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# Microbial fuel cell sensors for water quality early warning systems: Fundamentals, signal resolution, optimization and future challenges



Yong Jiang<sup>a</sup>, Xufei Yang<sup>b</sup>, Peng Liang<sup>a,\*</sup>, Panpan Liu<sup>a</sup>, Xia Huang<sup>a</sup>

<sup>a</sup> State Key Joint Laboratory of Environment Simulation and Pollution Control School of Environment, Tsinghua University, Beijing 100084, PR China
<sup>b</sup> Department of Environmental Engineering, Montana Tech of the University of Montana, Butte, MT 59701, USA

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## ABSTRACT

An early warning system is important to guarantee human health and ecological safety. Microbial fuel cell (MFC) sensor can achieve a self-sustainable monitoring without additional transducer or power sources. It would not limited by the main bottleneck of other contemporary MFC technologies, i.e., the low current density output, and is believed one of the most promising applications in the niche market of MFC technologies. This review is limited to MFC sensors for water quality early warning systems only, with emphasis on biochemical oxygen demand (BOD) and toxicity sensors. A comprehensive summary and discussion on sensor fabrication, operation, data representation, and optimization are provided. The MFC sensor is particularly promising to serve as a self-powered sensing device for in-situ and on-line environmental monitoring, as proved both in laboratory and field test. In addition, the main hurdles and future perspectives are discussed, as well as potential future research, which includes the following: separately lowering the detection limit or improving the sensitivity as well as lowering the recovery time of biofilm after a certain shock; developing the kinetic and/ or empirical model in combining with the detection algorithm to distinguish the signal interference of complex aquatic environment, especially when the shock of BOD and toxicity occur simultaneously.

#### 1. Introduction

An early warning system used in the continuous monitoring of water quality plays a central role in the operation of modern drinking water and wastewater treatment plants, as it provides essential data to human operators and/or automated control systems to secure the proper operation of the plants and to protect human health and ecosystems from hazardous water pollutants. Conventional monitoring of water quality is typically done with physiochemical methods. Despite their extensive use and great success, the physicochemical methods have some significant limitations - most notably, the measured pollutant concentrations do not readily reflect the actual response of humans and other organisms to a given water quality. To address this issue, generic biosensors have been increasingly implemented as a supplementary tool for water quality assessment. These sensors work based on the physiological response of living indicator organisms, such as bivalves, protozoans, algae, fish, and luminescent microorganisms, to water pollutants and therefore they can evaluate the biological effects associated with a wide range of biological and chemical mixtures through a rapid and cost effective method [1]. Over the last decade, the microbial fuel cell (MFC) and its derivative technologies have gained growing interest, as they not only enable the recovery of energy [2], and value-added products from wastewater [3–7], but also provide a new research platform for geochemistry, electrochemistry, and other disciplines [8,9].

A search in the Web of Science database with the selection of "microbial fuel cell" and "sensor" as the Topic, and 2000–2017 (until Mar. 2017) as the Year Published, yielded 282 publications. They cover a broad range of research topics in relation to MFC sensors, such as enhancing sensor sensitivity, optimizing sensor structure, and monitoring a specific aquatic environment. Several broadly-scoped review papers are available, providing an overview of MFC sensors and their different applications, including the water monitoring, screening of electrogenic microorganisms, identification of corrosive biofilms, and detection of pathogens [10–13]. This review intends to provide an overview of current research of MFC sensor and to address the challenges and perspectives for this biotechnology. Being more specific, this review focuses on MFC sensors in water quality early warning systems only, especially those for biochemical oxygen demand (BOD) and toxicity monitoring. A comprehensive summary and discussion on

E-mail address: liangpeng@tsinghua.edu.cn (P. Liang).

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<sup>\*</sup> Corresponding author.

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Nomenclature		IR	inhibition ratio
		MDC	microbial desalination cell
AD	anaerobic digestion	MEA	membrane-electrode assembly
ANN	artificial neural networks	MEC	microbial electrolysis cell
BOD	biochemical oxygen demand	MFC	microbial fuel cell
BVM	Butler-Volmer-Monod	MLSS	mixed liquor suspended solids
CE	Coulombic efficiency	M3C	microbial three-electrode system
CEM	cation exchange membrane	OCV	open circuit voltage
COD	chemical oxygen demand	PMS	power management system
CP	constant anode potential	QC	quality control
CV	cyclic voltammetry	RO	reverse osmosis
CY	Coulombic yield	SDS	sodium dodecyl sulfate
DO	dissolved oxygen	UASB	upflow anaerobic sludge blanket
EET	extracellular electron transfer	VFAs	volatile organic acids
EMS	energy management system	VOCs	volatile organic compounds
EPS	extracellular polymeric substances	WHO	World Health Organization
ER	constant external resistance	$\Delta I$	current change
HRT	hydraulic retention time		

MFC sensor fabrication, operation, and optimization will be provided. Several pivotal performance indicators to describe water monitoring processes using MFC sensors were summarized and discussed for a better quality of data representation. The progress of MFC sensor related to the special monitoring requirements were highlighted and summarized. Next, the challenges and limitations of using MFC sensors in complex aquatic environments (which involves the interrelations of many parameters) will be presented, followed by a discussion of possible solutions to those challenges based on the existing knowledge of detection principles, signal processing, and mathematic models.

#### 2. Working principles of MFC sensors

The MFC sensor is an attractive new type of electrochemical microbial biosensor, as it has different working principles and advantages from other electrochemical microbial biosensors based on conductometric, amperometry, potentiometric, or voltammetric transducers [14]. It utilizes electroactive microorganisms as the probe – the presence or a change in the level of target analytes would affect the microorganisms' electron transfer processes, thus creating an electric signal. Different from many other MFC applications, the MFC sensor does not focus on high current density output, but instead focuses on a change in the cell's output under different environmental conditions. The MFC sensor is expected to be one of the most promising applications of MFC technologies [12].

MFC sensors have been used in various areas such as water monitoring, screening of electrogenic microorganisms, identification of corrosive biofilms, and detection of pathogens [15-17]. Among them, the most extensively explored application is monitoring of water quality, especially BOD and toxicity. The working principle of MFC sensors for water monitoring is depicted in Fig. 1. An anode biofilm serves as the sensing and transducing element. Electrogenic microorganisms inside the anode biofilm oxidize organic substrates in the water to be monitored, and then convey the released electrons to the anode via multiple pathways, a collection of which is termed extracellular electron transfer (EET) [8,18]. The processes occurring within the anode biofilm are complex and highly variable, involving numerous biochemical electrochemical reactions. But in general, they can be simplified into three steps: (1) substrate transport and microbial turnover, (2) formation of reduced mediators or redox component complexes, and (3) oxidation of reduced mediators or redox component complexes by the electrode [19-21]. For BOD monitoring, as organic substrates are consumed as the feedstock/fuel for electricity generation, the substrate concentration in water naturally affects the sensor's current output [22]. For toxicity monitoring, as a toxic

component in water can suppress the activity of electrogenic microorganisms, its presence leads to a decrease in the sensor's current output when exceeding a certain concentration [23].

Compared to conventional biosensors, the MFC sensor has several major advantages [24,25]: (i) the water samples monitored provide inoculants and organic substrates needed by anode microorganisms; (ii) as the sensing element, the anode biofilm in the MFC sensor is capable of innate reproduction and self-healing, which significantly improves the sensor's robustness and self-sustainability; (iii) the MFC sensor requires no additional transducer or power source, as it generates and outputs electric signals directly; and (iv) no extra nutrients, substrates, or microorganisms are needed during sensor operation, which simplifies the management and maintenance of the MFC sensor and reduces relevant cost. Commercial MFC sensors for water quality monitoring have been available since 2000. Examples include the HATOX-2000 biomonitoring system and the HABS-2000 online biochemical oxygen demand (BOD) analyzer (KORBI Co., Ltd., Seoul, Korea). Recently, MicrobeElectric announced their SMART (Subsurface Microbial Activity in Real Time) technology (http:// www.microbeelectric.com/) for monitoring the presence or spread of organic contaminants in subsurface environments.



Fig. 1. Working principles of MFC sensors: (A) a classical MFC sensor and a signal acquisition system, (B) the MFC sensor for BOD monitoring, (C) the MFC sensor for toxicity monitoring.

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