable R_{in} is critical for reducing the possibility of fault signals of MFC sensors. But large volume (normally 20–150 mL) of wastewater contained the existing MFC sensors may cause unstable R_{in}, and increase the possibility of fault signals. Moreover, these MFC sensors need at least 1–2 weeks to acclimate electrogenic bacteria, meaning that they have to be inoculated long time before the occurrence of shocks, which is unrealistic for monitoring unexpected wastewater shocks.

A new type paper-based MFC, which packed carbon cloth and paper-based proton exchange membrane (PEM) together, could solve the problem of MFC sensors (Fraiwan et al., 2013a,b; Nguyen et al., 2014). The paper-MFC utilized both sides of carbon cloth as anode and cathode, which substantially reduced the MFC volume from milliliter (mL) to microliter (μL). However, this paper-MFC is still impractical for on line monitoring. Ferricyanide was used as the electron acceptor in cathode, which is not suitable for real-world application due to its toxicity and high cost. An additional hydrophilic paper reservoir (size: 4 cm × 3 cm) was used to shorten the acclimation time (Fraiwan et al., 2013a,b; Nguyen et al., 2014), which made the paper-MFC configuration complicated and difficult for direct installation in WWTPs. Most importantly, low mechanical strength of paper reservoir and water leakage of carbon cloth posed obstacles for *in situ* monitoring.

The objective of this study was to develop a simple compact membrane MFC (MMFC) sensor by stacking two flat filter membranes without the PEM and paper reservoir. The flat MMFC sensors possess four major breakthroughs over traditional MFC sensors (Chang et al., 2005; Kumlanghan et al., 2007; Wang et al., 2014; Liu et al., 2014) and paper-MFCs (Fraiwan et al., 2013a,b; Nguyen et al., 2014). MMFC sensors minimize the size to microliter (μL), which is expected to substantially reduce the variability of R_{in} and the possibility of fault signals. In addition, oxygen in the air is used as the electron acceptor in the MMFC sensors, which simplifies MMFC configuration. The unique flat structure of MMFCs makes the direct installation on wastewater facilities possible and serves as an "on line sticker sensor" for real time *in situ* wastewater quality monitoring. Moreover, microporous membranes could solve water leakage and enhance mechanical strength. High hydrophilicity of membranes is expected to facilitate bacterial adhesion and shorten acclimation time. Finally, the flat MMFC is studied as the shock sensor, while the paper-MFC was still targeted as power generation.

There were five tasks in this study. First, the flat MMFC sensors were installed as a sticker in a batch mode test chamber to examine its acclimation duration and voltage output. Second, the responses of the MMFC sensors to two toxic shocks (chromium and nickel) were determined at different concentrations. Third, OCP of the MMFC sensors was measured and correlated with the sensor performance. Fourth, the biofilm morphology and the contact angles of membranes were compared with carbon cloth (common anode materials for MFCs) to elucidate the advantage of MMFC sensors. Finally, the long-term robustness of flat MMFC sensors was examined through 1-month operation. The stability of sensor signals was validated using coefficient of variance statistical analysis.

2. Methods

2.1. Fabrication of flat MMFC sensor

The anode and cathode of the flat MMFC sensor were fabricated on filter membranes (Mixed Cellulose Ester Membranes, diameter: 4.7 cm, pore size: 0.22 μm, Millipore) (Fig. 1a). Specifically, multiple lines (thickness: <1 mm) of carbon ink (Microcircuit Material, DuPont) were painted on the filter membranes using a brush to effectively transfer electrons generated by electrogenic bacteria growing on membranes. The anode membrane was coated with plain carbon ink, while the cathode membrane was coated with plain carbon ink plus a top layer of platinum (Pt as the catalyst, loading: 0.5 mg/cm^2) (Nguyen et al., 2014). The resistance of stacked membranes was measured across the membrane (the longest distance) using a multimeter (Fig. 1a). Before the assembly, the anode membrane was soaked into a single chamber MFC (SCMFC volume: 300 mL) for 3 h to acclimate microorganisms on the membrane surface. The SCMFC had been operated for several weeks treating wastewater taken from the influent of the University of Connecticut WWTP (COD: 250–350 mg L^{-1} and BOD: 100–300 mg L^{-1}). The microorganisms acclimated on the anode were intrinsic in wastewater, so that MMFCs would not be a pollution source for wastewater. Next, the anode and cathode membranes were stacked together with the sides of coated carbon ink facing outside (Fig. 1b). Copper wires were bonded on the top bulk area of membranes for multimeter connection. To elucidate the importance of bacterial attachment for MMFC sensors, a control membrane was soaked into deionized water for 3 h and then assembled with a cathode membrane. The voltage of this blank control was compared with MMFC sensors.

2.2. Test chamber setup and shock tests

A test chamber made of plexiglass was used to simulate a wastewater facility (Fig. 1c). The MMFC sensor (volume: <200 μL, diameter: 5 cm) was inserted firmly into one side of the test chamber as an "on line sticker", with the cathode membrane facing to air (oxygen as the electron acceptor) and the anode membrane facing to wastewater in the container (substrates in wastewater as electron generator). The surface structure of the MMFC sensor was observed after 1-month operational period to examine the robustness and mechanical strength of membranes. Throughout the test period, the chamber was full of anoxic wastewater, with the redox potential (ORP) below −350 mV.