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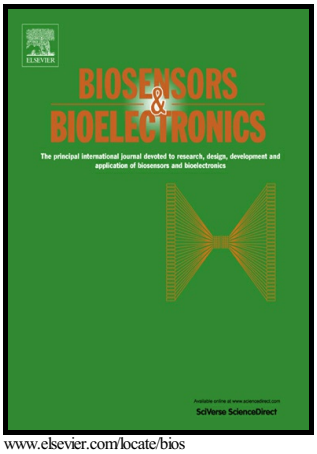

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A novel microbial fuel cell sensor with biocathode sensing element

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Abstract:

The traditional microbial fuel cell (MFC) sensor with bioanode as sensing element delivers limited sensitivity to toxicity monitoring, restricted application to only anaerobic and organic rich water body, and increased potential fault warning to the combined shock of organic matter/toxicity. In this study, the biocathode for oxygen reduction reaction was employed for the first time as the sensing element in MFC sensor for toxicity monitoring. The results shown that the sensitivity of MFC sensor with biocathode sensing element (7.4 ± 2.0 - 67.5 ± 4.0 mA $\%^{-1}$ cm^{-2}) was much greater than that showed by bioanode sensing element (3.4 ± 1.5 - 5.5 ± 0.7 mA $\%^{-1}$ cm^{-2}). The biocathode sensing element achieved the lowest detection limit reported to date using MFC sensor for formaldehyde detection (0.0005%), while the bioanode was more applicable for higher concentration (>0.0025%). There was a quicker response of biocathode sensing element with the increase of conductivity and dissolved oxygen (DO). The biocathode sensing element made the MFC sensor directly applied to clean water body monitoring, e.g., drinking water and reclaimed water, without the amending of background organic matter, and it also decreased the warning failure when challenged by a combined shock of organic matter/toxicity.

Keywords:

Biosensor, biocathode, toxicity, sensitivity, signal interference, microbial fuel cell

1. Introduction

The early warning device is critical to detect the existence and to mitigate the impact of contamination, which is important to guarantee the water environmental security and the public health (Liu et al., 2016). The use of generic biosensor based early warning device is a more practical option, compared with physicochemical analysis methods, to link the bioavailable concentration of the known or even unknown chemical contaminations with the biological effect (Su et al., 2011). The microbial fuel cell (MFC) sensor is an attractive new type of electrochemical microbial biosensor, which uses the biofilm-electrode as the sensing element (Kim et al., 2007). The most distinct advantage of MFC sensor is that it works self-sustaining without additional signal transducer or external power source, which is generally required in other types of biosensors (Chen et al., 2016; Stein et al., 2011; Sun et al., 2015).

The bioanode was used as the sensing element in traditional MFC sensors for water monitoring (Kim et al., 2007). The electrogenic microorganisms on this bioanode degrade the organic matter and release protons and electrons, and the protons and electrons are further transferred to the cathode through the internal ion transport and the external circuit, respectively (Jiang et al., 2014; Kannan 2016; Nealson and Rowe 2016). At the cathode, the electrons combine with the protons and different electron accepters, e.g., oxygen, to accomplish the reduction reaction (Zhang et al., 2016). The sudden presence of, or a change in the concentration of target analytes in the exposed aquatic environmental affects the electrogenic microorganisms' metabolic activity, and is reflected as a change of the output electric signal (Jiang et al., 2015; Kim et al., 2007).

The output electric signal of the bioanode sensing element is greatly affected by

various water quality parameters during toxicity monitoring, e.g., the concentration of organic matter and dissolved oxygen (DO). It is essential that the water sample remains organic matter rich and in anaerobic condition for stabilizing the baseline signal using the bioanode sensing element (Stein et al., 2010; Stein et al., 2011). A change in the concentration of organic matter can directly affect the output electric signal since it acts like the fuel for the bioanode. Moreover, a combined shock of organic matter and toxicity could happen in practical water monitoring. For instance, the accidental discharge of industrial wastewater, like those from livestock farms and petrochemical factory, will simultaneously increase the concentration of organic matter and toxicity (Abourached et al., 2013). The positive and negative effects caused by the increasing in organic matter and toxicity, respectively, tends to a potential fault warning (Jiang et al., 2016a; Liu et al., 2014). To minimize the influence of organic matter on toxicity monitoring, external organic matter with a constant concentration as high as over saturation should be manually added into the water sample, which increases the operation complexity of MFC sensor. What's worse, the dilution effect caused by the mixing of the water sample and artificial organic matter rich solution, dramatically decrease the sensitivity of MFC sensor (Kim et al., 2006). As the sensitivity of previous reported MFC sensor generally fails to meet the requirement of water quality standard, the additional organic matter amending largely restrict the practical application of MFC sensor using bioanode sensing element for organic matter deficient water body (Patil et al., 2010). The DO could act as an additional competitive electron acceptor for the bioanode sensing element, thus decrease the electric signal output of MFC sensor. In practice, additional respiratory inhibitor, e.g., azide, or deoxidation preprocessing is required to obtain higher sensitivity when the DO of the water sample exceeded certain limits

(Chang et al., 2005; Quek et al., 2015). However, the addition of inhibitor is strictly limited because of the potential environmental leakage.

The biocathode has been extensively used in MFC and its derivative technologies to catalyze the reduction of various substrates, e.g., oxygen, proton, carbon dioxide and short chain fatty acids, for electric power or value-added chemical production (Bergel et al., 2005; Jeremiasse et al., 2010; Jiang et al., 2013). Recently, the biocathode has also been used for the quantification of fumarate, an important indicator of food products, based on the catalytic ability of *Shewanella oneidensis* MR-1 for fumarate reduction (Si et al., 2015). The using of biocathode for oxygen reduction reaction (ORR) was attractive because of its low cost and long-term stability without degradation in performance, compared with inorganic catalysts, e.g., Pt cathode (Xia et al., 2013). The biocathodes both in the pure culture (e.g., *Acidithiobacillus ferrooxidans*) and mixed culture have shown the ability of oxygen reduction reaction (ORR) in MFC (Carbajosa et al., 2010). For example, an MFC incorporated with a biocathode for ORR was reported to be successfully operated as long as 6 months (Zhang et al., 2012). Another study revealed that using a biocathode for ORR could produce considerable power density even comparable to that produced by a two-chamber MFC with Pt cathode (Xia et al., 2013). For MFC sensor, in contrast to the traditional bioanode sensing element, the biocathode sensing element requires no organic matter amending in water sample for baseline signal output, and thus reduces the operational complexity (Bergel et al., 2005; Xia et al., 2013). The application range of the MFC sensor using biocathode sensing element could be expanded from anaerobic/organic matter rich aquatic environment to aerobic/organic matter deficient water body. Moreover, the biocathode sensing element is expected to greatly reduce the false early warning caused by an organic matter/toxicity combine

shock, since the increase of organic matter and toxicity both negatively affect the electric signal output. In this regard, the biocathode sensing element would be more adapted for complex aquatic environment monitoring.

In this study, a novel MFC sensor for water monitoring was constructed using the ORR biocathode as the sensing element for the first time. The performance of biocathode sensing element was systematically compared with a traditional bioanode sensing element. The effects of DO and the conductivity of water sample on the sensor's performance were explored. The sensor was challenged by the combined shock of organic matter/toxicity to evaluate the performance of this novel device for complex aquatic environment monitoring.

2. Materials and Methods

2.1. MFC sensor construction and startup

Four MFC sensors were constructed with a cation exchange membrane (CMI7000, Membranes International Inc., Glen Rock, NJ, USA) to separate the anode and cathode chamber. The cubic anode chamber and cathode chamber held identical dimensions, made from a cubic blocks with a cylindrical interior, with a length of 1 cm and a diameter of 3 cm. To enrich the biofilm in a short time, the graphite felt based electrodes (Sanye Carbon Co., Ltd., Beijing, China) with a diameter of 3 cm and a thickness of 0.3 cm were used as the anode in identical MFCs (Jiang et al., 2016a). After the enrichment of biofilms, half of the graphite felt based electrodes were used as the bioanode sensing element for the MFC sensors, while the remaining served as the traditional biocathode sensing element, as previous study indicated that acetate oxidizing mixed culture based biofilm-electrode also catalyzed the ORR after the reversion of polarity (Cheng et al., 2009). Saturated calomel electrodes (SCE, 242 mV versus the standard hydrogen electrode; Leici Co. Ltd., Shanghai, China) were

inserted near the bioanode and biocathode, respectively, as the reference electrode. All potentials reported here are relative to this SCE reference electrode. The anolyte was prepared by dissolving 0.82 g sodium acetate, 0.13 g KCl, 0.125 g NH_4Cl, 12.5 mL trace minerals solution, and 5 mL vitamin solution in 1 L of 5 mM PBS solution (Jiang et al., 2016b). The catholyte was modified from the anolyte by replacing the sodium acetate with 2 g $NaHCO_3$ and supplied with DO using external aeration system. Both the anolyte and catholyte were recirculated at a constant flow rate of 6 mL min^{-1} using a multichannel peristaltic pump. The anode and cathode were connected with a potentiostat (CHI 1030B, Chenhua Co., Shanghai, China) in two-electrode mode, by setting the potential of 0 V to model the condition of a minimized external resistor, as a lower external resistor generally lead to a higher sensitivity for MFC sensor (Stein et al., 2012).

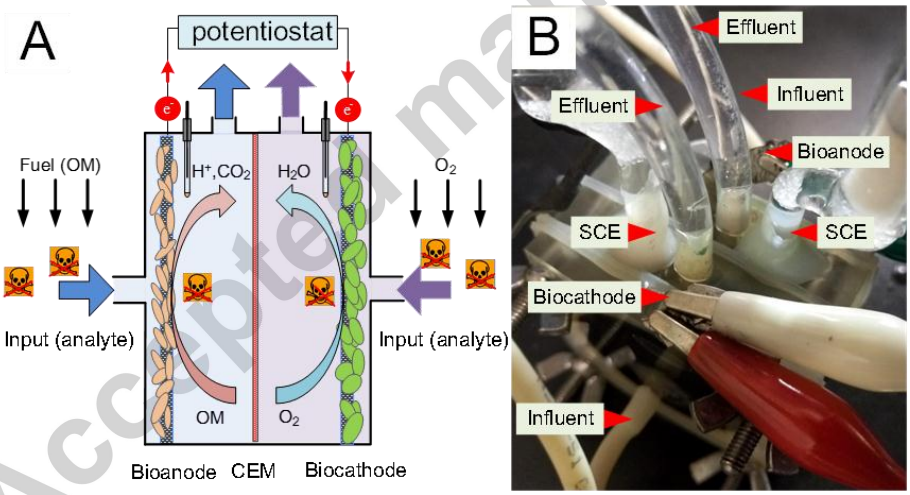


Fig. 1. The schematic diagram (A) and prototype (B) of the MFC sensor. Both the bioanode and biocathode could be used as the sensing element.

2.2. Biosensor tests.

After the startup process, the MFC sensors were fed with a continuous flow of influent, using the biocathode and bioanode sensing element respectively, as a comparative experiment for water monitoring. For both bioanode and biocathode, the

water sample was forced to flow through the porous carbon felt, in order to stimulate the mass transfer process inside the biofilm and thus to improve the sensitivity (Jiang et al., 2015). The MFC sensor was firstly challenged with the single shock of toxicity by adding formaldehyde with final volume concentrations from 0.0005% to 0.01% into the continuous flow of water sample. Then it was further challenged with the combined shock of organic matter/toxicity by changing the concentration of acetate and formaldehyde simultaneously. The fresh medium containing no toxicity was introducing to the MFC sensor in the recovery period before each concentration change of the formaldehyde. The using of biocatalysts for oxidation of formaldehyde in MFC has not been reported. The addition of the formaldehyde showed no obvious change in the conductivity of the water sample. The MFC sensors were all allowed to get fully recovery after toxicity detection by circularly introducing fresh medium overnight using an external stationary tank. In order to make a stable aquatic condition (i.e., the pH and substrate concentration) during this recovery process, the liquid volume of the tank was selected as large as 4 L, which is more than 600 times larger than the chamber of the MFC sensor. All experiments were conducted in duplicates and performed at the room temperature (25 ± 1ºC).

2.3.Electrochemical analyses and calculations.

The current of the MFC sensor was recorded every 10 s as the output electric signal. The electrochemical activity of the biocathode for ORR and the bioanode for acetate oxidizing was investigated by cyclic voltammetry (CV, scan rate: 1 mV s^{-1}). The electrochemical impedance spectroscopy (EIS) measurement was conducted with the frequency ranging from 100,000–0.010 Hz, and with the voltage amplitude of 10 mV (Ter Heijne et al., 2011). The EIS measurement results were simulated by Zview software (Scribner Associates Inc., Southern Pines, NC, USA) based on the equivalent

circuit model. All electrochemical tests were conducted using an Autolab electrochemical workstation (PGSTAT 128N, Metrohm Autolab, The Netherlands). The current change (ΔI) was defined as the current drop after the exposure to toxic agents. The sensitivity of the MFC sensor defined as a change in electric signal (current density) per unit change in the toxic agent concentration (Stein et al., 2012):

$$sensitivity = \frac{\Delta I}{\Delta c \times A}$$

Where Δc (%) is the change in the formaldehyde concentration, and A (cm^2) the electrode surface area (7 cm^2 for both the bioanode and biocathode).

3. Results and discussion

3.1.Sensitivity of biocathode MFC sensor to toxicity.

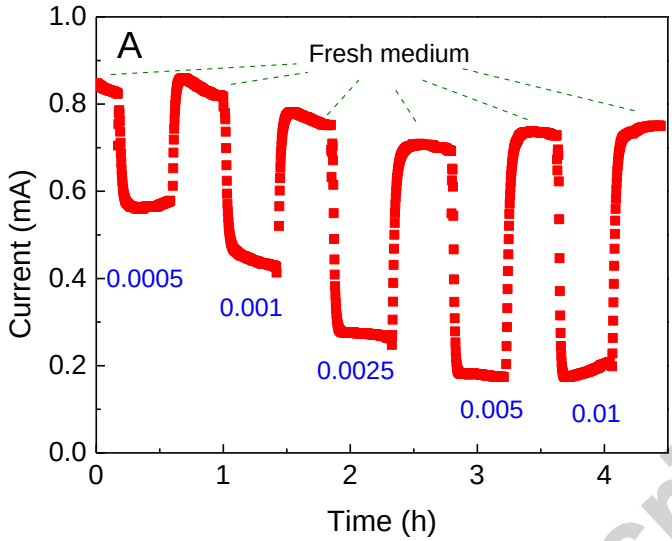
After the start-up stage, the biocathode and bioanode sensing element delivered good performance for ORR and acetate oxidizing, respectively, as investigated by CV (Fig. S1). Then the MFC sensor was challenged with influent containing specific concentration of formaldehyde. Using the biocathode sensing element, an immediate decrease in current output was observed after exposed to formaldehyde, and it almost fully recovered when exposed to fresh medium without formaldehyde (Fig.2A). Using the bioanode sensing element, a small hardly measurable change in current output was observed after exposed to formaldehyde with a lower concentration from 0.0005% to 0.0025% (Fig.2B), revealing that the bioanode sensing element might be more adapted for high concentration formaldehyde detection (>0.0025%). Moreover, the current output using the bioanode sensing element just stopped the downward trends after the exposure to fresh water, and could not get fully recovered. It was shown that the base line of electric signal output of the biocathode sensing element (0.75 ± 0.05 mA) was generally higher than that of the bioanode sensing element (0.45 ± 0.04 mA). The difference might be attributed to the change of batch type circulating during

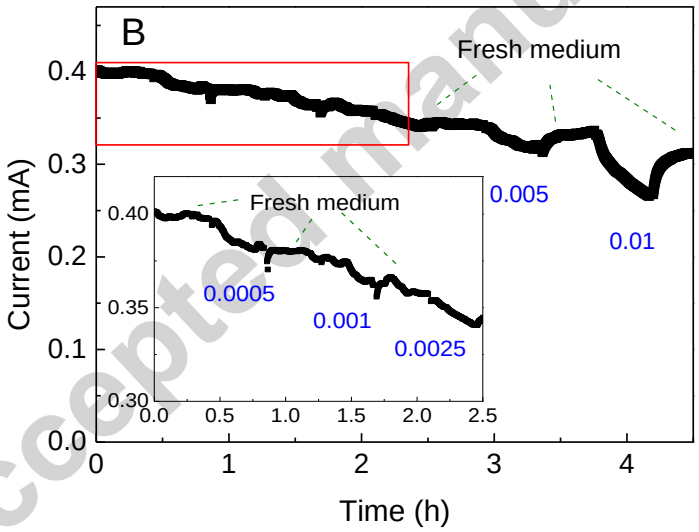
recovery stage to the throughput of sample stream mode for biosensor tests, and the bioanode might be more susceptible to the wash out of the metabolite such as the endogenous shuttle (Logan 2009).

The ΔI after the addition of formaldehyde was shown in Fig.2C as a performance comparison of bioanode and biocathode sensing element. The ΔI of both the biocathode and bioanode sensing element showed an increasing trend when the formaldehyde concentration increased from 0.0005% to 0.005%. Further increasing the formaldehyde concentration to 0.01%, the ΔI of biocathode sensing element remained stable, while the bioanode sensing element delivered a continuous increase. The linearity range of the biocathode sensing element for formaldehyde detection is 0.0005%~0.005% with a correlation of $R^2 = 0.83$. The sensitivity of MFC sensor with biocathode sensing element (7.4 ± 2.0 - 67.5 ± 4.0 mA $\%^{-1}$ cm^{-2}) was much greater than that showed by bioanode sensing element (3.4 ± 1.5 - 5.5 ± 0.7 mA $\%^{-1}$ cm^{-2}).

Different biofilm structure, reaction type, and the mass transfer could all contribute to the result that the biocathode sensing element improved the sensitivity of MFC sensor. The biofilm structure difference was ignorable in this study since the biocathode and bioanode sensing element were all pre-attached with the biofilm under same anodic conditions before the reversion of polarity (Pous et al., 2016). Both the biocathode and bioanode, and their chambers held identical dimensions, and the sample stream was both forced to flow through the porous carbon felt, which minimized the difference of mass transfer process. However, as shown in the EIS test (Fig. S2), the mass transfer resistance of the acetate degradation bioanode was 10 times higher than the ORR biocathode (Table S1). This great difference in mass transfer resistance was reasonable as it was determined also by the operation potential of the electrode, together with the flow pattern (Ter Heijne et al., 2011). Thus, the

improvement of sensitivity with the application of biocathode sensing element was mainly attributed to the difference of reaction type and the mass transfer.





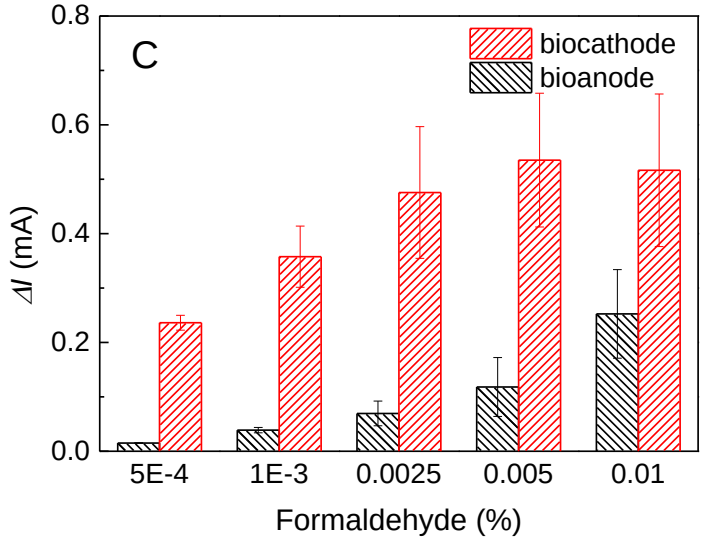


Fig. 2. The current output MFC sensor when challenged with influent containing specific concentration of formaldehyde using the biocathode (A) and bioanode (B), as the sensing element. The change in current (*ΔI*) observed following the addition of formaldehyde (C). The concentration of formaldehyde (%) were marked in the figure.

The Table 1 summarized the detection limit using the MFC sensor for formaldehyde detection. Compared to previous studies using MFC sensor based on bioanode sensing element, the biocathode sensing element in this study shows superior performance with the lowest detection limit. The bioanode sensing element here only delivered a small and hardly measurable change in current output after exposed to formaldehyde of 0.0005%, thus might be more applicable for higher concentration of formaldehyde detection (>0.0025%).

Table 1. Summary of MFC sensor for formaldehyde detection.

Sensing element	inoculation	chamber	detection limit	Ref.
bioanode	*Pseudomonas aeruginosa*	double	1.8%	(Yang et al., 2015)
bioanode	*Geobacter sulfurreducens*	double	0.1%	(Dávila et al., 2011)
bioanode	*Shewanella oneidensis*	single	0.01%	(Wang et al., 2013)
bioanode	*S. oneidensis*	double	0.001%	(Lee et al., 2015)
bioanode	MFC effluent	double	0.0025%	This study
biocathode	MFC effluent	double	0.0005%	This study

3.2. Effect of conductivity and DO.

The conductivity of the influent greatly affected the current output of the biocathode sensing element based MFC sensor (Fig. S3), as it implicated the Ohmic resistance (Logan et al., 2006). The saturate conductivity for current output was above 2000 μS cm^{-1} (Fig. S4), thus the following tests were conducted using deionized water and 1.5 g L^{-1} NaCl amended deionized water (2800 μ S cm^{-1}) for formaldehyde detection. The sensitivity increased by 3~11 times after the amending of 1.5 g L^{-1} NaCl (Fig.3). The sensitivity of the MFC sensor using the catholyte (Fig.2) with lower conductivity (1900 μ S cm^{-1}) was still 1~2 times higher than that using NaCl amended deionized water (Fig. 3). These results indicated that other water quality parameters, e.g., the buffer capacity, could also affect the performance of the biocathode sensing element. However, the distinguished response of biocathode sensing element to deionized water contaminated with low concentration of formaldehyde was much more attractive. These results indicated that the biocathode sensing element based MFC sensor could be directly applied in clean water monitoring, e.g., drinking water and reclaimed water after advanced treatment, without any amending or pretreatment.

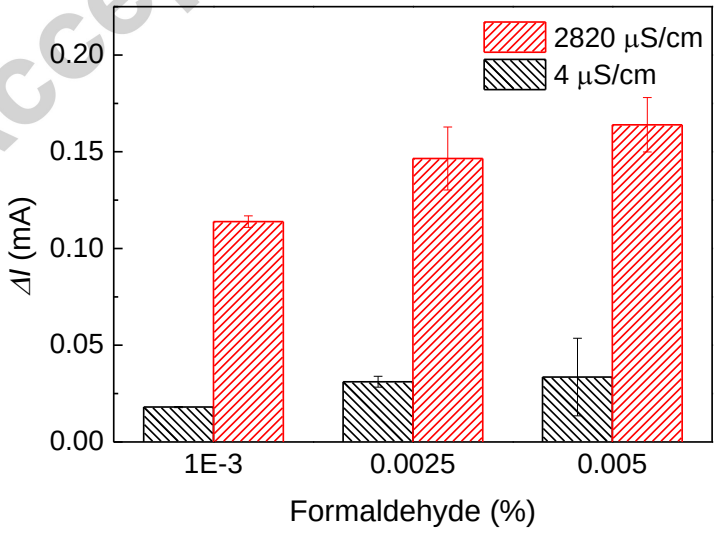


Fig. 3. The effect of conductivity on the performance of MFC sensor using biocathode sensing element. Deionized water (4 μS cm^{-1}) and 1.5 g L^{-1} NaCl amended deionized water (2800 μ S cm^{-1}) were used here.

The DO of the influent is used as the reduction substrate for cathodic current generation. An increase in current output with the increase of DO was observed in the biocathode sensing element based MFC sensor (Fig. S5). There was only a slight response when bubbling the influent with nitrogen gas (Fig. 4), compared to that with air bubbled influent (Fig. 2). Moreover, the electric signal output became susceptible to some uncertainties, e.g., the disturbance caused by influent switch, reflected as a large level of noise. In fact, during the normal operation of the MFC sensor, the DO of the effluent decreased to about 1.5 mg L^{-1}, even when a high DO level of about 8 mg L^{-1} was maintained in the cathodic influent. These results indicated that the biocathode sensing element based MFC might not be directly used in anaerobic water body without oxygen supply.

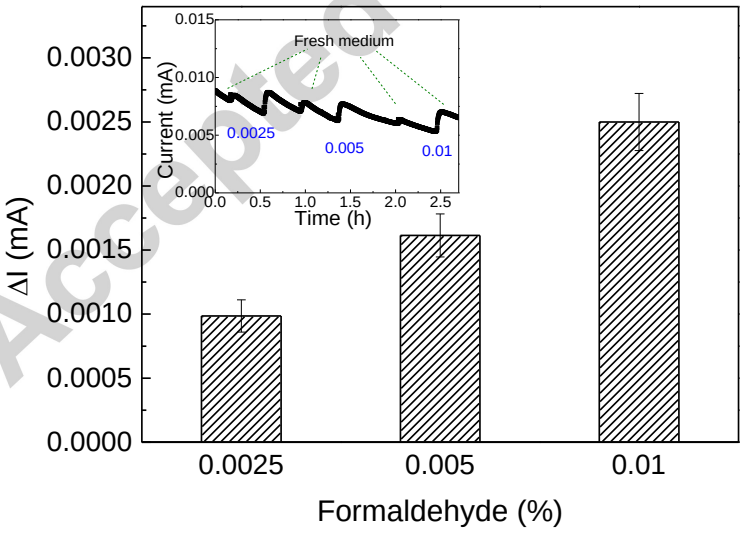


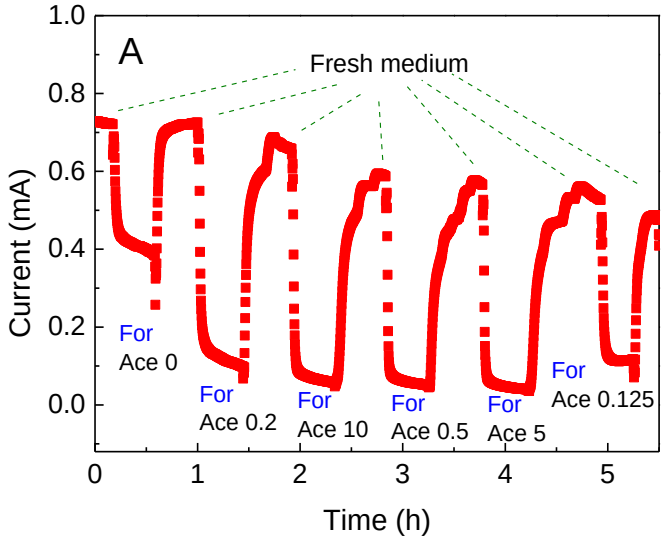
Fig. 4. The effect of dissolved oxygen (DO) on the performance of MFC sensor using biocathode sensing element. Here the nitrogen instead of air was used to bubble the influent, and decreased the DO from 8 mg L^{-1} to about 0.5 mg L^{-1}.

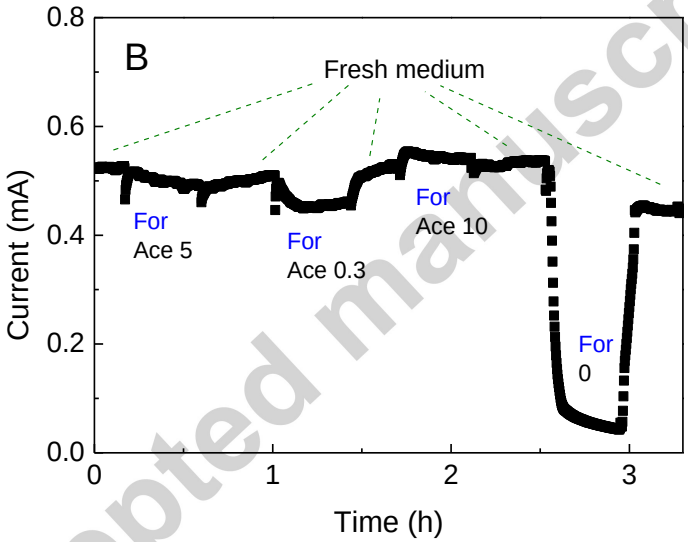
3.3. The challenge of a combined shock of organic matter/toxicity.

A combined shock of organic matter/toxicity could simultaneously happen when there are several sewage outlets along the recipient water body. The effect of organic matter to the signal output using different sensing element were evaluated here. After a steady state of the MFC sensor was observed, the biocathode and bioanode sensing element both showed an immediate response in current output when challenged with different concentration of acetate as a model organic matter (Fig. S6). The biocathode sensing element delivered a decrease in current output, while the anode sensing element showed an increase in current output, with the increase of the acetate concentration. It was reasonable as the organic matter can serve as an additional electron donor besides the electrode for the biocathode, while the organic matter served as the fuel for the bioanode with the electrode served as the electron accepter (Hamelers et al., 2011).

Using the biocathode sensing element, when the formaldehyde concentrations remained at 0.0005% in the fresh medium, the increase of acetate from 0.125 mM to 0.5 mM in the combined shock could largely increase the response of biocathode sensing element, compared with the single exposure of formaldehyde. Further increasing the acetate to as high as 10 mM could not further decrease the current output (Fig.5A). When the formaldehyde remained at a higher concentrations of 0.005%, the increase of acetate from 0.2 mM to 10 mM in the shock only led to a slight further decrease of current output, compared with the single exposure of formaldehyde (Fig. S7). Using the bioanode sensing element, when the formaldehyde concentrations remained at 0.005% and the acetate concentration remained at 0.3 mM in the fresh medium, the increase of acetate from 0.3 mM to 10 mM in the shock could largely obliterate the declining tendency of current output, compared with the single exposure of formaldehyde (Fig. 5B). For instance, the MFC sensor delivered

even an increase of current output when challenged with a combined shock of acetate 10 mM/ formaldehyde 0.005%. It is noticeable that when the background concentration of the organic matter doped to zero, the bioanode sensing element lacking of fuel generally delivered a weak current output close to 0 mA (Di Lorenzo et al., 2009). The coexisting of organic matter obviously showed a different effect on the biocathode and bioanoce sensing element for toxicity monitoring (Fig. 5C). Using the traditional bioanode sensing element based MFC sensor, the positive and negative effects caused by the increasing in organic matter and toxicity, respectively, led to a mask of the response and an increase in potential fault warning. One of the common used method to assure the normal operation of MFC sensor using bioanode sensing element for toxicity monitoring is to set a saturated background concentration of organic matter, which is much higher that the concentration of the potential shock (Fig. S8). In this case, the bioanode sensing element based MFC sensor alone could not be simultaneously used for the organic matter (demanding background organic matter free) and toxicity monitoring (demanding background organic matter over saturated) (Jiang et al., 2016a; Liu et al., 2014). Using this biocathode sensing element based MFC sensor, the increasing in organic matter and toxicity both caused negative effects, thus avoided the failure rate of early warning when challenged with a combined shock of organic matter/toxicity. Moreover, a single biocathode sensing element based MFC sensor was expected to be simultaneously used for the organic matter and toxicity monitoring, with no background organic matter required.





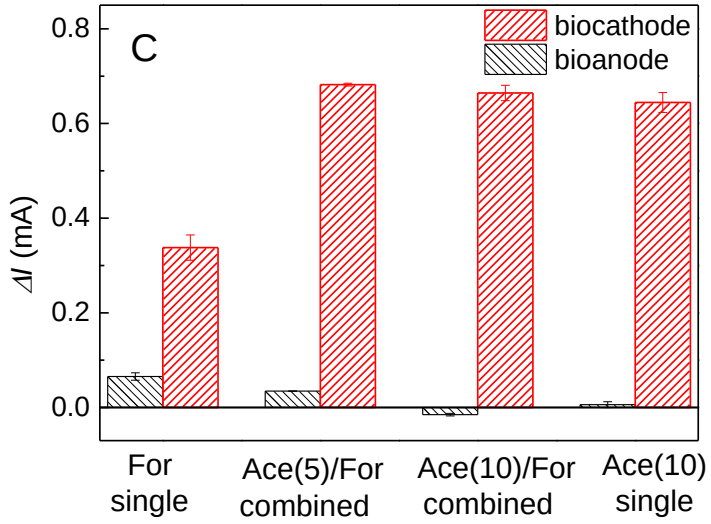


Fig. 5. The current output MFC sensor when challenged with a combined shock of organic matter/toxicity using the biocathode (A) and bioanode (B), as the sensing element. The change in current (*ΔI*) observed following the addition of single shock of formaldehyde, acetate and their combined shocks (C). The typical concentration of formaldehyde (For) was 0.0005% for biocathode while it was 0.005% for bioanode, because the biocathode was much more sensitivity. The concentration of acetate (Ace) of the fresh medium for bioanode was fixed at 0.3 mM to model the unsaturated condition. The concentration of acetate (mM) in the shocks were marked in the figure.

This study for the first time demonstrated the availability of the biocathode sensing element for MFC sensor based early warning device. Compared with traditional bioanode sensing element for MFC sensor, the novel electrochemical microbial biosensor developed in this study has several advantages. First, the sensitivity of MFC sensor using biocathode sensing element is 2-12 times that of bioanode sensing element, with a lowest detection limit achieved for formaldehyde detection using MFC sensor. Secondly, no additional background organic matter amending was required for toxicity monitoring. Thirdly, the biocathode sensing element delivered a proximately stable sensitivity for organic matter detection compared with the bioanode sensing element. The biocathode sensing element based MFC sensor alone was expected to be simultaneously used for the organic matter and

toxicity monitoring, and to avoid the failure rate of early warning when challenged with a combined shock of organic matter/toxicity.

Using the biocathode sensing element, the application area of MFC sensor based early waring device expanded from anaerobic/organic matter rich condition to aerobic/organic matter deficient water body. For instance, it could be directly used in clean water for on line monitoring without any amending or pretreatment. Moreover, it also expanded the specific application area and improved the reference meaning using the MFC sensor for wastewater treatment process monitoring. Although many different types of microorganisms were reported to produce varying level of current, the dominate bacteria on the bioanode for current generation is often limited to few kind of species, e.g., *Geobacter sulfurreducens* (Zhu et al., 2014). Moreover, the difference between the microorganisms on the bioanode and the practical function microorganisms of the wastewater treatment process will inevitably result indifferent toxic effects (Xiao et al., 2015). On the contrary, various microorganisms could become the dominate bacteria inside the biocathode to accomplish various functions. Future research will focus on evaluating the application of biocathode sensing element based MFC sensor for wastewater treatment process monitoring by using other types of biocathode besides the ORR biocathode here, e.g., denitrification biocathode and methanogens biocathode.

The MFC sensors in this study have been operated for about 2 months after the startup period, and no significant degradation in electric signal output was observed. The biocathode in MFC, though not for sensor application, was reported to be successfully operated for 4 to 6 months (Xia et al., 2012; Zhang et al., 2012). This MFC sensor using the biocathode as the sensing element thus could be directly deployed in water/wastewater systems without replacement for at least half a year.

The MFC sensors in this study have shown good reproducibility. During the whole biosensor test process, the biocathode and the bioanode sensing elements were both separately challenged with toxicity shocks using various concentration of formaldehyde for more than 30 times. As shown in Fig. 2A and 5A, the MFC sensor using the biocathode as the sensing element could get fully recovered within half an hour by replacing the influent with a toxicity free fresh medium, attributed to the self-renewal and regenerative capacity of microorganisms.

The performance of biocathode sensing element based MFC is largely affected by the DO, and further study will be carried out to provide a stable and energy saving method for DO supply. The bioanode is suggested to retain for further optimization of the biocahode sensing element based MFC sensor, as the bioanode can provide a self-sustaining initial electron source for the biocathode. The presence of the membrane can maintain a stable performance by separating the biocathode sensing element from the direct contact with high concentrations of organic matter, which is used as the fuel for the bioanode, and thus prevent the growth of autotrophic microorganism inside the biocathode (Xia et al., 2013). In laboratory test and mechanism research, however, three-electrode system could also be employed using the biocahode sensing element based biosensor. The MFC sensor is generally used as a generic biosensors to provide a warm for the existence of bioavailable total toxicity, not for specifying the pollutants. In this regard, the accurate response is more important than the selectivity especially for MFC sensor. In this study, the accurate response of MFC sensor was improved using biocathode as the sensing element, based on the results that the sensitivity was largely increased, and it also decreased the warning failure when challenged by a combined shock of organic matter/toxicity. The MFC sensor using the biocathode sensing element could also be used for detecting

other types of toxicants. But the effect of the abiotic electrochemical reduction like Cu(II) on the response of MFC sensor should be carefully evaluated in the future studies.

4. Conclusion

The sensitivity of MFC sensor with biocathode sensing element (7.4 ± 2.0 - 67.5 ± 4.0 mA $\%^{-1}$ cm^{-2}) was much greater than that showed by bioanode sensing element (3.4 ± 1.5 - 5.5 ± 0.7 mA $\%^{-1}$ cm^{-2}). There was an increased response of biocathode sensing element with the increase of conductivity and DO. The biocathode sensing element made the MFC sensor directly applied to clean water monitoring without the amending of organic matter, and decreased the warning failure when challenged by a combined shock of organic matter/toxicity. Future research would include the application of biocathode sensing element for practical field test, and the effect of abiotic electrochemical reduction of some toxicants like e.g. Cu(II) on the response of MFC sensor.

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Highlights

- The sensitivity was increased by 1~15 times using the biocathode sensing element
- Biocathode could be directly used in clean water monitoring without amending
- A single device could be simultaneously used for the OM and toxicant monitoring
- Biocathode decreased the warning failure for a combined shock of OM/toxicant