Chemosphere 203 (2018) 21–25

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Short Communication

A novel microbial fuel cell sensor with a gas diffusion biocathode sensing element for water and air quality monitoring

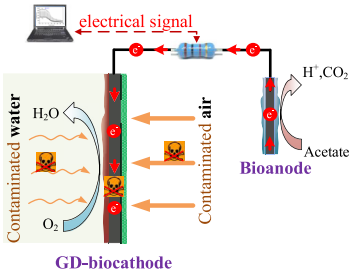
Yong Jiang [a], Peng Liang [a, *], Xia Huang [a], Zhiyong Jason Ren [b, **]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, PR China
[b] Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, CO 80309, USA

HIGHLIGHTS

- Gas diffusion biocathode sensing element was fabricated in uncomplicated method.
- MFC sensor was directly used in monitoring of aerobic and anaerobic water bodies.
- MFC sensor was for the first time used for air pollution monitoring.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 December 2017
Received in revised form
20 March 2018
Accepted 24 March 2018
Available online 26 March 2018

Handling Editor: E. Brillas

Keywords:
Biosensor
Biocathode
Sensitivity
Formaldehyde
Waterproof breathable membrane

ABSTRACT

Toxicity monitoring is essential for the protection of public health and ecological safety. Microbial fuel cell (MFC) sensors demonstrated good potential in toxicity monitoring, but current MFC sensors can only be used for anaerobic water monitoring. In this study, a novel gas diffusion (GD)-biocathode sensing element was fabricated using a simple method. The GD-biocathode MFC sensor can directly be used for formaldehyde detection (from 0.0005% to 0.005%) in both aerobic and anaerobic water bodies. Electrochemical analysis indicated that the response by the sensor was caused by the toxic inhibition to the microbial activity for the oxygen reduction reaction (ORR). This study for the first time demonstrated that the GD-biocathode MFC sensor has a detection limit of 20 ppm for formaldehyde and can be used to monitor air pollution. Selective sensitivity to formaldehyde was not achieved as the result of using a mixed-culture, which confirms that it can serve as a generic biosensor for monitoring gaseous pollutants. This study expands the realm of knowledge for MFC sensor applications.

1. Introduction

Environmental toxicity monitoring is important for the protection of public health and ecological safety. There has been a growing interest in developing microbial fuel cell (MFC) based sensors, as they self-generate electric signals with biodegradable substrates, provide real-time data, and are at low cost (Sun et al., 2015; Wang et al., 2015; Jiang et al., 2018). The traditional MFC sensor has a bioanode sensing element and has been used successfully for toxicity monitoring in anaerobic water. When using the bioanode sensing element, microorganisms conduct the outward extracellular electron transfer (EET) process by transferring electrons obtained from substrates to the anode (Pandey et al.,

* Corresponding author.
** Corresponding author.
E-mail addresses: liangpeng@tsinghua.edu.cn (P. Liang), zhiyong.ren@colorado.edu (Z.J. Ren).

https://doi.org/10.1016/j.chemosphere.2018.03.169
0045-6535/

2016; Kumar et al., 2017; Saratale et al., 2017; Zhao et al., 2018). The electric signal is obtained as the electrons further flow throughout an external circuit to the cathode. The presence of toxic compounds causes a decrease in microbial activity which causes the electric signal to change (Alaraj et al., 2014; Grattieri and Minteer, 2018). However, the bioanode sensing element can only be used for anaerobic water monitoring. In addition, its performance for toxicity monitoring is negatively affected by the variation in the concentration of organic matter (Jiang et al., 2016a, 2017c; Jin et al., 2016; ElMekawy et al., 2018). Our pervious study has proven that the use of a biocathode sensing element solved the problem of false negative due to the combined signals mixed with organic degradation and toxicity, and it achieved increased sensitivity (Jiang et al., 2017b). It is also known that microorganisms can conduct inward EET process by transferring electrons obtained from the cathode for oxygen reduction reaction (ORR) (Li et al., 2017). The working principle of the biocathode sensing element is that the presence of toxic compounds is expected to decrease the activity of microorganisms on the biocathode. The biocathode sensing element requires a sufficient supply of oxidants, such as oxygen, whereas the bioanode sensing element requires a sufficient supply of reductants, such as hydrocarbons.

External aeration (EA) is commonly used to supply oxygen for a biocathode via air sparging (Wu et al., 2016). However, the EA-biocathode MFC sensor was potentially restricted by the loss of volatile pollutants. Moreover, the method is energy intensive so is not suitable to achieve energy self-sustainability (Grattieri and Minteer, 2018). Although not designed for environmental monitoring, it shows that a MFC with a gas diffusion (GD) biocathode could produce a power density comparable to that of platinum (Xia et al., 2013; Lu et al., 2016).

In this study, a novel structure of GD-biocathode sensing element sensitive to the analyte was constructed. Bioanode separated by a piece of membrane was used as the counter electrode, which maintained the advantage of MFC sensor as a typical type of self-powered biosensor (Jiang et al., 2015; Grattieri and Minteer, 2018). Moreover, the performance of the GD-biocathode MFC sensor for gaseous pollution monitoring was further evaluated.

2. Materials and methods

2.1. MFC sensor construction and startup

The GD-biocathode sensing element was fabricated by the polarity reversion of the bioanode (Fig. 1a) to abstain sufficient biomass loading to catalyze the ORR (Cheng et al., 2009). Briefly, the cultivated bioanodes were assembled with commercial waterproof breathable membrane (WBM) (Ningbo Shanquan Building Material Co., Ltd., CHN) as the GD-biocathode sensing element (Xing et al., 2015). A pair of bioanode and GD-biocathode was installed into the two-chamber MFC sensor (7 mL for each chamber with a cross sectional area of 7 cm^2) (Fig. 1b). The EA-biocathode MFC sensor (Fig. 1c) was constructed as the control test by just replacing the WBM with a blind plate and using an air pump to supply oxygen into the catholyte.

For water monitoring, the MFC sensors were running with anolyte and catholyte with a feeding rate of 6 mL min^{-1} controlled by a peristaltic pump. The anolyte was prepared by dissolving 1 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 50 mM PBS solution (Lovley and Phillips, 1988; Jiang et al., 2016b). The catholyte was modified from the anolyte by replacing the sodium acetate with 1 g $NaHCO_3$. The anode and cathode were connected with an external resistor of 300 Ω with a data acquisition system. The 300 Ω of the external resistance was the optimized value, as the MFC sensor could only achieve a stable operation when the value of the external resistor was higher than this value (Huggins et al., 2015). A bottle contained 500 mL of anolyte was circulating with the anode chamber to keep a constant concentration of acetate.

For air monitoring, the GD-biocathode MFC sensor was further

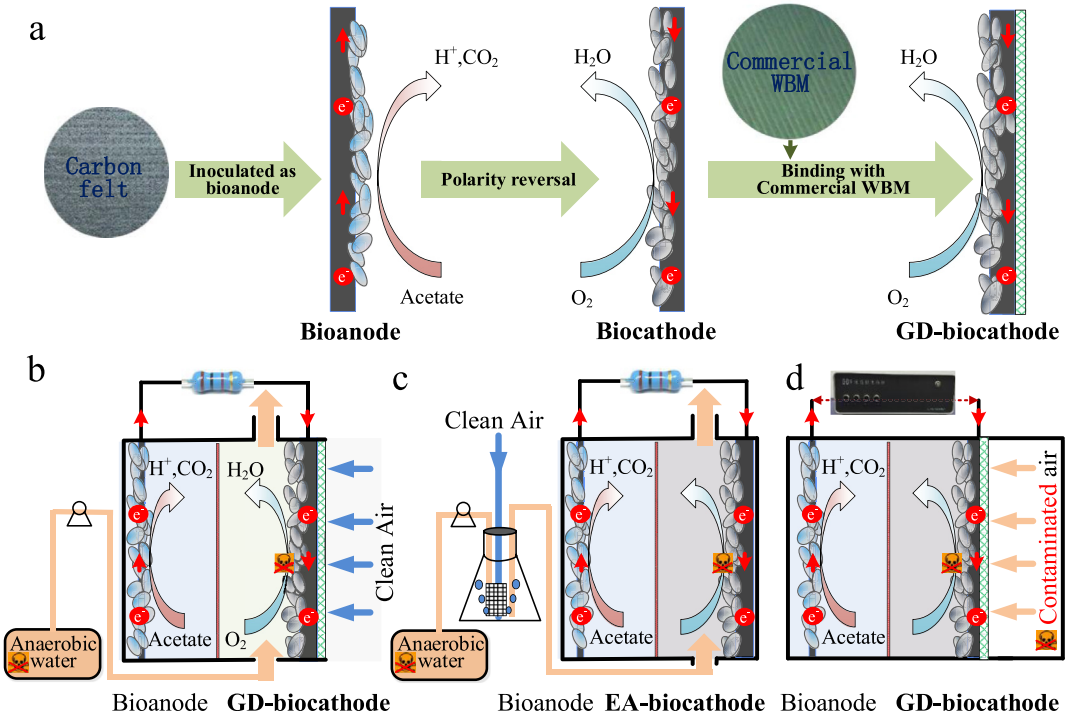


Fig. 1. The schematic illustration for the fabrication process of GD-biocathode (a). Water monitoring achieved by the GD-biocathode MFC sensor (b), and EA-biocathode MFC sensor (c). Air monitoring achieved by the GD-biocathode MFC sensor (d).

equipped with a 28 mL air-chamber for passive polluted air transfer (Fig. 1d). A glass bottle containing aqueous analyte solution was sealed on the bottom of the air-chamber, to obtain the polluted air with a defined concentration. No extra bottle or pump was connected to the MFC sensor to avoid the dilution of gaseous pollution. It should be noted that a potentiostat (CHI 1000B, Chenhua Co., Shanghai, China) with higher sensitivity for electric current measurement was applied here for air monitoring, because the output electric current was limited by the stop of water disturbance. All MFC sensor reactors were run in duplicate.

2.2. Biosensor tests

Formaldehyde was selected as the model toxic agent, as it was frequently used in studies of both water and air monitoring (Li et al., 2016; Szulejko and Kim, 2016). The water contamination was created by adding formaldehyde with final concentrations from 0.0005% to 0.005% (weight/weight) into the continuous flow of catholyte. The catholyte was bubbled with air gas and nitrogen gas, respectively, to simulate aerobic (dissolved oxygen, DO > 6 mg L^{-1}) and anaerobic (DO < 0.5 mg L^{-1}) conditions. The air pollution was created by the headspace above the aqueous solutions, with the concentration calculated from the concentration in solution according to the respective Henry constants at room temperature (Dong and Dasgupta, 1986; Hämmerle et al., 2010).

2.3. Electrochemical analyses and calculations

The electrochemical activity of the biocathode was investigated by cyclic voltammetry (CV, scan rate: 1 mV s^{-1}). The current change (ΔI) and inhibition ratio (IR) were defined as the current drop, and the percentage of current drop, respectively (Shen et al., 2013).

3. Results and discussion

3.1. MFC sensor for water monitoring

The EA-biocathode MFC sensor could be effectively used for aerobic water monitoring, as evidenced by a decrease of output current density when challenging with formaldehyde from 0.0005% to 0.005% (Fig. 2a). In contrast, when using EA-biocathode MFC sensor for anaerobic water monitoring, the output current signal was negligible, and no response was observed. The GD-biocathode MFC sensor could be used for formaldehyde detection in both aerobic and anaerobic water (Fig. 2b). This was attributed to the outstanding performance of WBM for passive oxygen transfer (Xing et al., 2015). The enhancement of baseline current signal output using GD-biocathode MFC sensor was in agreement with the polarization curves and power density curves (Fig. SM-1), and also the current output in steady state (Fig. SM-2), respectively. It was shown that an enhancement of baseline current signal output could not necessarily promote an increase in current change (ΔI) from the MFC sensor (Fig. 2c). However, the use of GD-biocathode MFC sensor clearly shows that as pollutant concentrations increase ΔI also increases, which was important for quantitative monitoring (Jiang et al., 2017a; Prévoteau and Rabaey, 2017; Zeng et al., 2017). For instance, the ΔI of GD-bicathode was increased from 0.011 ± 0.002 to 0.016 ± 0.009 mA, with the formaldehyde

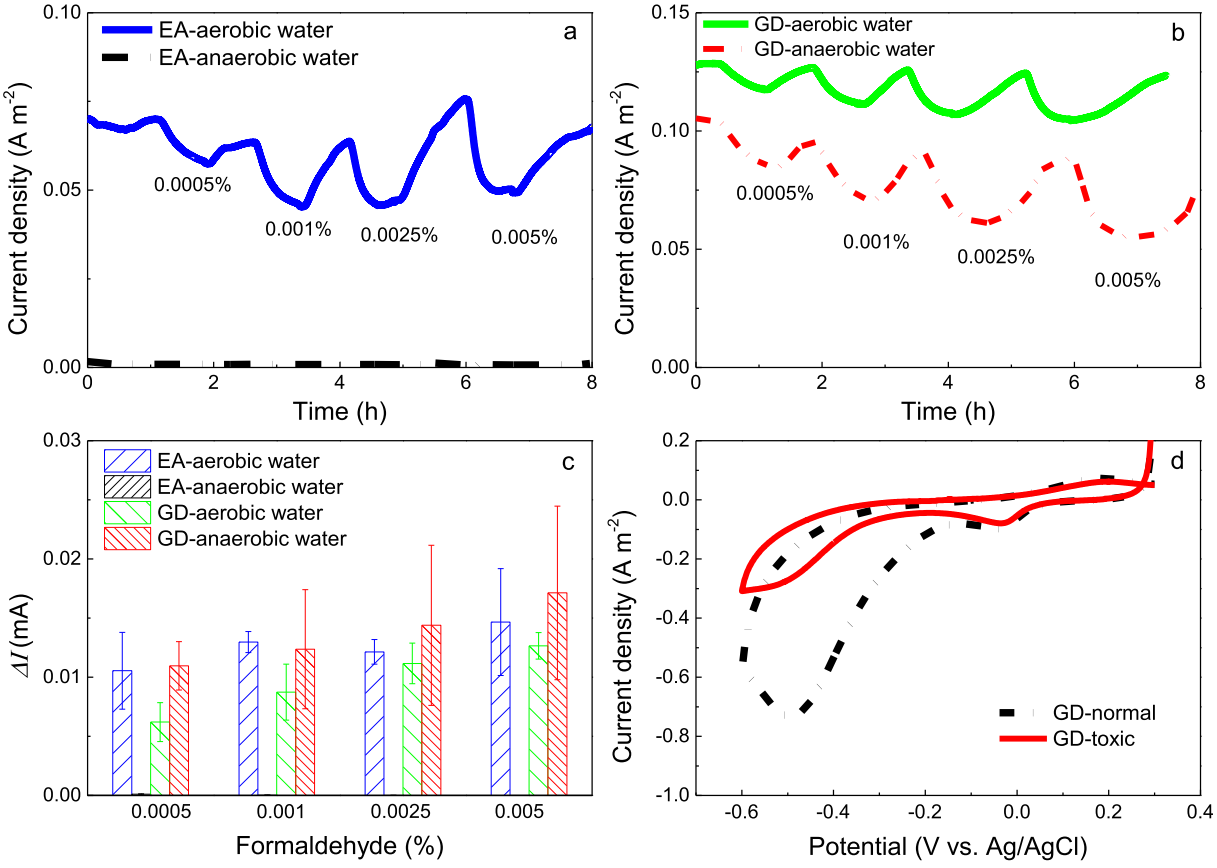


Fig. 2. The output electric signal during formaldehyde detection in both aerobic and anaerobic water using EA-biocathode (a) and GD-biocathode MFC (b). The current change (ΔI) observed with different concentrations of formaldehyde (c). The cyclic voltammetry (CV) curves of GD-biocathode before and after formaldehyde adding (d). The standard deviation is reported by double-experiments running in parallel.

concentration increased from 0.0005% to 0.005% in anaerobic water sample. The CV curves further indicated that the response of GD-biocathode MFC sensor to formaldehyde was caused by the toxic inhibition to the microbial activity for oxygen reduction reaction (ORR) (Fig. 2d). The standard deviations generated by double-experiments running in parallel are high and the results agree with previous studies (Li et al., 2016; Yang et al., 2016). The standard deviations could be reduced by optimizing the structure of the reactor (Jiang et al., 2017c).

3.2. MFC sensor for air monitoring

The response of the GD-biocathode MFC sensor to different concentrations of formaldehyde, reported as ppm (as volume) in the headspace of the air-chamber, was evaluated (Fig. 3). When exposed to 20 ppm of formaldehyde, the MFC sensors showed a quick response with a maximum *IR* increase to 27.0% after 60 min of exposure duration (Fig. 3a). The *IR* further increased to 45.8% when the formaldehyde increased to 35 ppm. The GD-biocathode MFC sensor could also serve as a generic biosensor for determination of other gaseous pollutants such as dichloromethane and ethyl alcohol, within 10 min of exposure duration (Fig. 3b). However, the repeatability of the GD-biocathode MFC sensor was limited based on its present configuration and operation mode (Fig. SM-3). In the third exposure duration, no response to 35 ppm of formaldehyde was observed, and it could only respond to formaldehyde present at much higher concentrations. This was mostly due to the fact of the formaldehyde molecules failing to be eliminated from the three-phase reaction interface without water disturbance in a timely manner (Yang et al., 2016).

In this study, the bioanode was integrated into the self-powered MFC sensor with the biocathode sensing element. In real-world applications, the use of the large ratio of anolyte volume/catholyte volume could also be adopted, to avoid the negative influence caused by the consumption of organic matter. Moreover, it could be simpler to use a counter electrode or a polarized system with a given abiotic counter reaction (e.g. zinc oxidation and water oxidation) to solve the potential problem of varying electron donor concentrations. In addition, the optimization of the configuration and operating mode was further required to increase the repeatability of the GD-biocathode MFC sensor.

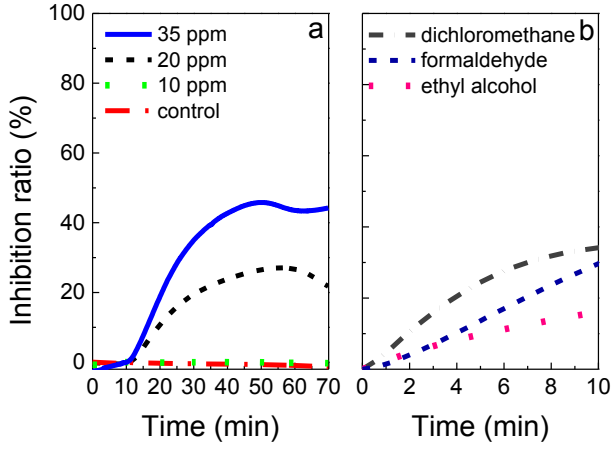


Fig. 3. The response of GD-biocathode MFC sensor to different concentration of formaldehyde, reported as ppm (as volume) in the headspace of the air-chamber (a). The MFC sensor for quantitative detection, by putting a drop of pure dichloromethane, formaldehyde (37 wt% commercial solution), and pure ethyl alcohol, respectively, into the air-chamber for volatilization (b).

4. Conclusion

A novel GD-biocathode sensing element was fabricated using a simple method. The GD-biocathode MFC sensor can be used for formaldehyde detection in both aerobic and anaerobic water. This study for the first time demonstrated that the GD-biocathode MFC sensor has a detection limit of 20 ppm for formaldehyde and can be used to monitor air pollution. Further work would include optimizing the structure to increase the repeatability.

Acknowledgments

This work was supported by the National Science Foundation of China (NSFC No. 51778324, 51422810), and Chinese Scholarship Council (CSC) State Scholarship Fund of China. We thank Mr. Scott Singer for his comments and text editing to improve the English level.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.03.169.

References

Alaraj, M., Ren, Z.J., Park, J.-D., 2014. Microbial fuel cell energy harvesting using synchronous flyback converter. J. Power Sources 247, 636–642.
Cheng, K.Y., Ho, G., Cord-Ruwisch, R., 2009. Anodophilic biofilm catalyzes cathodic oxygen reduction. Environ. Sci. Technol. 44, 518–525.
Dong, S., Dasgupta, P.K., 1986. Solubility of gaseous formaldehyde in liquid water and generation of trace standard gaseous formaldehyde. Environ. Sci. Technol. 20, 637–640.
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, 302–313.
Grattieri, M., Minteer, S.D., 2018. Self-powered biosensors. ACS Sens. 3, 44–53.
Hämmerle, M., Hilgert, K., Achmann, S., Moos, R., 2010. Direct monitoring of organic vapours with amperometric enzyme gas sensors. Biosens. Bioelectron. 25, 1521–1525.
Huggins, T.M., Pietron, J.J., Wang, H., Ren, Z.J., Biffinger, J.C., 2015. Graphitic biochar as a cathode electrocatalyst support for microbial fuel cells. Bioresour. Technol. 195, 147–153.
Jiang, Y., Liang, P., Liu, P., Bian, Y., Miao, B., Sun, X., Zhang, H., Huang, X., 2016a. Enhancing signal output and avoiding BOD/toxicity combined shock interference by operating a microbial fuel cell sensor with an optimized background concentration of organic matter. Int. J. Mol. Sci. 17, 1392.
Jiang, Y., Liang, P., Liu, P., Miao, B., Bian, Y., Zhang, H., Huang, X., 2017a. Enhancement of the sensitivity of a microbial fuel cell sensor by transient-state operation. Environ. Sci.: Water Res. Technol. 3, 472–479.
Jiang, Y., Liang, P., Liu, P., Wang, D., Miao, B., Huang, X., 2017b. A novel microbial fuel cell sensor with biocathode sensing element. Biosens. Bioelectron. 94, 344–350.
Jiang, Y., Liang, P., Liu, P., Yan, X., Bian, Y., Huang, X., 2017c. A cathode-shared microbial fuel cell sensor array for water alert system. Int. J. Hydrogen Energy 42, 4342–4348.
Jiang, Y., Liang, P., Zhang, C., Bian, Y., Sun, X., Zhang, H., Yang, X., Zhao, F., Huang, X., 2016b. Periodic polarity reversal for stabilizing the pH in two-chamber microbial electrolysis cells. Appl. Energy 165, 670–675.
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. Renew. Sustain. Energy Rev. 81, 292–305.
Jin, X., Angelidaki, I., Zhang, Y., 2016. Microbial electrochemical monitoring of volatile fatty acids during anaerobic digestion. Environ. Sci. Technol. 50, 4422–4429.
Kumar, G., Saratale, R.G., Kadier, A., Sivagurunathan, P., Zhen, G., Kim, S.H., Saratale, G.D., 2017. A review on bio-electrochemical systems (BESs) for the syngas and value added biochemicals production. Chemosphere 177, 84–92.
Li, F., Zheng, Z., Yang, B., Zhang, X., Li, Z., Lei, L., 2016. A laminar-flow based microfluidic microbial three-electrode cell for biosensing. Electrochim. Acta 199, 45–50.
Li, X., Lu, Y., Luo, H., Liu, G., Zhang, R., 2017. Microbial stratification structure within cathodic biofilm of the microbial fuel cell using the freezing microtome method. Bioresour. Technol. 241, 384–390.

Lovley, D.R., Phillips, E.J., 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Appl. Environ. Microbiol. 54, 1472–1480.
Lu, L., Hou, D., Wang, X., Jassby, D., Ren, Z.J., 2016. Active H_2 harvesting prevents methanogenesis in microbial electrolysis cells. Environ. Sci. Technol. Lett. 3, 286–290.
Pandey, P., Shinde, V.N., Deopurkar, R.L., Kale, S.P., Patil, S.A., Pant, D., 2016. Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery. Appl. Energy 168, 706–723.
Prévoteau, A., Rabaey, K., 2017. Electroactive biofilms for sensing: reflections and perspectives. ACS Sens. 2, 1072–1085.
Saratale, R.G., Saratale, G.D., Pugazhendhi, A., Zhen, G., Kumar, G., Kadier, A., Sivagurunathan, P., 2017. Microbiome involved in microbial electrochemical systems (MESs): a review. Chemosphere 177, 176–188.
Shen, Y.J., 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.
Sun, J.Z., 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. Water Sci. Technol. 71, 801–809.
Szulejko, J.E., Kim, K.-H., 2016. A practical approach to estimate emission rates of indoor air pollutants due to the use of personal combustible products based on small-chamber studies. Chemosphere 144, 1451–1458.
Wang, H., Luo, H., Fallgren, P.H., Jin, S., Ren, Z.J., 2015. Bioelectrochemical system platform for sustainable environmental remediation and energy generation. Biotechnol. Adv. 33, 317–334.
Wu, S., Li, H., Zhou, X., Liang, P., Zhang, X., Jiang, Y., Huang, X., 2016. A novel pilot-scale stacked microbial fuel cell for efficient electricity generation and wastewater treatment. Water Res. 98, 396–403.
Xia, X., Tokash, J.C., Zhang, F., Liang, P., Huang, X., Logan, B.E., 2013. Oxygen-reducing biocathodes operating with passive oxygen transfer in microbial fuel cells. Environ. Sci. Technol. 47, 2085–2091.
Xing, D., Tang, Y., Mei, X., Liu, B., 2015. Electricity generation of microbial fuel cell with waterproof breathable membrane cathode. J. Power Sources 300, 491–495.
Yang, W., Wei, X., Fraiwan, A., Coogan, C.G., Lee, H., Choi, S., 2016. Fast and sensitive water quality assessment: a μL-scale microbial fuel cell-based biosensor integrated with an air-bubble trap and electrochemical sensing functionality. Sensor. Actuator. B Chem. 226, 191–195.
Zeng, L., Li, X., Shi, Y., Qi, Y., Huang, D., Tade, M., Wang, S., Liu, S., 2017. $FePO_4$ based single chamber air-cathode microbial fuel cell for online monitoring levofloxacin. Biosens. Bioelectron. 91, 367–373.
Zhao, N., Li, X., Jin, X., Angelidaki, I., Zhang, Y., 2018. Integrated electrochemical-biological process as an alternative mean for ammonia monitoring during anaerobic digestion of organic wastes. Chemosphere 195, 735–741.