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Enhancing the response of microbial fuel cell based toxicity sensors to Cu(II) with the applying of flow-through electrodes and controlled anode potentials

Yong Jiang [a], Peng Liang [a,*], Changyong Zhang [a], Yanhong Bian [a], Xufei Yang [b], Xia Huang [a], Peter R. Girguis [c]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control School of Environment, Tsinghua University, Beijing 100084, PR China
[b] Division of Atmospheric Sciences, Desert Research Institute, Reno, NV 89512, USA
[c] Harvard University, Organismic and Evolutionary Biology, Cambridge, MA, USA

HIGHLIGHTS

- Flow-through anode improved the sensitivity of MFC-based toxicity sensors.
- Better sensitivity was achieved when operating with a constant anode potential.
- Quasi steady-state *j*-V tests help optimize the anode potential.
- Abiotic electrochemical reactions of toxic agents affect the response of sensors.

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ABSTRACT

The application of microbial fuel cell (MFC)-based toxicity sensors to real-world water monitoring is partly impeded by the limited sensitivity. To address this limitation, this study optimized the flow configurations and the control modes. Results revealed that the sensitivity increased by ~15–41 times with the applying of a flow-through anode, compared to those with a flow-by anode. The sensors operated in the controlled anode potential (CP) mode delivered better sensitivity than those operated in the constant external resistance (ER) mode over a broad range of anode potentials from −0.41 V to +0.1 V. Electrodeposition of Cu(II) was found to bias the toxicity measurement at low anode potentials. The optimal anode potential was approximately −0.15 V, at which the sensor achieved an unbiased measurement of toxicity and the highest sensitivity. This value was greater than those required for electrodeposition while smaller than those for power overshoot.

1. Introduction

On-line monitoring of water toxicity plays an important role in providing safe drinking water and securing the proper operation of wastewater treatment plants. Generic biosensors with indicator organisms such as fish, *Daphnia* and luminescent microorganisms have been developed to measure the joint toxicity of multiple contaminants. More recently, increasing attention has been paid to the potential use of microbial fuel cells (MFCs) for toxicity measurement (Kim et al., 2007; Patil et al., 2010; Shen et al., 2013). MFCs utilize the capability of electrogenic microorganisms to degrade organic matter for electricity generation (Jiang et al., 2013; Liang et al., 2013; Logan et al., 2006). Electrogenic microorganisms exposed to toxic components in water exhibit reduced electrochemical activity, leading to a decrease in the MFCs' electricity generation. Accordingly, the output voltage or current of an MFC can be used as a qualitative or quantitative measure of toxic agents in water samples, thereby exempting the use of an additional transducer (Stein et al., 2011). MFC-based toxicity sensors have gained growing interest due to their quick response, long-term stability and robustness (Kim et al., 2007; Stein et al., 2011; Xiao et al., 2015).

Many previous MFC-based toxicity sensors delivered relatively poor sensitivity, compared to conventional technologies based on such as planktonic cells (Patil et al., 2010). In an MFC-based toxicity sensor, the anodic biofilm forms a mass-transfer barrier for both the toxic agents to be measured and the nutrients required by

* Corresponding author. Tel.: +86 10 62796790.
E-mail address: liangpeng@tsinghua.edu.cn (P. Liang).

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microbial growth. This may significantly limit the sensor's measurement sensitivity. To promote the mass transfer in the anodic chamber, increasing the water stirring speed or flow rate was often applied. However, the promotion effect tapered off when the stirring intensity or flow rate reaches a certain level. The other way to enhance the mass transfer is to optimize the flow mode inside the anodic chamber. This is of particular importance for on-line, real-time monitoring as it demands water samples to be continuously fed to a sensor's sensing zone – in this case, the MFC's anodic biofilms. For typical electrochemical sensors, two flow modes/electrode configurations are usually adopted: flow-through and flow-by electrodes. In the former case, water samples are ducted to flow through a porous electrode; while in the latter case, the samples flow "openly" in a direction parallel to the electrode surface. Previous studies revealed that using a flow-through anode could markedly enhance the diffusion of protons in the anodic biofilm and alleviate the limited availability of substrates to microorganisms (Torres et al., 2008), thus elevating the MFC's output current and power density (Cheng et al., 2006; Katuri et al., 2011). We expect that a flow-through electrode will similarly improve the sensitivity of MFC-based toxicity sensors. To our knowledge, no relevant experiments have been performed to date.

The sensitivity of MFC-based toxicity sensors is also affected by their control mode (Stein et al., 2012a). Two types of control modes are currently employed by most MFC-based toxicity sensors. The first one stands for the simplest setup – an external resistor with a fixed resistance is connected to the MFC's anode and cathode, and the measurement is done by tracking the voltage drop along the resistor (Di Lorenzo et al., 2014; Kim et al., 2007; Shen et al., 2013). The second one represents an upgraded version – in addition to the setup in the first case, the anode potential is regulated using a potentiostat and remains constant during monitoring (Liu et al., 2014; Patil et al., 2010; Stein et al., 2010; Wang et al., 2013). For simplicity, the two control modes were designated as ER (constant external resistance) and CP (controlled anode potential) hereafter. The sensitivity of MFC-based toxicity sensors can be optimized by adjusting the values of ER and/or CP. Previous studies (Shen et al., 2012; Stein et al., 2012a,b) observed better sensitivity at low ER and/or high CP values; however, the ranges of the test CP values were quite limited. There lacks a systematic investigation of the two control modes over a broad range of anode potentials.

The sensitivity of MFC-based toxicity sensors is further affected by the types of the toxic agents to be monitored (Stein et al., 2011). Four types of toxic inhibition mechanisms, i.e., noncompetitive inhibitors, electron acceptors, reaction products, and redox complex binders, have been distinguished using kinetic models (Stein et al., 2012c). The abiotic electrochemical reactions of the toxic agents may also bias the toxicity measurement. Li et al. (2014) reported that metal species such as Fe(III) and Cr(VI) – with their redox potentials higher than the typical operating potentials of MFC anodes – were partly deposited on the anode surface during the heavy metal wastewater treatment. Zhang et al. (2014) observed a reduction of V(V) on the MFC anode under anaerobic conditions. These abiotic electrochemical reactions not only alter the concentrations of the target toxic agents but also result in an electric current that interferes with the current-based toxicity measurement. Despite of their importance, the effect of the abiotic electrochemical reactions on the sensor response has not been well studied.

In this study, we explored the application of flow-through mode to enhancing the sensitivity of MFC based toxicity sensors. Two control modes were compared and the anode potential was optimized to further improve the MFC sensor's sensitivity. The Cu(II) toxicity-induced current signals and the electrodeposition-induced signals were distinguished, thereby enabling an unbiased measurement of Cu(II) toxicity.

2. Methods

2.1. Construction of the microbial fuel cell

A typical two-chamber MFC was constructed as the toxicity sensor (Fig. 1). The MFC's anode and cathode chambers were separated by a cation exchange membrane (CMI7000, Membranes International Inc., USA), with the liquid volumes of 6.7 mL and 28 mL, respectively. The cathode was a carbon-fiber brush of 3 cm long and 3 cm in diameter. The anode was made of cylinder-shaped graphite felt (Sanye Carbon Co. Ltd., Beijing, China) of 1.5 cm in diameter and a thickness of 0.6 cm. The wall of the anode chamber was drilled with two holes – one on the end plate and the other on the top plate – serving as the liquid inlet and outlet, respectively. A saturated calomel electrode (SCE, 242 mV versus a standard hydrogen electrode; Leici Co. Ltd., Shanghai, China) was inserted near the anode as the reference electrode. All potentials presented were referenced to the SCE.

2.2. Startup of the microbial fuel cell

The MFC was inoculated with a mixed culture collected from the effluent of acetate-fed MFCs in our laboratory (Zhang et al., 2015). During startup, the anolyte contained (per liter) 1.64 g sodium acetate (NaAc), 0.31 g NH_4Cl, 2.2 g KH_2PO_4, 1.7 g $K_2HPO_4{\cdot}3H_2O$, 0.1 g $CaCl_2{\cdot}2H_2O$, 0.1 g $MgCl_2{\cdot}6H_2O$, 12.5 mL trace minerals solution, and 5 mL vitamins solution (Lovley and Phillips, 1988). The catholyte contained (per liter) 16.64 g $K_3Fe(CN)_6$, 4.4 g KH_2PO_4, and 3.4 g $K_2HPO_4{\cdot}3H_2O$. Both the anolyte and catholyte were prepared and replaced on a daily basis, and were recirculated at a constant flow rate of 2.8 mL min^{-1} using a multichannel peristaltic pump. The anolyte was forced to flow through the porous anode, and the resulting hydraulic retention time (HRT) was ~2.4 min in the anodic chamber. The anode potential was controlled at −0.4 V using an eight-channel potentiostat (CHI 1030B, Chenhua Instruments Co. Ltd., Shanghai, China). The MFC can be configured to work in the flow-by-anode mode. In this configuration, the liquid inlet on the end plate was sealed with a rubber stopper, and the anolyte was fed in from the bottom of the anode chamber where a spare hole was drilled.

2.3. Biosensor test

After the enrichment of anodic biofilms, the MFC was fed with anolyte containing (per liter) 0.82 g NaAc and 0.31 g NH_4Cl. The biosensor test was performed with the following steps: First, two identical MFCs (with the same internal resistance and open-circuit voltage) were each connected to an external resistor with fixed resistance. The output voltages and anode potentials were measured to ensure that the two MFCs worked stably and

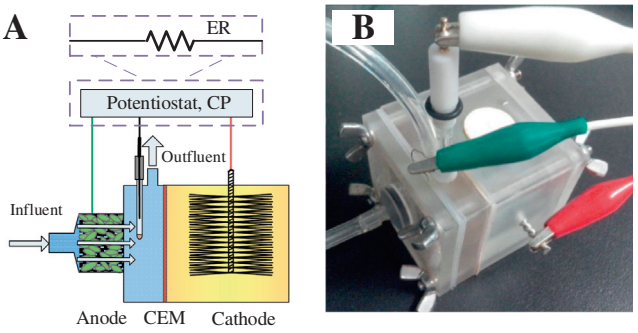

Fig. 1. (A) Schematic and (B) photo of a microbial fuel cell (MFC)-based toxicity sensor equipped with a flow-through anode and a carbon-brush cathode.

were comparable for the subsequent experiments. Secondly, after stabilization for 2 h, the anode and the reference electrode of one MFC were connected to the CHI1030B potentiostat, with which the anode potential was controlled to be constant at a desired voltage, i.e., CP value. The other MFC remained unchanged during this step. Thirdly, after 30 min, the two MFCs were challenged with anolytes containing 2 mg L^{-1} Cu(II) (Note: copper chloride, $CuCl_2$) for 2 h to achieve an equilibrium. The concentration was selected according to the World Health Organization (WHO) guideline value for copper in drinking water. Finally, the MFCs were drained and fed freshly-prepared anolyte solutions without Cu(II), allowing the anodic biofilms to recover from the impairment caused by Cu(II) toxicity. The MFCs' internal resistance and output voltage were measured periodically to ensure the biofilms were entirely recovered before conducting the next test. All the experiments (including startup and biosensor tests) were performed in at 30 ± 1 °C. An MFC without bacterial inoculation was used as the negative, i.e., abiotic control.

2.4. Analyses

For MFCs working with in the ER mode, the voltage drop across the external resistor was measured every 5 s using a data acquisition system (DAQ2213, ADLINK, Beijing, China), and the electric current was determined based on the Ohm's law; while the anode potential was measured against the SCE reference electrode. For MFCs working in the CP mode, the anode potential and current were recorded by the potentiostat. The surface morphology and elemental composition of the MFC anode before and after Cu(II) tests were examined using a scanning electron microscope (SEM, TESCAN LYRA 3 XMH FIB/FE-SEM, Brno, Czech Republic) equipped with energy-dispersive X-ray spectroscopy (EDX).

For short-term amperometric (*j*-V) tests, the anode potential was increased stepwise every 15 min from −0.55 V to +0.15 V. The current was measured every 1 s, and the average of the final 100 current readings was calculated for every potential step. The sensitivity of MFC-based toxicity sensors is usually defined as a decrease in electric current per unit concentration of a target toxic agent, but when the sensors are challenged with the same concentration of the toxic agent (as in this case) it is proportional to a change in current (ΔI) (Stein et al., 2012b).

3. Results and discussion

3.1. Effect of the flow modes on the sensor response

To evaluate the effect of the flow modes on the response of the MFC-based sensor, the anode potential was set at −0.41 V, −0.07 V and 0.1 V, respectively, to represents the typical low, medium and high potentials. As shown in Fig. 2, after challenging the MFC sensors with Cu(II) for 2 h, the values of ΔI fell into the range of ~0.76–1.55 mA for the sensors with a flow-through anode, and ~0.02–0.06 mA for the ones with a flow-by anode. In the former case, the sensors' sensitivity was higher by ~15–41 times. According to Cheng et al. (2006), using flow-through electrode can facilitate the mass transport of substrates/nutrients and, thus, an increase in current generation (I_{nor}). In this study, the values of I_{nor} in the flow-through mode (~0.20–1.69 mA) were ~2–14 times those in the flow-by mode (~0.09–0.14 mA). The better sensitivity (ΔI) of MFC sensors with the applying of a flow-through anode may also be attributed to the enhanced mass transport of Cu^{2+} ions.

3.2. Effect of control modes on the sensor response

Two identical MFCs were selected to evaluate the effect of different control modes on the sensors' sensitivity. Before the challenge of toxicity agent, one of the MFC controlled by ER was connected to an external resistor with fixed resistance from 3000 Ω to 50 Ω. Thus the anode potential was measured. Then other one MFC controlled by CP was fixed at the same anode potential. The parameters in different control modes was shown in Table S1. With an increase in the anode potential, the changes in the ΔI in the two control modes followed a similar pattern (Fig. 3). In both modes, the ΔI increased as the anode potential increased from −0.41 V to −0.1 V, and then decreased. At every tested anode potential, the ΔI was higher for the CP-controlled MFC sensors than the ER-controlled ones. Fig. 4 shows the temporal changes in the sensors' anode potentials and output currents when they were operated in the CP or ER mode. The anode potential kept constant before and after the dosing of Cu(II) with the applying of the CP mode. Comparatively, when the ER mode was applied, adding Cu(II) led to an increased anode potential; here, we designated the anode potential at the beginning of the sensor operation as the initial anode potential. Fig. S1 shows that after >24-h cultivation with a Cu(II)-free anolyte, the sensor's output current went back to the "healthy" levels prior to Cu(II) test. Fig. S2 compares the initial and final states (including anode potential and output current) of the MFC sensors operated at different initial anode potentials. The final anode potentials increased to ~0.1–0.15 V when the ER mode was applied. The increased anode potential allows the electrogenic microorganisms to gain more energy from the degradation of substrates and accordingly increase their substrate consumption rate (Cheng et al., 2008; Wei et al., 2010). An increased substrate consumption rate often results in a

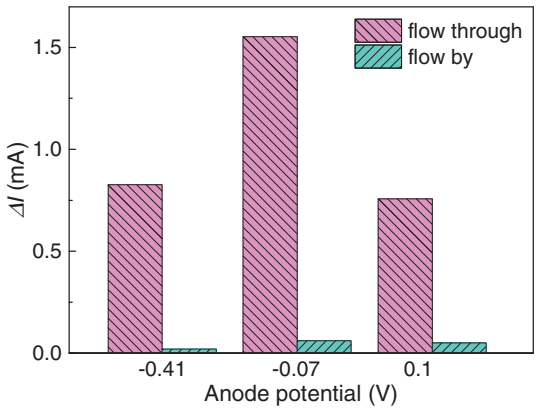

Fig. 2. Effect of the flow modes on the changes in current density.

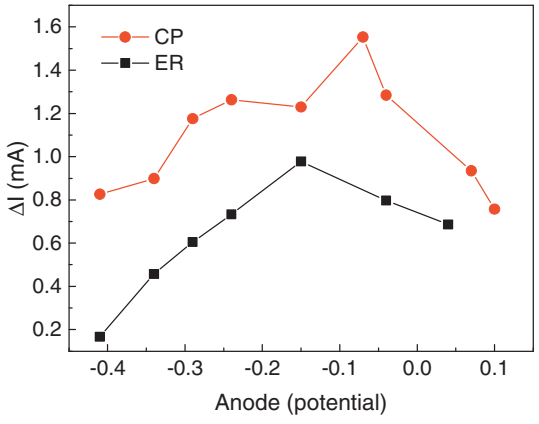

Fig. 3. Effect of the control modes on the changes in current density. For the sensors operated in the external resistance (ER) modes, the *x*-axis represents the initial stabilized anode potential.

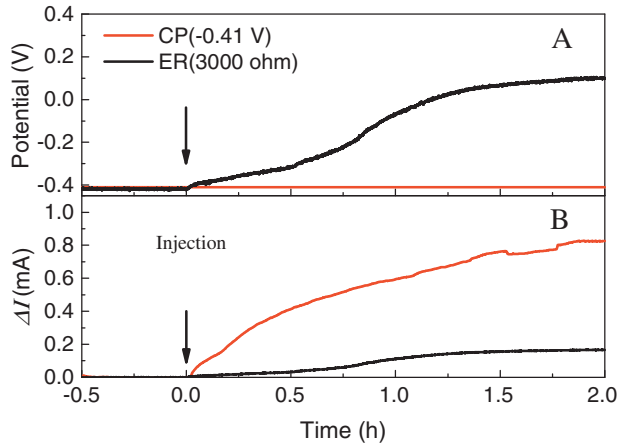

Fig. 4. (A) Anode potential and (B) change in the output current (ΔI) of an MFC-based toxicity sensor when operated in the constant anode potential (CP) and constant external resistance (ER) modes. In both control modes, the sensor was challenged with 2 mg L^{-1} Cu(II) injected at t = 0.5 h.

larger output current, which however may offset the current drop caused by the toxic agent of interest and therefore bias the toxicity measurement. This is a limitation of the ER mode.

The decrease of ΔI at high anode potentials (Fig. 3 and Fig. S2) indicates the occurrence of power overshoot, i.e., a decline in the MFC's anode performance at large current density (Hong et al., 2011). To further study this phenomenon and to optimize the anode potential for better sensor sensitivity, a short-term j-V test was conducted. This quasi-steady-state method was previously employed by Stein et al. (2011), and a detailed description of the method can be found in their paper. Briefly, the ΔI predicted by the j-V test was calculated by subtracting the polarization curves derived under non-toxic conditions from those obtained under toxic conditions (Fig. S3). The results of the short-term j-V test agreed well with those from multiple CP-mode tests – the latter tests were much more time-consuming because each test studied only a single fixed anode potential and was performed after the sensor output reached equilibrium. The short-term j-V test also revealed the occurrence of power overshoot when the anode potential exceeded −0.1 V. The optimal anode potential was slightly lower (approximately −0.15 V), as given by the test.

3.3. Abiotic electrochemical reactions of Cu(II)

A negative current was observed when the sensors were operated in the CP mode and at the CP values below −0.17 V (Fig. S2). During the abiotic control experiments, a drop in electric currents down to negative values was also noted at low CPs ($\leqslant$−0.07 V) (Fig. S4). The occurrence of negative currents indicates that the overall current drop (ΔI) could be caused by both the toxicity effects and abiotic electrochemical reduction of Cu(II). No negative current was seen for sensors operated in the ER mode; however, this does not exclude the possible occurrence of abiotic electrochemical reactions as the negative current resulted from those reactions could be masked by the toxicity-induced current change.

The reduction of Cu(II) during electrodeposition leads to the formation of metallic copper (Cu) and cuprous oxide (Cu_2O).

$$Cu^{2+} + 2e^- \rightarrow Cu \ (E^0 = 0.095\ V) \quad (1)$$

$$2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+ \ (E^0 = -0.035\ V) \quad (2)$$

The redox potentials of the two reactions are both greater than the anode potential of typical MFCs. Such a potential difference has been utilized by some researchers to build a metallurgical MFC for copper recovery by coupling the anodic oxidation of organic substrates with the cathodic reduction of copper ions (Heijne et al., 2010; Tao et al., 2011). Based on the Nernst equation, $E(Cu^{2+}/Cu)$ and $E(Cu^{2+}/Cu_2O)$ were calculated to be −0.041 V and 0.115 V, respectively, at pH of 7.0 and Cu(II) concentration of 2 mg L^{-1}. The calculated redox potentials were consistent with the abiotic control experiments, in which a negative current was observed at CPs $\leqslant$−0.07 V (Fig. S4). The electrodeposition of Cu(II) was evidenced by the SEM and elemental analyses of the MFC anodes with and without (i.e., abiotic control) biofilms. During the test, the anode potential was set at −0.41 V and Cu(II) was dosed for 2 h (Fig. S5). Spherical particles, identified by the EDX analysis as metallic copper, were formed on the fiber surface during the abiotic control experiments. Solid copper-containing particles were also found to embed in the biofilms that covered the MFC's anode surface. The presence of copper particles and the coexistence of other elements (e.g., S, P, Fe, and Zn) suggest the concurrence of biofilms and Cu electrodeposition. A monolayer biofilm structure was observed. A similar phenomenon was reported by Harrington et al. (2014) in their recent study of bioelectrochemical systems with carbon felt flow-through electrode. Electrogenic microorganisms tended to form a monolayer biofilm structure when the anolyte was forced to flow through the anode, especially when the anode was made of carbon felt or other materials with similarly small internal passages (i.e., 16 μm for MWCNT/CHI scaffolds) (Katuri et al., 2011). This implies that the enhanced sensitivity of MFC sensors with the applying of a flow-through anode may be related to a thinner biofilm structure on the anode surface.

Based on the discussions above, a schematic mechanism was proposed for the Cu(II) reactions occurring in the MFC-based toxicity sensors (Fig. 5). There were two types of reactions associated with Cu(II): (1) toxic reactions with electrogenic microorganisms; and (2) abiotic electrochemical reduction reactions, i.e., electrodeposition. The former reactions suppress the current generation by electrogenic microorganisms; while the latter ones cause a negative current, thereby biasing the measurement of Cu(II) toxicity.

The toxicity-related current changes, i.e., "true" signals, can be calculated by subtracting the ΔI values measured during the abiotic control experiments (Fig. S4) from those measured during the Cu(II)-challenge tests operated in the CP mode (Fig. 3). It is important to note that no similar subtraction/correction can be done for the sensors operated in the ER mode because of the varying anode potentials. The toxicity-related ΔI, in general, followed a similar trend to the total ΔI (toxicity plus electrodeposition). It

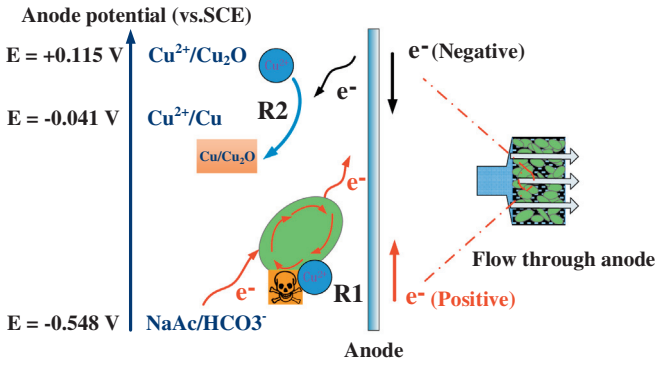

Fig. 5. Schematic of reactions taking place at the flow-through anode during Cu(II) detection. Two types of reactions occurred during this process: R1 represents a collection of toxic reactions that decreased the electrogenic activity of anode microorganisms; and R2 refers to abiotic electrochemical reactions that reduced Cu(II) to Cu(I) or Cu(0).

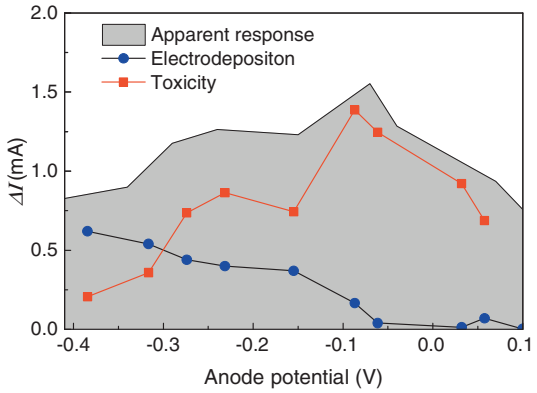

Fig. 6. Effect of the anode potential on the partitioning of ΔI between abiotic electrochemical reactions and toxic reactions.

increased as the anode potential increased from −0.41 V to −0.1 V but then decreased as the anode potential further increased to 0.1 V (Fig. 6). The toxicity-related ΔI values at low CPs ($\leqslant$−0.1 V) were found to be consistent with those predicted by a kinetic model developed by Stein et al. (2011) for heavy-metal toxicity MFC sensors. The decrease in the toxicity-related ΔI at high anode potentials could be related to the occurrence of power overshoots.

Noticeably, even after such subtraction, the MFC sensors operated in the CP mode still delivered better sensitivity than those operated in the ER mode. At the anode potential of −0.41 V, −0.24 V and 0.07 V, the toxicity-related ΔI values of the CP-controlled sensors were 0.21 mA, 0.86 mA and 0.92 mA, respectively; while the ΔI values of the ER-controlled sensors were 0.17 mA, 0.73 mA and 0.68 mA, respectively. Cu(II) electrodeposition became insignificant as the anode potential further increased to 0.07 V (Yu et al., 2010), enabling an unbiased measurement of Cu(II) toxicity. In addition to Cu(II), cautions should be taken when applying MFC-based toxicity sensors to other toxic agents such as V (V), Cr (VI), Ag (I), Hg (II) and azide, with redox potentials higher than the operating anode potentials of typical MFCs. Furthermore, the effect of electrodeposition on the cytotoxicity to the electrogenic microorganisms (Hubenova et al., 2011) and the long-term operation of the sensor should be taken into consideration in the future research.

4. Conclusions

The sensitivity of the MFC-based toxicity sensor can be enhanced with applying of a flow-through anode compared to the flow-by anode. MFCs operated with a controlled anode potential (CP) have higher sensitivity compared to the ones with a constant external resistance (ER). The optimal anode potential depends on the target analyte and its associated toxic and abiotic electrochemical reactions. But in general, it should be selected to avoid electrochemical reduction as well as power overshoots. Future research will be carried out to study the sensor response and develop a general kinetic model for toxic agents with various redox potentials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.04.127.

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