

Elsevier required licence: © <2019>.

This manuscript version is made available under the CC-BY-NC-ND 4.0 license

<http://creativecommons.org/licenses/by-nc-nd/4.0/>

The definitive publisher version is available online at

<https://www.sciencedirect.com/science/article/pii/S0048969719356074?via%3Dihub>

Microbial fuel cell-based biosensor for online monitoring wastewater quality: A critical review

Minh Hang Do¹, Huu Hao Ngo^{1,*}, Wenshan Guo¹, Soon Woong Chang², Dinh Duc Nguyen^{2,3}, Yiwen Liu¹, Sunita Varjani⁴, Mathava Kumar⁵

¹*Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NWS 2007, Australia*

²*Department of Environmental Energy Engineering, Kyonggi University, 442-760, Republic of Korea*

³*Institution of Research and Development, Duy Tan University, Da Nang, Vietnam*

⁴*Gujarat Pollution Control Board, Gandhinagar - 382010, Gujarat, India*

⁵*Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, Tamilnadu, India - 600 036*

* Corresponding author: E-mail address: H. H. Ngo; E-mail address: ngohuuhaol21@gmail.com

ABSTRACT

Recently, the application of the microbial fuel cell (MFC)-based biosensor for rapid and real-time monitoring wastewater quality is very innovative due to its simple compact design, disposability, and cost-effectiveness. This review represents recent advances in this emerging technology for the management of wastewater quality, where the emphasis is on biochemical oxygen demand, toxicity, and other environmental applications. In addition, the main challenges of this technology are discussed, followed by proposing possible solutions to those challenges based on the existing knowledge of detection principles and signal processing. Potential future research of MFC-based biosensor has been demonstrated in this review.

Keywords Microbial fuel cell-based, biosensor, biochemical oxygen demand, wastewater quality monitoring, challenges.

1. Introduction

Assessing the quality of wastewater is an integral part of the operation of wastewater treatment plants, as it provides essential data to evaluate the level of treatment required to guarantee human health and ecological safety (Liu et al., 2016). Currently, most chemical tests for wastewater quality monitoring are performed off-site and cause long-term delays for wastewater treatment plants (WWTPs). The on-line sensors have become critical for monitoring wastewater influent quality as they can provide online early warning systems for timely precautions and solutions. Recently, technology using microbial fuel cell (MFC)-based biosensors has proved to be innovative for the rapid and real-time monitoring of wastewater quality due to the simple compact design, disposability, and cheapness.

The development of biosensors in recent years has opened up a great perspective to the onsite, simplified and cost-effective monitoring of water quality. A biosensor is defined by

IUPAC as an analytical device that integrates a biologically derived recognition of molecules such as enzymes, antibodies, phages, aptamers, or single-stranded DNA with a suitable physicochemical transducer such as electrochemical, optical, thermometric, piezoelectric, and magnetic (Iqbal et al., 2000).

Microbial fuel cells (MFCs) are devices that use bacteria as catalysts to oxidize organic and inorganic matter and generate electrical current. (Hernández-Flores et al., 2015; Surya Ramadan and Purwono, 2017). Microbial fuel cells, in general, can be regarded as a form of a biosensor, where microorganisms in the anode chamber function as a biological recognition element, whereas proton exchange membranes and electrodes act as a transducer (Peixoto et al., 2011). The bacteria can sense the sudden present or a change in the level of target analytes and then give the response on its output electric current (Corbella et al., 2019; Do et al., 2018; Modin and Aulenta, 2017; Mustakeem, 2015; Sun et al., 2015; Wang et al., 2015).

The current generation is dependent on microbial respiration and proportional to the fuel concentration. Thus, MFCs have been utilized as biosensor to measure the parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), volatile fatty acids (VFAs) and toxins in wastewater (Hsieh et al., 2016; Jin et al., 2017; Wang et al., 2014; Xu et al., 2015). The unique advantage of MFC based biosensor is that it can be worked without additional signal transducer or external power source, which is commonly required in other types of biosensors (Chen et al., 2016; Stein et al., 2011; Sun et al., 2015).

The application of microbial fuel cell-based biosensors for wastewater quality management has been considerable in recent years (ElMekawy et al., 2018; Zhou et al., 2017). A search

utilizing keywords ‘microbial fuel cell’ and ‘biosensor’ in the Web of Science database retrieved 362 publications on this scenario for the period from 2010 to 2019. However, they only confirmed the existence of a wide range of research topics about MFC sensors, including optimizing sensor structure, improving sensor sensitivity, and monitoring for a specific aquatic environment. This review is, therefore, to provide: (i) recent advances made in MFC-based biosensor technology for the management of wastewater quality, which focuses on biochemical oxygen demand, toxicity, and other environmental applications; and (ii) the challenges of MFC-based biosensors and the proposed possible solutions to those challenges based on the existing knowledge of detection principles and signal processing.

2. General feature of Microbial fuel cell-based biosensor

Based on the configuration, microbial fuel cell-based biosensor can be classified into two types: single - chamber MFCs and double-chamber MFCs. Dual-chamber MFCs consist of anode and cathode chambers separated by a proton exchange membrane (PEM), while single-chamber MFCs are mainly composed of anodic chamber and air cathode (Hernández-Fernández et al., 2015). In the anode chamber, microbes oxidize added substrates generate electrons and protons in the process. Electrons are transferred to the anode (negative terminal) and then flew to the cathode (positive terminal) through an external resistor to produce the electric current (Corbella et al., 2019; Do et al., 2018). The H^+ and other cation (e.g. Na^+ , K^+) migrated to the cathode chamber and combined with electron acceptor (e.g. O_2) to form water (Zhou et al., 2017). Figure 1 (a,b,c) describes the architecture, basic principle and basic component of MFCs based biosensor.

Figure 1

The component and structure of the developed biofilm in the anode play an integral role in the operation of the MFC-based biosensor (Cheng et al., 2008). These biosensors rely on electroactive biofilms that are capable of transferring electrons extracted from the metabolic oxidation of organic substrates to an electrode (Yang et al., 2012). Hence, it is very crucial to identify the character, structure, and composition of the biofilm to get better performance of MFCs and get clearer of the electron transfer mechanism (Yang et al., 2012). The bacterial community at the anode is mainly affected by the type of substrates used and ultimately influences the current generation (Zhang et al., 2011b). Denaturing gradient gel electrophoresis (DGGE) has been utilized for microbial community structure in MFCs. However, Kan et al. (2011) concluded that DGGE is not very sensitive and impossible to detect communities with less than 1% representation, which results in the underestimation of strains. Zhi et al. (2014) also illustrated that pyrosequencing had been used as a next-generation technique for microbial communities in a double chamber MFCs. The result illustrated that rare compositions of the microbial communities can be found which may affect the performance in terms of bioelectricity production.

Currently, most MFC-based biosensor studies were set up at the lab-scale. It is necessary to enhance MFC performance by optimization of the operating conditions. Table 1 summarizes the best performance of critical environmental parameters of MFC, such as pH, organic loading rate, feeding, rate, temperature.

Table 1

In the light of biosensor for monitoring water quality, there are some critical parameters that affect the energy generation of MFCs. The main objective of MFCs-based biosensor is to focus on the correlation between the signal output (e.g., voltage, current) and changes in the

level of target analytes (e.g., BOD, COD, toxicity) (Abrevaya et al., 2015a). The high sensitivity detection of the desired compounds is therefore one of the important targets of the MFC-based biosensor. On this theme, the sensitivity of an MFC-based biosensor is known as the change of electrical signal per unit of the alteration in analyte content concentration. It is generally influenced by the surface area of the anode (Eq. 1) (Di Lorenzo et al., 2014).

$$Sensitivity = \frac{\Delta I}{\Delta c \times A} \quad (1) \quad (\text{Zhou et al., 2017})$$

ΔI (μA): change of the current output.

Δc ($mmol\ l^{-1}$): change of the analyte content.

A (cm^2): surface area of the anode area.

In addition, Stein et al. (2010) also demonstrated that the sensor should produce a stable and constant current output which is namely the baseline. A baseline current is needed to prevent false-positive alarms caused by other factors (e.g. anode potential, pH) than a toxic compound present in the water fed to anode of the MFC-based biosensor. The anodic potential and pH are the environmental parameter which has the most influence on overpotential toward measured current. Consequently, overpotential control plays an integral part in getting a stable baseline current (Stein et al., 2010).

MFC-based biosensor devices have overcome the limitation of the traditional whole-biosensor in which an external power source and costly equipment are indispensable (Peixoto et al., 2011). Thus, the MFC technology can lead to a cost-effective, simple, and completely meet the requirement for long-term and remote sensing. Xu et al. (2015) has utilized biosensor as a converter used by weak voltage for monitoring water quality in real-time. A

comparative table (Table 2) illustrated the significance of the achievements in the light of already published literature.

Table 2

3. Analytical applications of MFC biosensor

3.1. Microbial fuel cell-based biosensor for BOD monitoring

One of the most widely utilized and important parameters for the assessment of water quality is Biochemical Oxygen Demand (BOD). The conventional BOD test has certain benefits such as being a universal method of measuring most wastewater samples, and no expensive equipment is needed. However, this method requires time from 5-7 days and depend on trained persons, and consequently, it is not suitable for online process monitoring. Thus, it is necessary to develop an alternative method that capable overcome the weakness of the conventional BOD test. One promising alternative is to utilize an MFC for real-time and on-line BOD monitoring. Fast determination of BOD could be completed by the microbial fuel cell-based biosensor.

The most basic of biosensor device is based on a double-chamber MFC, in which the anaerobic anodic compartment plays a role as the detection part. MFC BOD sensor can be operated with or without membrane, e.g., proton exchange membrane (PEM) acting as the separator. In an MFC-based BOD sensor, the BOD concentration can be correlated with either charge or current. As the organic matter is utilized as the fuel for an MFC to create current, the change of organic matter's concentration in wastewater directly affects the output electricity. In particular, the steady-state current output usually correlates with the concentration of the organic matter, while the charge output correlates with the total amount of organic matter (Kim et al., 2003; Peixoto et al., 2011).

With the inoculation of different kinds of activated sludge, the enrichment time for anodic biofilm lasts from 3 to 8 weeks. After performing the mature anode biofilm, the wastewater (analyte input) is injected into the anode chamber and the MFC output fluctuation is controlled using simple devices and serves as the biosensor output. Basically, the BOD concentration is correlated with the maximum current output or total charge output. The BOD concentration can be monitored with rapid response times, varying from 5 min to 10 h and with high stability. Figure. 2 shows the basic mechanism of MFC based BOD biosensor.

Figure 2

The use of MFC as a BOD sensor was first reported in 1977 (Karube et al., 1977), where pure culture *Clostridium butyricum* plays a role of sensing element to transfer electron using hydrogen as the electron acceptor. The authors revealed that the measured current reached saturation at about 400 mg L⁻¹ BOD. The next utilization of MFCs as a BOD sensor was studied by Kim et al. (2003), using wastewater as a source of electrogenic bacteria. The biosensor gave a good correlation between the current measured with the BOD value.

The MFC's performance as a BOD sensor could be improved by reducing O₂ diffusion through a cation-specific membrane utilizing a cathode with enhanced catalytic activity and the membrane being smaller in size. This oligotrophic-type MFC was described as having good operational stability, efficient repeatability and reproducibility, but calibration curves were not presented. Currents of about 3 mA for 6 mg L⁻¹ BOD, relative to the baseline noise allow us to speculate on the detection limit being approximately 1 mg L⁻¹ BOD (Kang et al., 2003)

Di Lorenzo et al. (2009) developed a single chamber MFC with an air-cathode, and it was tested as a BOD biosensor using a carbon cloth anode to further increase the linear range to

350 mg BOD L⁻¹. They reported that an air-cathode MFC is superior to the two-chamber system as the former is a simpler system while having the potential for recycling and chemical regeneration of catholyte.

In a later study, Hsieh and Chung (2014) investigated a mediator-less MFC biosensor inoculated with a mixture of six bacteria strains to quickly determine BOD concentration. A good relationship between BOD concentration and voltage output, high reproducibility and long-term stability for the MFC biosensor was observed. This developed MFC biosensor had the ability to degrade complex organic compounds and surviving toxic conditions. The described MFC biosensor successfully measured BOD concentration below 240 mg L⁻¹ in real wastewater samples.

Recently, more researchers have been attended to improve MFC performance. A novel bio-electrochemical open-type biosensor for in situ monitoring of BOD during intermittent aeration was designed by Yamashita et al. (2016). This novel biosensor generated similar levels of current under both aerating and non-aerating environments and confirmed a logarithmic correlation ($R^2 > 0.9$) of current BOD concentration up to 250 mg/L. This biosensor will have various practical applications, such as automatic control of aeration intensity and the *in situ* monitoring of natural water environments. Kharkwal et al. (2017) investigated a novel MFC-based biosensor for continuous monitoring of BOD in real wastewater. To curtail the material costs, MnO₂ was tested as a cathode catalyst for oxygen reduction in a single chamber air-cathode MFC. In this study, a good linear relationship was detected between the voltage and BOD in both a sodium acetate solution and real domestic wastewater (DWW). The long-term stability of the BOD biosensor was estimated to be more than 1.5 years. Table 3 summarized the MFC based BOD sensor.

Table 3

Yang et al. (2013) showed that the reaction time is one of the most important parameters that reflect the accuracy and measuring the speed of BOD sensor. If it is too short, the biochemical reaction will be incomplete. Otherwise, longer reaction time is not available for the practical performance of MFC. This researcher shows that the response time of the single-chamber MFC-type BOD sensor was gained after 132 minutes with the BOD concentration 200 mg/L. Moreover, it was noted that the lower the BOD concentration, the shorter was the reaction time.

Reported start-up times for MFCs vary depending on the substrates examined and the reactor architecture, ranging from 10s of hours to several months (Feng et al., 2008; Liu et al., 2008). Wang et al. (2009) have investigated the application of fixed potentials to the anode. They decreased the start-up time by applying an anodic positive poised potential. Zhang et al. (2017) found that external resistances had a significant effect on the startup of MFC. Four double-chamber MFCs with serpentine flow fields in the anode and cathode were conducted in the experiment with the external resistance at 10 Ω , 50 Ω , 250 Ω , and 1000 Ω . The authors indicated that MFCs with higher external resistance would have a faster startup process. With increasing external resistance from 10 Ω to 1000 Ω , the lag period of MFCs decreased from approximately 3 to 0.6 days. After the lag phase, rapid increases were observed in the cell voltage of all MFCs operated at different external resistances. MFC-1000 reached a voltage peak of 0.74 V on day 2.5. The voltage peak for MFC-250, MFC-50, and MFC-10 was observed on days 3.2, 4.0 and 5.0, respectively. Therefore, it is feasible to startup MFC at a higher external resistance and then gradually switch to lower external resistance to obtain high current.

The effect of an external resistance applied to the MFC has recently received attention as the growth of electro-active bacteria can be controlled by changing the external resistance. In general, MFC performance increases by decreasing the applied external resistance. Liu et al. (2005) demonstrated that when a low external resistance applied, higher maximum power output was obtained. Aelterman et al. (2008) reported that a significant increase in the continuous current generation and consequently the power generation when the external resistance reduced from 50 Ω to 25 Ω and then to 10.5 Ω .

One of the most important and most investigated factors is the anode potential at which the MFC is operated because it controls the theoretical energy gain of microorganisms (Wagner et al., 2010). Maximizing the power output is one of the main challenges for scaling up this technology. Many factors, such as loading rate, flow rate, temperature and start-up time have a key role in achieving a higher power output (Jadhav and Ghangrekar, 2009).

To shorten the response time of the BOD biosensor, the dynamic behavior of MFC was analyzed and optimized. Moon et al. (2004) suggested that the fuel feeding rate of MFC should be maintained at 0.53 ml min⁻¹, leading to the shortest response time. The experiment results also showed that the response time could dramatically reduce from 36 min to 5 min while the anode volume of MFC decreased from 25 ml to 5 ml.

MFC-based BOD biosensors can potentially be applied to the rapid estimation of biodegradable organic matter in wastewaters. High reproducibility, good performance utilizing a variety of organic matter as fuel substances and short response time are the salient advantages for an MFC- based BOD biosensor. Similar to MFCs for the generation of power, diverse factors affect the stability and sensitivity of MFC-based BOD sensors, encompassing

DO concentration in the cathode chamber, external resistance, and effluent flow rate. Optimization of the various operating conditions can enhance the BOD sensors' performance. Jiang et al. (2018) illustrated that an MFC sensor's performance was also affected by the construction of the sensor and its efficiency in monitoring and controlling the flow regime of wastewater. Sensors should in fact be better constructed based on the given water monitoring requirements and signal resolution considerations.

Abrevaya et al. (2015b) indicated that the drawbacks of biosensors due to the limitation in the types of bacteria, organic substances present and the metabolic rates are lower than those in other typical biosensors. Therefore, future research should pay more attention in selecting better electrogenic microorganisms or microbial biofilm consortia that are capable of metabolizing different organic substances.

The leakage of oxygen from the cathode to the anode chamber is another challenge, which lowers coulombic efficiency (CE) and subsequently the sensor's electrical signal output. The main limitation of MFC based BOD sensor is the diffusion oxygen through the proton exchange membrane into the anodic chamber (Feng et al., 2013; Liu et al., 2011; Moon et al., 2005). Leakage oxygen into the anodic chamber may affect the growth of obligate anaerobes and results in a loss. New MFC membranes have been developed to overcome the problems caused by oxygen inhibition. Ayyaru and Dharmalingam (2014) investigated the single-chamber MFC that utilized sulfonated polyether ketone (SPEEK) membrane for BOD monitoring in wastewater. By utilizing this new membrane, the BOD sensing range can be 62.5% higher and lower oxygen permeability than that of Nafion membrane. The system was further improved by making a double membrane electrode assembly (MEA) with an

increased electrode surface area, which provides a high surface area for electrically active bacteria.

In a single-chamber MFC sensor without a membrane, the pH gradient across the membrane was eliminated (Modinand Wilén, 2012). However, I. et al. (2008) revealed that the pH gradient inside the anode biofilm is still an unresolved problem when the sensor was utilized for monitoring low buffer capacity wastewater. The lack of membrane in this configuration substantially aggravates the issue of oxygen leakage (from cathode to anode), stimulates the growth of heterotrophic organism on the anode, causing a reduction of the electric signal to MFC BOD sensor (Feng et al., 2013). This configuration can be further modified to meet the specific monitoring requirements. For example, a three-chamber bioelectrochemical sensor developed from microbial desalination cell (MDC) was constructed to monitor the VFAs in the AD process (Jin et al., 2016). Moreover, a submersible MFC was developed for in-situ, real-time measurement of BOD in anaerobic wastewater at multiple depths. This MFC sensor can be submerged in wastewater as a passive monitoring device so as no pumping of water samples is needed (Peixoto et al., 2011; Zhang and Angelidaki, 2011).

There may be absolutely confident that further research and developments are required to overcome the above problems. In order to improve BOD biosensors, it needs to develop new technologies, new biomaterials, and optimization of the biosensors system.

3.2. Microbial fuel cell-based biosensor for toxicity

Toxicity is one of the most important parameters for water quality inspection, as the toxic compounds cause harmful effects to the health of the human beings. Therefore, toxicity detection is an integral in wastewater treatment, drinking water processing and water

environmental monitoring (Dávila et al., 2011; Stein et al., 2012c). A recently developed sensor is the MFC-based biosensor, in which bacteria act as the sensor for toxic components in water (Kim et al., 2007b; Stein et al., 2010).

Toxic substances have an inhibitory effect on the metabolism of microorganisms particularly on the transfer rate of electrons to the electrode. Presence of toxic substances can therefore decrease the current compared to a situation without toxic compounds present. This means that the microbial fuel cell is utilized as an online biosensor for the presence of toxic compounds in water. Depending on the type of substrates being monitored, MFC-based toxicity biosensors can be divided into two categories: heavy metal biosensors and organic matter biosensors (Zhou et al., 2017)

The major advantage of MFC based biosensor is that it does not requires a transducer to read the signal and convert it to an electrical signal since the measures signal is already an electric current. Figure. 3 illustrates the mechanism of MFC-based biosensor for toxicity.

Figure 3

When a MFC runs under correct conditions, the voltage generated is correlated with the amount of a given substrate. Biosensors with single strains show several advantages over systems integrating bacterial consortia, such as selectivity and stability. One of the limitations of such sensors is that the detection range usually exceeds the actual pollution level. Thus, improving their sensitivity is the most important for widespread application.

An inhibition rate has been demonstrated to show the effect of a toxic substance fed into the MFC-based biosensor, which can be calculated using the follow Michaelis-Menten equation:

$$I(\%) = \frac{|CY_{nor} - CY_{tox}|}{CY} * 100 \quad (2)$$

CY_{nor} and CY_{tox} represent the Coulombic yield in normal wastewater and toxic sample, respectively (Kim et al., 2007b)

CY is the Coulombic yield in each peak and it is calculated by integrating the electrical output over time.

For toxicity biosensor, the time for incubation with the toxicity is an important parameter that determines the performance of the biosensor. The longer time for incubation, the more risky for microorganism and thus resulted in higher inhibition ration. Hence, optimization of the incubation time was optimal to the toxicity biosensor (Yang et al., 2018)

The electric signal output of MFC sensors is depended on water quality parameters, including temperature, pH, BOD, conductivity, electron acceptors (nitrate and sulfate), and the type and concentration of toxic agents (Peixoto et al., 2011; Zhang and Angelidaki, 2011). The application of MFC sensor based on the bio-cathode sensing element can help prevent signal interference, simply because biofilms hold a diverse redox potential, different of reactions, and a different electrons, as well as ions flow direction, compared with anode biofilm (Jafary et al., 2015; Si et al., 2015). Table 4 below shows a brief summary on MFC-based toxicity sensor.

Table 4

A novel biomonitoring system utilizing MFC for detecting the inflow of toxic substances into water systems has been developed by (Kim et al., 2007b). Researchers indicated that addition of various kinds of toxic substrates such as Diazinon (an organophosphate insecticide), Pb,

Hg, and polychlorinated biphenyls (PCBs) caused significant decrease in MFC current output. The inhibition ratio caused by inflow of these used toxic substances (1 mg L^{-1}) were 61%, 46%, 28%, and 38%, respectively when compared to the control. When real wastewater was inoculated, more significant current decreases and higher inhibition ratio were observed. When mixed heavy metals (1 mg L^{-1} and $1 \text{ mg}^{-1} \text{ Pb}$) were applied, the inhibition ratio was 76% (Kim et al., 2007b). Furthermore, the MFC-based biosensors were successfully applied for fast monitoring of acidic toxicity (Shen et al., 2012), formaldehyde acute toxicity (Dávila et al., 2011), surfactant toxicity (sodium dodecyl sulfate (Stein et al., 2012b)) and toxicity caused by heavy metals (such as nickel and copper) (Shen et al., 2013; Stein et al., 2012c). Stein et al. (2010) revealed that control of anodic overpotential is needed to detect toxic events and prevent false positive alarms. Anodic overpotential and thus current is influenced by anode potential, pH, substrate and bicarbonate concentration. To investigate the influence of anode potential on current, microorganism were cultivated in an MFC with a set anode potential -0.4 V vs Ag/AgCl. The anode potential was decreased from -0.4 V to -0.45 V , increased to -0.15 V and decreased to -0.45 V with steps of 0.025 V .

Dávila et al. (2011) showed a miniaturized MFC (working volume of $144 \text{ } \mu\text{m}$ per compartment) as formaldehyde biosensor. It consists on a proton exchange membrane placed between two micro fabricated silicon plates that act as current collectors. An array of square $80 \mu\text{m} \times 80 \mu\text{m}$ vertical channels, $300 \mu\text{m}$ deep, have been defined through the plates over an area of $6 \text{ mm} \times 6 \text{ mm}$. *Geobacteraceae sulfurreducens* was utilized to form the anodic biofilm to oxidize organic carbon in the effluent. The maximum power density of the micro-fabricated MFC can reach $6.5 \text{ } \mu\text{W cm}^{-2}$, which is significantly higher than the maximum power density of $4.4 \text{ } \mu\text{W cm}^{-2}$ in a macro-size fuel cell.

Recently, Yang et al. (2018) developed a dual signal bioelectrochemical system based biosensor utilizing the model of *Shewanella oneidensis* MR-1. It was found that beside the current output signal, this biosensor could considered the lag phase time (Δt) for cell adaptation is another indicator for the toxicity of 3,5-dichlorophenol (DCP). This is the first whole-cell-based toxicity biosensor with a dual-signal confirmation to give a more reliable detection results for toxicity detection and wastewater quality assessment.

Furthermore, how to specifically detect the target analyse would be another challenge encountered for a biosensor in. It is optimal to improve the sensitivity of a biosensor for toxicity in wastewater. Liu et al. (2014) showed that there might occur simultaneously sudden changes in BOD and toxicity when sudden changing in BOD concentration. In a MFC-based sensor, the current density decreases with respect to the toxicity of the toxic agents, while increase with an increase in BOD. The sudden changes of BOD concentration may therefore reduce the responses of MFC sensors for toxicity.

Utilizing MFC-based biosensor for detecting toxic compounds in wastewater has many advantages compared with other biosensors in terms of stability, simplicity, portable and cost effective detection device. Nevertheless, there are still shortcomings that limit their practical application, encompassing low sensitivity, high cost of proton exchange membrane and cathode catalyst. This issue needs to optimization in terms of control modes and flow configurations (Jiang et al., 2015). Hence, many question regarding the MFC as toxicity sensor are still left. More specific research is necessary regarding design, control, and operation and the effect of these issues on sensitivity, robustness and reproducibility of the sensor. Further work needs to be done to determine the sensitivity and response of the sensors to different toxic compounds.

3.3. Other applications of microbial fuel cell-based biosensor

a. MFC based biosensor for monitoring Volatile fatty acids (VFAs)

Currently, biogas is considered as a promising renewable alternative energy to replace fossil fuels. Nevertheless, the anaerobic digestion (AD) process is unstable which causes the limitation in this technology application. To solve this issue, volatile fatty acids (VFAs) are revealed as crucial indicators for monitoring biogas generation (Falk et al., 2015)

Traditional methods for VFA detection including High-performance liquid chromatography (HPLC), gas chromatography (GC), colorimetric testing and titration, are complex and consist of numerous stages (Raposo et al., 2013; Siedlecka et al., 2008). Thus, it is necessary to develop a portable VFA detection for AD process monitoring.

Kaur et al. (2013) indicated that the correlation between VFA concentration and current output can be evaluated using the MFC technology. They illustrated that it is possible to distinguish among different kinds of VFA utilizing voltammetry and coulombic efficiency. The results presented a good linear relationship between the charge and individual VFA species concentration from 5-40 mg L⁻¹.

Based on the principle of microbial desalination cells, Jin et al. (2016) developed an innovative three chamber-VFA biosensor. Two linear relationships were observed between current densities and VFA levels from 10-30 mM (0.04 to 8.50 mA/m², R²=0.97) and then from 30-200 mM (8.50 to 10.80 mA/m², R²=0.95). The simple and efficient biosensor showed promising potential for online, inexpensive, and reliable measurement of VFA levels during AD and other anaerobic processes (Jin et al., 2016).

Currently, MFC-based VFA biosensors is considered as one of the most suitable device for monitoring anaerobic digestion simply because of its high sensitivity and wide range of response. Nevertheless, there has some issues that should be solved in future works, encompassing the effects of fermentation metabolites and other variation of divergent inhibitors. Furthermore, the behaviors of electroactive biofilms in anodic chamber under different conditions are worth of further investigation. As a result, the onsite operation of MFC-based VFA biosensors needs to be further exploration, especially regarding their durability over long terms operation (Tuoyu et al., 2017).

b. Monitoring of microbial activities

Liu et al. (2011) illustrated that MFC-based sensors can also monitor microbial activities and the number of microorganism in situ by utilizing relationship between the current and the microorganisms. The basic methods used to determine microbial activities is through the measurement of microbial respiration. The other method utilized to monitoring microbial activities is through using other suitable parameters to replace the biomass concentration as an expression of the active microorganism concentration.

Tront et al. (2008) revealed the use of MFCs as groundwater monitoring sensors. The author designed and evaluated columns filled with glass beads (3.5mm), in which *Geobacter sulfurreducens* used an external electron acceptor to metabolize acetate. Current generation was mirrored by bulk phase acetate concentration, and a correlation ($R^2=0.92$) was developed between current values (0-0.3 mA) and acetate concentration (0-2.3 mM). The electrical signal produced by the presented MFC provided real-time data for electron donor availability and biological activity. These results have practical impact on the future development of a

biosensor for inexpensive real-time monitoring of in situ bioremediation processes. The unresolved problems is the design of a system that could be buried and also cope with the possibly large distance between reductive and oxidative conditions for in-well use during groundwater monitoring.

A wall-jet microbial fuel cell was developed for the monitoring of anaerobic digestion (Liu et al., 2011). MFC signal showed a good correlation with online measurements (pH, gas flow rate). These result suggested that the MFC signal can reflect the dynamic variation of the anaerobic digestion, and potentially be a valuable tool for monitoring and control of bioprocess.

Yifeng and Irini (2011) selected the concentration of adenosine-triphosphate (ATP), which could show the total number of living microorganism, investigated the relationship between ATP concentration and current density. The results presented that the current density had a linear relationship with the concentration of active microorganism from 0 to 6.52 nmol ATP/L.

c. Monitoring of corrosive biofilms

Microbiologically influenced corrosion (MIC) is a serious problem in many industries such as oil and gas industry as well as water utilities (Xu et al., 2013). AlAbbas et al. (2013) revealed that MIC accounts for 20% of all corrosion damage. MIC is mainly caused by microbial biofilms due to their metabolic activities or metabolites, especially by anaerobic microbes. Most anaerobic MIC attacks can be divided into two types, namely respiration and fermentation. Type I MIC includes microorganisms that perform anaerobic respiration. *Sulfate Reducing Bacteria (SRB)* respiration normally utilizes sulfate as the terminal electron acceptor. Organic carbons such as volatile fatty acids are often used as electron donors. Type

II MIC involves secrete corrosive metabolism such as organic acids. It is easy to detect this bio corrosion simply because it normally includes a low pH. Oil and gas pipelines are always anaerobic since oxygen is removed to prevented excessive corrosion of carbon steel. A solid-state anode provides electrons to feed the cathodic biofilm. If a corrosive biofilm, such as an SRB biofilm, attached to the cathode the electronegenic biofilm will transfer the biofilm to the cytoplasm of sessile cells to reduce sulfate (Xu and Gu, 2014).

4. Challenges and future perspective of microbial fuel cell-based biosensor for wastewater quality detection

Microbial fuel cell technology is considered as an innovative tool for wastewater quality assessment. MFC based biosensors illustrate significant applications in monitoring BOD, toxic substances, oxygen demand, VFA and anaerobic digester performances. The most advantage of MFC-based biosensors is that it does not need a transducer to read and convert the signal to an electric signal (Stein et al., 2012a). These unique characteristics facilitate the fabrication of disposable and portable biosensor devices, which perfectly meet the requirement for long-term and remote sensing.

Despite tremendous improvements made in the last two decades such as enhancing sensor sensitivity, optimizing sensor structure, and monitoring a specific aquatic environment, MFCs still several bottlenecks encountered in their practical application and scale-up. These main drawbacks are the limitation of electron transfer between microorganism and electrodes, membrane resistance in the proton transportation process, various overpotential unsatisfactory mixing and turbulence in each compartment. The distance between electrodes and the specific surface of the anode, cathode or separator are key factors on which the internal resistance of the system and the power density directly depend (Oliveira et al., 2013).

Researchers also demonstrated that MFC-based biosensors can be integrated with artificial neural networks (ANNs) to identify specific chemicals in water samples. On this theme, Di Lorenzo et al. (2014) indicated that MFC assembly and the testing system must be simple and direct, that enabling straightforward start-up and maintenance of the technology. Using a single chamber MFC has overcome difficulties in operating costs, especially when controlling a second feed solution and this has led to reduced capital costs in the design process (ElMekawy et al. al., 2013). Furthermore, single chamber MFCs are also easier to miniaturize (Yang et al., 2013). Although little research has been done on small-scale single chamber air-cathode MFCs as biosensors, the development and manufacture of micro-scale MFCs biosensors still needs to be improved for toxicant detection efficiency (Di Lorenzo et al., 2014; Liu et al., 2014).

The electrode material is a key aspect in the development of MFC's performance so as it is crucial to modify the anode and cathode material. Microbial fuel cells are normally made of plastic and carbonaceous materials utilized as electrodes. The costs involved in manufacturing can be reduced by miniaturization and by using 3D printing techniques (Di Lorenzo et al., 2009). Modification of the anode using different materials has been a successful approach for improving power production. Several methods have been developed that are based on adding mediators to the anode. For example, by immobilizing neutral red onto the surface of a woven graphite electrode, the maximum power density increased from 0.02 to 9.1 mW m⁻² in an MFC with a pure culture of *Shewanella putrefaciens*.

Ordinarily, microbial fuel cells are normally made of plastic and carbonaceous materials utilized as electrodes. The cost of manufacturing can be decreased by miniaturization and by using 3D printing techniques (Di Lorenzo et al., 2009). Otherwise, MFCs use an expensive

proton exchange membrane, normally made from Nafion or Ultrex, which are difficult to source in developing regions. Latex condom (Winfield et al. 2014), prefabricated latex gloves (Winfield et al., 2013) and cast ceramics (Behera et al., 2010) have been employed as an alternative material as membranes with very promising results. Cristiani et al. (2013); Santoro et al. (2013) have also investigated membrane-less MFC with anodic/cathodic biofilms, providing a higher power generation. However, future research should pay attention more to using these materials for sensing purposes.

To improve the performance of MFC, many studies recently have been focusing on the MFC system integration such as the combination of multi anode/cathode or multi cells of MFCs, integrated with other physical/chemical process, and extend MFCs with other biological processes. These combinations can obtain higher power density compare to a single anode/cathode. A multi anode/cathode was developed by (Jiang et al., 2010). They inserted multi graphite rods in a bed filled with activated carbon granules as an anode to pair with a single cathode. A new sediment MFC which has two cathodes was illustrated by (Chen et al., 2012). This work proved that the excreted oxygen from the rice rhizosphere could serve as a biocathode that is comparable in efficiency with an air cathode. The advantage of this biocathode is that it can be decreased in the distance between the cathode and anode, leads to changes in internal resistance. However, these integrations also more expensive to build and have difficulty in maintaining stable operations (Eom et al., 2011; Jiang et al., 2010).

It is necessary to improve the performance of MFCs before they can be scaled up as their practical implementation is still not feasible. Therefore, the global objective pursued by the researchers is the development and evaluation of low cost catalysts for improving electron

acceptor reduction (new cathodes), new biocompatible anodes and membrane, and novel configurations (Hernández-Fernández et al., 2015).

5. Conclusion

Microbial fuel cell based biosensors are considered as a portable and cost-effective detection device for in situ, online monitoring wastewater quality. Although MFC-based biosensor can measure various of analytical targets in real-time, it needs to be improved in their stability, sensitivity, repeatability and selectivity. In order for MFCs to be fully realized for wastewater quality monitoring, future researchers must focus on fabricating low cost and simple design by utilizing inexpensive electrode and membrane materials. By this way, the total cost of MFC biosensor will be reduced towards enhancing the economically competitive and productive scaled up commercial units. Additionally, more work is required on developing a self-sustaining and wireless MFC for remote areas with poor infrastructure.

Acknowledgement

This review research was supported by the Centre for Technology in Water and Wastewater (CTWW), University of Technology, Sydney (UTS, FEIT - RIA NGO) and in part by i) the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20183020141270) and ii) the Korean Ministry of Environment as a “Global Top Project” (Project No. 2016002200005).

Reference

- Aaron, D., Tsouris, C., Hamilton, C.Y., Borole, A.P. (2010). Assessment of the Effects of Flow Rate and Ionic Strength on the Performance of an Air-Cathode Microbial Fuel Cell Using Electrochemical Impedance Spectroscopy. *Energies*, **3**(4), 592-606.
- Abrevaya, X.C., Sacco, N.J., Bonetto, M.C., Hilding-Ohlsson, A., Cortón, E. (2015a). Analytical applications of microbial fuel cells. Part I: Biochemical oxygen demand. *Biosensors Bioelectron.*, **63**, 580-590.
- Abrevaya, X.C., Sacco, N.J., Bonetto, M.C., Hilding-Ohlsson, A., Cortón, E. (2015b). Analytical applications of microbial fuel cells. Part II: Toxicity, microbial activity and quantification, single analyte detection and other uses. *Biosensors Bioelectron.*, **63**, 591-601.
- Aelterman, P., Versichele, M., Marzorati, M., Boon, N., Verstraete, W. (2008). Loading rate and external resistance control the electricity generation of microbial fuel cells with different three-dimensional anodes. *Bioresour. Technol.*, **99**(18), 8895-8902.
- Ahn, Y., Logan, B.E. (2010). Effectiveness of domestic wastewater treatment using microbial fuel cells at ambient and mesophilic temperatures. *Bioresour. Technol.*, **101**(2), 469-475.
- AlAbbas, F.M., Williamson, C., Bhola, S.M., Spear, J.R., Olson, D.L., Mishra, B., Kakpovbia, A.E. (2013). Influence of sulfate reducing bacterial biofilm on corrosion behavior of low-alloy, high-strength steel (API-5L X80). *Int. Biodeterior. Biodegrad.*, **78**, 34-42.
- Ayyaru, S., Dharmalingam, S. (2014). Enhanced response of microbial fuel cell using sulfonated poly ether ether ketone membrane as a biochemical oxygen demand sensor. *Anal. Chim. Acta*, **818**, 15-22.

- Behera, M., Ghangrekar, M.M. (2009). Performance of microbial fuel cell in response to change in sludge loading rate at different anodic feed pH. *Bioresour. Technol.*, **100**(21), 5114-5121.
- Behera, M., Jana, P.S., Ghangrekar, M.M. (2010). Performance evaluation of low cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode. *Bioresour. Technol.*, **101**(4), 1183-1189.
- Behera, M., Murthy, S.S.R., Ghangrekar, M.M. (2011). Effect of operating temperature on performance of microbial fuel cell. *Water Science and Technology*, **64**(4), 917-922.
- Biffinger, J.C., Pietron, J., Bretschger, O., Nadeau, L.J., Johnson, G.R., Williams, C.C., Nealson, K.H., Ringeisen, B.R. (2008). The influence of acidity on microbial fuel cells containing *Shewanella oneidensis*. *Biosensors Bioelectron.*, **24**(4), 900-905.
- Chang, I.S., Jang, J.K., Gil, G.C., Kim, M., Kim, H.J., Cho, B.W., Kim, B.H. (2004). Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. *Biosensors Bioelectron.*, **19**(6), 607-613.
- Chen, Z., Huang, Y.-c., Liang, J.-h., Zhao, F., Zhu, Y.-g. (2012). A novel sediment microbial fuel cell with a biocathode in the rice rhizosphere. *Bioresour. Technol.*, **108**, 55-59.
- Chen, Z., Niu, Y., Zhao, S., Khan, A., Ling, Z., Chen, Y., Liu, P., Li, X. (2016). A novel biosensor for p-nitrophenol based on an aerobic anode microbial fuel cell. *Biosensors Bioelectron.*, **85**, 860-868.
- Cheng, K.Y., Ho, G., Cord-Ruwisch, R. (2008). Affinity of Microbial Fuel Cell Biofilm for the Anodic Potential. *Environ. Sci. Technol.*, **42**(10), 3828-3834.
- Corbella, C., Hartl, M., Fernandez-gatell, M., Puigagut, J. (2019). MFC-based biosensor for domestic wastewater COD assessment in constructed wetlands. *Sci. Total Environ.*, **660**, 218-226.

- Cristiani, P., Carvalho, M.L., Guerrini, E., Daghighi, M., Santoro, C., Li, B. (2013). Cathodic and anodic biofilms in Single Chamber Microbial Fuel Cells. *Bioelectrochemistry*, **92**, 6-13.
- Dávila, D., Esquivel, J.P., Sabaté, N., Mas, J. (2011). Silicon-based microfabricated microbial fuel cell toxicity sensor. *Biosensors Bioelectron.*, **26**(5), 2426-2430.
- Di Lorenzo, M., Curtis, T.P., Head, I.M., Scott, K. (2009). A single-chamber microbial fuel cell as a biosensor for wastewaters. *Water Res.*, **43**(13), 3145-3154.
- Di Lorenzo, M., Scott, K., Curtis, T.P., Head, I.M. (2010). Effect of increasing anode surface area on the performance of a single chamber microbial fuel cell. *Chem. Eng. J.*, **156**(1), 40-48.
- Di Lorenzo, M., Thomson, A.R., Schneider, K., Cameron, P.J., Ieropoulos, I. (2014). A small-scale air-cathode microbial fuel cell for on-line monitoring of water quality. *Biosensors Bioelectron.*, **62**, 182-188.
- Do, M.H., Ngo, H.H., Guo, W.S., Liu, Y., Chang, S.W., Nguyen, D.D., Nghiem, L.D., Ni, B.J. (2018). Challenges in the application of microbial fuel cells to wastewater treatment and energy production: A mini review. *Sci. Total Environ.*, **639**, 910-920.
- ElMekawy, A., Hegab, H.M., Pant, D., Saint, C.P. (2018). Bio-analytical applications of microbial fuel cell-based biosensors for onsite water quality monitoring. *J. Appl. Microbiol.*, **124**(1), 302-313.
- Eom, H., Chung, K., Kim, I., Han, J.-I. (2011). Development of a hybrid microbial fuel cell (MFC) and fuel cell (FC) system for improved cathodic efficiency and sustainability: The M2FC reactor. *Chemosphere*, **85**(4), 672-676.
- Erable, B., Etcheverry, L., Bergel, A. (2009). Increased power from a two-chamber microbial fuel cell with a low-pH air-cathode compartment. *Electrochemistry Communications*, **11**(3), 619-622.

- Falk, H.M., Reichling, P., Andersen, C., Benz, R. (2015). Online monitoring of concentration and dynamics of volatile fatty acids in anaerobic digestion processes with mid-infrared spectroscopy. *Bioprocess Biosystems Eng.*, **38**(2), 237-249.
- Fan, Y., Hu, H., Liu, H. (2007). Sustainable Power Generation in Microbial Fuel Cells Using Bicarbonate Buffer and Proton Transfer Mechanisms. *Environ. Sci. Technol.*, **41**(23), 8154-8158.
- Feng, Y., Barr, W., Harper, W.F. (2013). Neural network processing of microbial fuel cell signals for the identification of chemicals present in water. *J. Environ. Manage.*, **120**, 84-92.
- Feng, Y., Wang, X., Logan, B.E., Lee, H. (2008). Brewery wastewater treatment using air-cathode microbial fuel cells. *Appl. Microbiol. Biotechnol.*, **78**(5), 873-880.
- Fornero, J.J., Rosenbaum, M., Cotta, M.A., Angenent, L.T. (2010). Carbon Dioxide Addition to Microbial Fuel Cell Cathodes Maintains Sustainable Catholyte pH and Improves Anolyte pH, Alkalinity, and Conductivity. *Environ. Sci. Technol.*, **44**(7), 2728-2734.
- Herbert-Guillou, D., Tribollet, B., Festy, D. (2001). Influence of the hydrodynamics on the biofilm formation by mass transport analysis. *Bioelectrochemistry*, **53**(1), 119-125.
- Hernández-Fernández, F.J., Pérez de los Ríos, A., Salar-García, M.J., Ortiz-Martínez, V.M., Lozano-Blanco, L.J., Godínez, C., Tomás-Alonso, F., Quesada-Medina, J. (2015). Recent progress and perspectives in microbial fuel cells for bioenergy generation and wastewater treatment. *Fuel Processing Technology*, **138**, 284-297.
- Hernández-Flores, G., Poggi-Varaldo, H.M., Solorza-Feria, O., Ponce-Noyola, M.T., Romero-Castañón, T., Rinderknecht-Seijas, N., Galíndez-Mayer, J. (2015). Characteristics of a single chamber microbial fuel cell equipped with a low cost membrane. *International Journal of Hydrogen Energy*, **40**(48), 17380-17387.

- Hsieh, M.-C., Cheng, C.-Y., Liu, M.-H., Chung, Y.-C. (2016). Effects of Operating Parameters on Measurements of Biochemical Oxygen Demand Using a Mediatorless Microbial Fuel Cell Biosensor. *Sensors*, **16**(1), 35.
- Hsieh, M.-C., Chung, Y.-C. (2014). Measurement of biochemical oxygen demand from different wastewater samples using a mediator-less microbial fuel cell biosensor. *Environ. Technol.*, **35**(17), 2204-2211.
- I., T.C., Andrew, K.M., E., R.B. (2008). Proton transport inside the biofilm limits electrical current generation by anode-respiring bacteria. *Biotechnol. Bioeng.*, **100**(5), 872-881.
- Ieropoulos, I., Winfield, J., Greenman, J. (2010). Effects of flow-rate, inoculum and time on the internal resistance of microbial fuel cells. *Bioresour. Technol.*, **101**(10), 3520-3525.
- Iqbal, S.S., Mayo, M.W., Bruno, J.G., Bronk, B.V., Batt, C.A., Chambers, J.P. (2000). A review of molecular recognition technologies for detection of biological threat agents. *Biosensors Bioelectron.*, **15**(11), 549-578.
- Jadhav, G.S., Ghangrekar, M.M. (2009). Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration. *Bioresour. Technol.*, **100**(2), 717-723.
- Jafary, T., Daud, W.R.W., Ghasemi, M., Kim, B.H., Md Jahim, J., Ismail, M., Lim, S.S. (2015). Biocathode in microbial electrolysis cell; present status and future prospects. *Renewable and Sustainable Energy Reviews*, **47**, 23-33.
- Jiang, D., Li, X., Raymond, D., Mooradain, J., Li, B. (2010). Power recovery with multi-anode/cathode microbial fuel cells suitable for future large-scale applications. *International Journal of Hydrogen Energy*, **35**(16), 8683-8689.
- Jiang, Y., Liang, P., Zhang, C., Bian, Y., Yang, X., Huang, X., Girguis, P.R. (2015). Enhancing the response of microbial fuel cell based toxicity sensors to Cu(II) with the

- applying of flow-through electrodes and controlled anode potentials. *Bioresour. Technol.*, **190**, 367-372.
- Jiang, Y., Yang, X., Liang, P., Liu, P., Huang, X. (2018). Microbial fuel cell sensors for water quality early warning systems: Fundamentals, signal resolution, optimization and future challenges. *Renewable and Sustainable Energy Reviews*, **81**, 292-305.
- Jin, X., Angelidaki, I., Zhang, Y. (2016). Microbial Electrochemical Monitoring of Volatile Fatty Acids during Anaerobic Digestion. *Environ. Sci. Technol.*, **50**(8), 4422-4429.
- Jin, X., Li, X., Zhao, N., Angelidaki, I., Zhang, Y. (2017). Bio-electrolytic sensor for rapid monitoring of volatile fatty acids in anaerobic digestion process. *Water Res.*, **111**, 74-80.
- Juang, D.F., Yang, P.C., Kuo, T.H. (2012). Effects of flow rate and chemical oxygen demand removal characteristics on power generation performance of microbial fuel cells. *International Journal of Environmental Science and Technology*, **9**(2), 267-280.
- Jung, S., Mench, M.M., Regan, J.M. (2011). Impedance Characteristics and Polarization Behavior of a Microbial Fuel Cell in Response to Short-Term Changes in Medium pH. *Environ. Sci. Technol.*, **45**(20), 9069-9074.
- Kan, J., Hsu, L., Cheung, A.C.M., Pirbazari, M., Neilson, K.H. (2011). Current Production by Bacterial Communities in Microbial Fuel Cells Enriched from Wastewater Sludge with Different Electron Donors. *Environ. Sci. Technol.*, **45**(3), 1139-1146.
- Kang, K.H., Jang, J.K., Pham, T.H., Moon, H., Chang, I.S., Kim, B.H. (2003). A microbial fuel cell with improved cathode reaction as a low biochemical oxygen demand sensor. *Biotechnol. Lett.*, **25**(16), 1357-1361.
- Karube, I., Matsunaga, T., Mitsuda, S., Suzuki, S. (1977). Microbial electrode BOD sensors. *Biotechnol. Bioeng.*, **19**(10), 1535-1547.

- Kaur, A., Kim, J.R., Michie, I., Dinsdale, R.M., Guwy, A.J., Premier, G.C. (2013). Microbial fuel cell type biosensor for specific volatile fatty acids using acclimated bacterial communities. *Biosensors Bioelectron.*, **47**, 50-55.
- Kharkwal, S., Tan, Y.C., Lu, M., Ng, H.Y. (2017). Development and Long-Term Stability of a Novel Microbial Fuel Cell BOD Sensor with MnO(2) Catalyst. *International Journal of Molecular Sciences*, **18**(2), 276.
- Kim, B., Chang, S., Moon, H. 2006. *Microbial Fuel Cell-Type Biochemical Oxygen Demand Sensor*.
- Kim, B.H., Chang, I.S., Cheol Gil, G., Park, H.S., Kim, H.J. (2003). Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. *Biotechnol. Lett.*, **25**(7), 541-545.
- Kim, J.R., Cheng, S., Oh, S.-E., Logan, B.E. (2007a). Power Generation Using Different Cation, Anion, and Ultrafiltration Membranes in Microbial Fuel Cells. *Environ. Sci. Technol.*, **41**(3), 1004-1009.
- Kim, M., Sik Hyun, M., Gadd, G.M., Joo Kim, H. (2007b). A novel biomonitoring system using microbial fuel cells. *J. Environ. Monit.*, **9**(12), 1323-1328.
- Kim, T., Han, J.-I. (2013). Fast detection and quantification of *Escherichia coli* using the base principle of the microbial fuel cell. *J. Environ. Manage.*, **130**, 267-275.
- Liu, B., Lei, Y., Li, B. (2014). A batch-mode cube microbial fuel cell based “shock” biosensor for wastewater quality monitoring. *Biosensors Bioelectron.*, **62**(Supplement C), 308-314.
- Liu, H., Cheng, S., Huang, L., Logan, B.E. (2008). Scale-up of membrane-free single-chamber microbial fuel cells. *Journal of Power Sources*, **179**(1), 274-279.
- Liu, H., Cheng, S., Logan, B.E. (2005). Production of Electricity from Acetate or Butyrate Using a Single-Chamber Microbial Fuel Cell. *Environ. Sci. Technol.*, **39**(2), 658-662.

- Liu, L., Tsyganova, O., Lee, D.-J., Su, A., Chang, J.-S., Wang, A., Ren, N. (2012). Anodic biofilm in single-chamber microbial fuel cells cultivated under different temperatures. *International Journal of Hydrogen Energy*, **37**(20), 15792-15800.
- Liu, S., Li, R., Smith, K., Che, H. (2016). Why conventional detection methods fail in identifying the existence of contamination events. *Water Res.*, **93**, 222-229.
- Liu, Z., Liu, J., Zhang, S., Xing, X.-H., Su, Z. (2011). Microbial fuel cell based biosensor for in situ monitoring of anaerobic digestion process. *Bioresour. Technol.*, **102**(22), 10221-10229.
- Martin, E., Savadogo, O., Guiot, S.R., Tartakovsky, B. (2010). The influence of operational conditions on the performance of a microbial fuel cell seeded with mesophilic anaerobic sludge. *Biochem. Eng. J.*, **51**(3), 132-139.
- Min, B., Román, Ó.B., Angelidaki, I. (2008). Importance of temperature and anodic medium composition on microbial fuel cell (MFC) performance. *Biotechnol. Lett.*, **30**(7), 1213-1218.
- Modin, O., Aulenta, F. (2017). Three promising applications of microbial electrochemistry for the water sector. *Environmental Science: Water Research & Technology*, **3**(3), 391-402.
- Modin, O., Wilén, B.-M. (2012). A novel bioelectrochemical BOD sensor operating with voltage input. *Water Res.*, **46**(18), 6113-6120.
- Moon, H., Chang, I.S., Jang, J.K., Kim, K.S., Lee, J., Lovitt, R.B., Kim, B. 2005. *On-line monitoring of low biochemical oxygen demand through continuous operation of a mediator-less microbial fuel cell.*
- Moon, H., Chang, I.S., Kang, K.H., Jang, J.K., Kim, B.H. (2004). Improving the dynamic response of a mediator-less microbial fuel cell as a biochemical oxygen demand (BOD) sensor. *Biotechnol. Lett.*, **26**(22), 1717-1721.

- Mustakeem, M. (2015). Electrode materials for microbial fuel cells: nanomaterial approach. *Materials for Renewable and Sustainable Energy*.
- Nimje, V.R., Chen, C.-Y., Chen, C.-C., Tsai, J.-Y., Chen, H.-R., Huang, Y.M., Jean, J.-S., Chang, Y.-F., Shih, R.-C. (2011). Microbial fuel cell of *Enterobacter cloacae*: Effect of anodic pH microenvironment on current, power density, internal resistance and electrochemical losses. *International Journal of Hydrogen Energy*, **36**(17), 11093-11101.
- Oliveira, V.B., Simões, M., Melo, L.F., Pinto, A.M.F.R. (2013). Overview on the developments of microbial fuel cells. *Biochem. Eng. J.*, **73**, 53-64.
- Patil, S.A., Harnisch, F., Kapadnis, B., Schröder, U. (2010). Electroactive mixed culture biofilms in microbial bioelectrochemical systems: The role of temperature for biofilm formation and performance. *Biosensors Bioelectron.*, **26**(2), 803-808.
- Patil, S.A., Harnisch, F., Koch, C., Hübschmann, T., Fetzer, I., Carmona-Martínez, A.A., Müller, S., Schröder, U. (2011). Electroactive mixed culture derived biofilms in microbial bioelectrochemical systems: The role of pH on biofilm formation, performance and composition. *Bioresour. Technol.*, **102**(20), 9683-9690.
- Peixoto, L., Min, B., Martins, G., Brito, A.G., Kroff, P., Parpot, P., Angelidaki, I., Nogueira, R. (2011). In situ microbial fuel cell-based biosensor for organic carbon. *Bioelectrochemistry*, **81**(2), 99-103.
- Quek, S.B., Cheng, L., Cord-Ruwisch, R. (2015). Microbial fuel cell biosensor for rapid assessment of assimilable organic carbon under marine conditions. *Water Res.*, **77**, 64-71.
- Raghavulu, S.V., Mohan, S.V., Goud, R.K., Sarma, P.N. (2009). Effect of anodic pH microenvironment on microbial fuel cell (MFC) performance in concurrence with aerated and ferricyanide catholytes. *Electrochemistry Communications*, **11**(2), 371-375.

- Raposo, F., Borja, R., Cacho, J.A., Mumme, J., Orupöld, K., Esteves, S., Noguerol-Arias, J., Picard, S., Nielfa, A., Scherer, P., Wierinck, I., Aymerich, E., Cavinato, C., Rodriguez, D.C., García-Mancha, N., Lens, P.N.T., Fernández-Cegri, V. (2013). First international comparative study of volatile fatty acids in aqueous samples by chromatographic techniques: Evaluating sources of error. *TrAC Trends in Analytical Chemistry*, **51**, 127-143.
- Rochex, A., Godon, J.-J., Bernet, N., Escudié, R. (2008). Role of shear stress on composition, diversity and dynamics of biofilm bacterial communities. *Water Res.*, **42**(20), 4915-4922.
- Santoro, C., Ieropoulos, I., Greenman, J., Cristiani, P., Vadas, T., Mackay, A., Li, B. (2013). Current generation in membraneless single chamber microbial fuel cells (MFCs) treating urine. *Journal of Power Sources*, **238**, 190-196.
- Shen, Y., Wang, M., Chang, I.S., Ng, H.Y. (2013). Effect of shear rate on the response of microbial fuel cell toxicity sensor to Cu(II). *Bioresour. Technol.*, **136**, 707-710.
- Shen, Y.J., Lefebvre, O., Tan, Z., Ng, H.Y. (2012). Microbial fuel-cell-based toxicity sensor for fast monitoring of acidic toxicity. *Water Sci. Technol.*, **65**(7), 1223-8.
- Si, R.-W., Zhai, D.-D., Liao, Z.-H., Gao, L., Yong, Y.-C. (2015). A whole-cell electrochemical biosensing system based on bacterial inward electron flow for fumarate quantification. *Biosensors Bioelectron.*, **68**, 34-40.
- Siedlecka, E.M., Kumirska, J., Ossowski, T., Glamowski, P., Gołębiowski, M., Gajdus, J., Kaczyński, Z., Stepnowski, P. (2008). Determination of Volatile Fatty Acids in Environmental Aqueous Samples. *Polish Journal of Environmental Studies*, **17**(3), 351-356.

- Stein, N.E., Hamelers, H.M.V., van Straten, G., Keesman, K.J. (2012a). On-line detection of toxic components using a microbial fuel cell-based biosensor. *Journal of Process Control*, **22**(9), 1755-1761.
- Stein, N.E., Hamelers, H.V.M., Buisman, C.N.J. (2012b). The effect of different control mechanisms on the sensitivity and recovery time of a microbial fuel cell based biosensor. *Sensors Actuators B: Chem.*, **171-172**, 816-821.
- Stein, N.E., Hamelers, H.V.M., Buisman, C.N.J. (2012c). Influence of membrane type, current and potential on the response to chemical toxicants of a microbial fuel cell based biosensor. *Sensors Actuators B: Chem.*, **163**(1), 1-7.
- Stein, N.E., Hamelers, H.V.M., Buisman, C.N.J. (2010). Stabilizing the baseline current of a microbial fuel cell-based biosensor through overpotential control under non-toxic conditions. *Bioelectrochemistry*, **78**(1), 87-91.
- Stein, N.E., Keesman, K.J., Hamelers, H.V.M., van Straten, G. (2011). Kinetic models for detection of toxicity in a microbial fuel cell based biosensor. *Biosensors Bioelectron.*, **26**(7), 3115-3120.
- Sun, J., Peter Kingori, G., Si, R.W., Zhai, D.D., Liao, Z.H., Sun, D.Z., Zheng, T., Yong, Y.-C. 2015. *Microbial fuel cell-based biosensors for environmental monitoring: A review*.
- Torres, C.I., Lee, H.-S., Rittmann, B.E. (2008). Carbonate Species as OH⁻ Carriers for Decreasing the pH Gradient between Cathode and Anode in Biological Fuel Cells. *Environ. Sci. Technol.*, **42**(23), 8773-8777.
- Tront, J.M., Fortner, J.D., Plötze, M., Hughes, J.B., Puzrin, A.M. (2008). Microbial fuel cell biosensor for in situ assessment of microbial activity. *Biosensors Bioelectron.*, **24**(4), 586-590.

- Tuoyu, Z., Huawen, H., Pu, L., Jian, X., Fake, T., Xiangkai, L. (2017). Microbial Fuels Cell-Based Biosensor for Toxicity Detection: A Review. *Sensors (14248220)*, **17**(10), 1-21.
- Vishwanathan, A.S., Rao, G., Siva Sankara Sai, S. (2013). A novel minimally invasive method for monitoring oxygen in microbial fuel cells. *Biotechnol. Lett.*, **35**(4), 553-558.
- Wagner, R.C., Call, D.F., Logan, B.E. (2010). Optimal Set Anode Potentials Vary in Bioelectrochemical Systems. *Environ. Sci. Technol.*, **44**(16), 6036-6041.
- Wang, H., Park, J.-D., Ren, Z.J. (2015). Practical Energy Harvesting for Microbial Fuel Cells: A Review. *Environ. Sci. Technol.*, **49**(6), 3267-3277.
- Wang, J., Zheng, Y., Jia, H., Zhang, H. (2014). Bioelectricity generation in an integrated system combining microbial fuel cell and tubular membrane reactor: Effects of operation parameters performing a microbial fuel cell-based biosensor for tubular membrane bioreactor. *Bioresour. Technol.*, **170**, 483-490.
- Wang, X., Feng, Y., Ren, N., Wang, H., Lee, H., Li, N., Zhao, Q. (2009). Accelerated start-up of two-chambered microbial fuel cells: Effect of anodic positive poised potential. *Electrochimica Acta*, **54**(3), 1109-1114.
- Wang, X., Gao, N., Zhou, Q. (2013). Concentration responses of toxicity sensor with *Shewanella oneidensis* MR-1 growing in bioelectrochemical systems. *Biosensors Bioelectron.*, **43**, 264-267.
- Winfield, J., Chambers, L.D., Stinchcombe, A., Rossiter, J., Ieropoulos, I. (2014). The power of glove: Soft microbial fuel cell for low-power electronics. *Journal of Power Sources*, **249**, 327-332.
- Winfield, J., Ieropoulos, I., Greenman, J., Dennis, J. (2011). The overshoot phenomenon as a function of internal resistance in microbial fuel cells. *Bioelectrochemistry*, **81**(1), 22-27.

- Winfield, J., Ieropoulos, I., Rossiter, J., Greenman, J., Patton, D. (2013). Biodegradation and proton exchange using natural rubber in microbial fuel cells. *Biodegradation*, **24**(6), 733-9.
- Xie, H., Wang, Q., Chai, Y., Yuan, Y., Yuan, R. (2016). Enzyme-assisted cycling amplification and DNA-templated in-situ deposition of silver nanoparticles for the sensitive electrochemical detection of Hg²⁺. *Biosensors Bioelectron.*, **86**, 630-635.
- Xu, D., Gu, T. (2014). Carbon source starvation triggered more aggressive corrosion against carbon steel by the *Desulfovibrio vulgaris* biofilm. *Int. Biodeterior. Biodegrad.*, **91**, 74-81.
- Xu, D., Li, Y., Song, F., Gu, T. (2013). Laboratory investigation of microbiologically influenced corrosion of C1018 carbon steel by nitrate reducing bacterium *Bacillus licheniformis*. *Corros. Sci.*, **77**, 385-390.
- Xu, Z., Liu, B., Dong, Q., Lei, Y., Li, Y., Ren, J., McCutcheon, J., Li, B. (2015). Flat microliter membrane-based microbial fuel cell as “on-line sticker sensor” for self-supported in situ monitoring of wastewater shocks. *Bioresour. Technol.*, **197**, 244-251.
- Yamashita, T., Ookawa, N., Ishida, M., Kanamori, H., Sasaki, H., Katayose, Y., Yokoyama, H. (2016). A novel open-type biosensor for the in-situ monitoring of biochemical oxygen demand in an aerobic environment. *Scientific Reports* (Nature Publisher Group), **6**, 38552.
- Yang, G.X., Sun, Y.M., Kong, X.Y., Zhen, F., Li, Y., Li, L.H., Lei, T.Z., Yuan, Z.H., Chen, G.Y. (2013). Factors affecting the performance of a single-chamber microbial fuel cell-type biological oxygen demand sensor. *Water Sci. Technol.*, **68**(9), 1914-9.
- Yang, S., Du, F., Liu, H. (2012). Characterization of mixed-culture biofilms established in microbial fuel cells. *Biomass Bioenergy*, **46**, 531-537.

- Yifeng, Z., Irini, A. (2011). Submersible microbial fuel cell sensor for monitoring microbial activity and BOD in groundwater: Focusing on impact of anodic biofilm on sensor applicability. *Biotechnol. Bioeng.*, **108**(10), 2339-2347.
- Yuan, Y., Zhao, B., Zhou, S., Zhong, S., Zhuang, L. (2011). Electrocatalytic activity of anodic biofilm responses to pH changes in microbial fuel cells. *Bioresour. Technol.*, **102**(13), 6887-6891.
- Zhang, L., Li, C., Ding, L., Xu, K., Ren, H. (2011a). Influences of initial pH on performance and anodic microbes of fed-batch microbial fuel cells. *Journal of Chemical Technology & Biotechnology*, **86**(9), 1226-1232.
- Zhang, L., Li, J., Zhu, X., Ye, D., Fu, Q., Liao, Q. (2017). Startup Performance and Anodic Biofilm Distribution in Continuous-Flow Microbial Fuel Cells with Serpentine Flow Fields: Effects of External Resistance. *Industrial & Engineering Chemistry Research*, **56**(14), 3767-3774.
- Zhang, Y., Angelidaki, I. (2012). Self-stacked submersible microbial fuel cell (SSMFC) for improved remote power generation from lake sediments. *Biosensors Bioelectron.*, **35**(1), 265-270.
- Zhang, Y., Angelidaki, I. (2011). Submersible microbial fuel cell sensor for monitoring microbial activity and BOD in groundwater: Focusing on impact of anodic biofilm on sensor applicability. *Biotechnol. Bioeng.*, **108**(10), 2339-2347.
- Zhang, Y., Min, B., Huang, L., Angelidaki, I. (2011b). Electricity generation and microbial community response to substrate changes in microbial fuel cell. *Bioresour. Technol.*, **102**(2), 1166-1173.
- Zhi, W., Ge, Z., He, Z., Zhang, H. (2014). Methods for understanding microbial community structures and functions in microbial fuel cells: A review. *Bioresour. Technol.*, **171**, 461-468.

Zhou, T., Han, H., Liu, P., Xiong, J., Tian, F., Li, X. (2017). Microbial Fuels Cell-Based Biosensor for Toxicity Detection: A Review. *Sensors (Basel, Switzerland)*, **17**(10), 2230.

Zhuang, L., Zhou, S., Li, Y., Yuan, Y. (2010). Enhanced performance of air-cathode two-chamber microbial fuel cells with high-pH anode and low-pH cathode. *Bioresour. Technol.*, **101**(10), 3514-3519.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Figure 1: (a) The mechanism for a basic Microbial Fuel Cell system; (b) Components of a biosensor; (c) Basic principles of MFC as a biosensor

Figure 2. Basic principles of MFC as a BOD biosensor

Figure 3. Mechanism of MFC-based toxicity monitoring

Table 1: The effect of environmental condition on the performance of MFC-based biosensor

Parameter	Best performance			Reference
pH	Anode	pH between 6-9		(Behera and Ghangrekar, 2009; Jung et al., 2011; Nimje et al., 2011; Patil et al., 2011; Yuan et al., 2011; Zhang et al., 2011a)
	Cathode	Low pH values		(Biffinger et al., 2008; Erable et al., 2009; Jadhav and Ghangrekar, 2009; Raghavulu et al., 2009; Winfield et al., 2011; Zhuang et al., 2010)
	pH control (buffers)	Most popular utilized	Phosphate	(Kim et al., 2007a; Min et al., 2008)
		Low cost	Bicarbonate	(Fan et al., 2007)
			Carbon dioxide	(Fornero et al., 2010; Torres et al., 2008)
Organic loading rate	Higher OLR			(Aelterman et al., 2008; Jadhav and Ghangrekar, 2009; Martin et al., 2010)
Feed rate	Higher feed rate			(Aaron et al., 2010; Aelterman et al., 2008; Di Lorenzo et al., 2010; Ieropoulos et al., 2010; Juang et al., 2012)
Temperature	30-45° C			(Ahn and Logan, 2010; Behera et al., 2011; Jadhav and Ghangrekar, 2009; Liu et al., 2012; Martin et al., 2010; Min et al., 2008; Patil et al., 2010)
Shear stress	Higher shear rate			(Herbert-Guillou et al., 2001; Rochex et al., 2008)

Table 2. Overview of MFC-based biosensor

Parameter measured	Type of MFC	Type of wastewater	Power, voltage or current	Measuring range	Reference
BOD	Mediator-less MFC	Artificial wastewater	3.7-5.2 mA	20-200 mg L ⁻¹	(Chang et al., 2004)

BOD	Single chamber MFC	Artificial wastewater	0.063-0.55 mA		(Di Lorenzo et al., 2009)
BOD	Submersible Microbial Fuel Cell (SMFC)	Domestic wastewater	72mW m ⁻²	17-183 mg O ₂ L ⁻¹	(Peixoto et al., 2011)
BOD	Mediator-less MFC	Artificial wastewater	0.7-1.9 mA	50-100 mg L ⁻¹	(Moon et al., 2004)
Quantification of E.coli	One chamber MFC		0.1-0.38 mA	-	(Kim and Han, 2013)
Microbial activity			0.6-12.4 A m ⁻²	0-13 nmol L ⁻¹	(Zhang and Angelidaki, 2011)
			0-0.3 mA		(Tront et al., 2008)
Dissolved oxygen	Submersible MFC	Domestic wastewater	5.6-462 mA m ⁻²	0-8.8 mg L ⁻¹	(Zhang and Angelidaki, 2012)
	Two chamber MFC		9.5-17 mW m ⁻³		(Vishwanathan et al., 2013)
Volatile fatty acid	H-type MFC		0.22-1.29 mA	0-40 mg L ⁻¹	(Kaur et al., 2013)
Anaerobic digestion process	wall-jet type MFC	Artificial wastewater	0.01-0.095 mA	-	(Liu et al., 2011)
Assimilable organic carbon	Two chamber MFC	Sea water	0-40 mA	0-75 mg L ⁻¹	(Quek et al., 2015)

Table 3. Microbial fuel cells used for the determination of BOD

Microbial source	Anode/Cathode	Mediator added	Membrane	Detection range (BOD ₅ , mg L ⁻¹)	Saturation signal	Measurement time (min)	Reference
<i>Clostridium</i>	Pt/Carbon	No	Anion	10-300 ^a	0.12 mA	70	(Karube et al.,

<i>butyricum</i>			exchange membrane				1977)
MFCs effluent	Graphite felt/ Graphite felt	No	Cation exchange membrane	2.58-206.4	1.1 mA	300-600	(Kim et al., 2003)
Consortium (activated sludge)	Graphite felt/ Graphite felt	No	Cation exchange membrane	20-100	7 mA ^a	60	(Chang et al., 2004)
MFCs effluent	No data	No	Cation exchange membrane	50-100	0.185 mA ^a	36	(Moon et al., 2004)
Consortium (river sediments)	Graphite felt/ Graphite felt/Pt	No	Cation exchange membrane	2-10	6 mA ^a	60	(Moon et al., 2005)
Consortium (river sediments)	Graphite felt/ Graphite felt/Pt	No	Cation exchange membrane	6	No data	180	(Kang et al., 2003)
Enriched consortium	Graphite felt/ Grafite felt	No	Cation exchange membrane	2.6-25 (current) 2.6-206 (charge)	1.1 mA 58 ⁰ C	30-600	(Kim et al., 2006)
Consortium (anerobic sludge)	Carbon cloth/ Toray paper/Pt	No	Cation exchange membrane	50-400 ^b	0.4 mA	40-120	(Di Lorenzo et al., 2009)
Domestic wastewater	Carbon paper/ Carbon	No	Proton exchange membrane	17-183	222 mA	30	(Peixoto et al., 2011)

paper

Consortium (primary clarifier)	Graphite felt/ Graphite felt	No	Cation exchange membrane	10-250	233 mA	40	(Zhang and Angelidaki, 2011)
Escherichia Coli	Glassy carbon/ Pt	Poly-neutral red	No	50-1000	0.001 mA	No data	(Liu et al., 2012)
Consortium (anaerobic and aerobic sludge)	Graphite rode/ Carbon paper with carbon nanoparticle s	No	No	32-1280	70°C	5-20 h	(Modin and Wilén, 2015)

Table 4. Microbial fuel cells used for the determination of toxicity

Type of MFC	Toxicant	Anode potential	Biofilm enrichment	Hydraulic retention time	Smallest concentration detected	Reference
Double chamber MFC	Diazinon (61%)	NA	Consortium (activated sludge)	20 min-2h	1-10 mg/L	(Kim et al., 2007)
	Hg, Pb	0.026-0.004 mA	Activated sludge			
Double chamber MFC	Sodium dodecyl sulfate	>-0.4 V (Ag/AgCl)	Enrich bacteria community from long-term operated MFC	NA	50 mg/L	(Stein et al., 2012b)
Double chamber MFC	Ni ²⁺	-0.4 V (Ag/AgCl)	Enrich bacteria community from long-term operated MFC	45 min	22.7	(Stein et al., 2012c)
Single chamber MFC	Cu ²⁺ (69.8%)	Without control	Wastewater (2 months)	1-20 min	5	(Shen et al., 2013)
Double chamber MFC	Cu ²⁺	-0.15 ~ -0.4 V (Ag/AgCl)	Enrich bacteria community from long-term operated MFC	~ 47 min	93	(Stein et al., 2010)
Double chamber MFC (microsize)	Formaldehyde	Without control	<i>Geobacter sulfurreducens</i>	NA	0.1%	(Dávila et al., 2011)
Three-electrode electrochemical cell (CE)	Formaldehyde (0.01%)	0.3 V saturated calomel electrode	<i>Shewanella oneidensis</i> MR-1	1-5h	0.01%	(Wang et al., 2013)

Graphical abstract

HIGHLIGHTS

- MFCs-based biosensor is an innovative technology for wastewater quality detection.
- No transducer is needed for MFC-based biosensors to read and convert the signal.
- MFCs sensor's limitations are sensitivity, irreproducibility, labor scaling and stability.
- Future research on improving electrodes' material and configurations is essential.

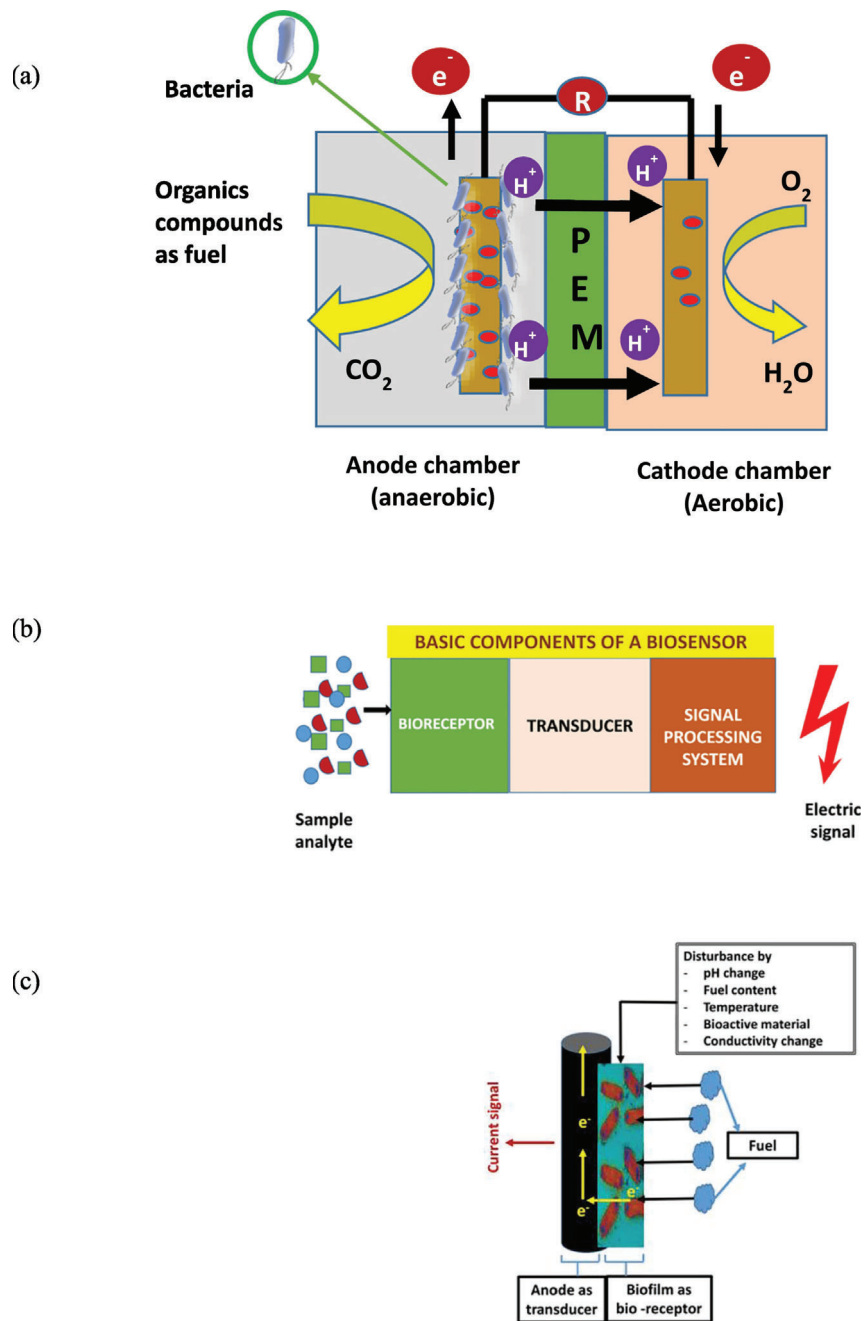


Figure 1

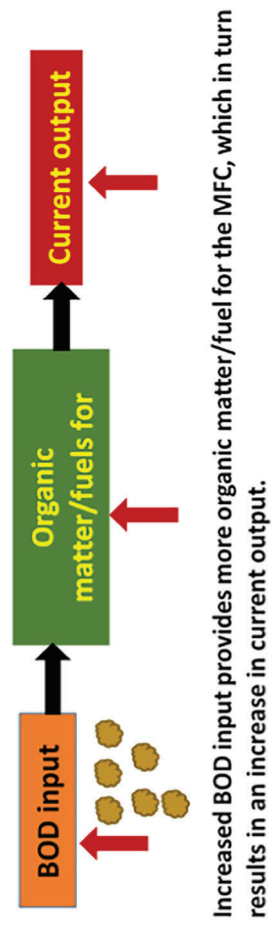


Figure 2

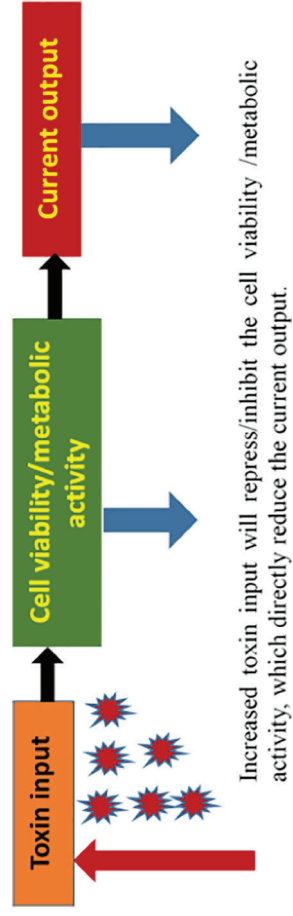


Figure 3