Chemosphere 264 (2021) 128532

Contents lists available at ScienceDirect

Chemosphere

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

Short Communication

Revisiting the bioelectrochemical system based biosensor for organic sensing and the prospect on constructed wetland-microbial fuel cell

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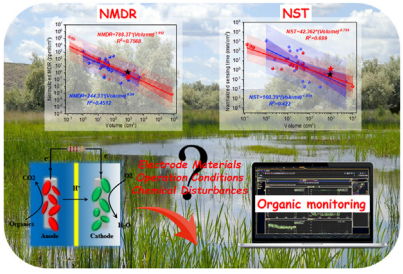
HIGHLIGHTS

- NMDR and NST are proposed as the criteria for BES based biosensor.
- Anodic material can significantly affect NMDR and NST of CW-MFC.
- Operation mode and HRT determine directly the NMDR and NST of CW-MFC.
- Normalized toxicity should be considered in CW-MFC based biosensor.
- Reduction potential of the disturbance plays a critical role in biosignal production.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 March 2020
Received in revised form
11 August 2020
Accepted 2 October 2020
Available online 5 October 2020

Handling Editor: Chang- Ping Yu

Keywords:
Constructed wetland
Bioelectrochemical system
Organic sensing
Normalization
Anodic material
Chemical shock

ABSTRACT

Bioelectrochemical system (BES) based biosensors for organic sensing has long been investigated. However, there is no uniform criterion to evaluate directly the performance of the BES based biosensors due to their different scale. Here, for the first time, we show that the normalized maximum detection range (NMDR) and normalized sensing time (NST) can potentially be used as the two criteria in BES based biosensors for organic sensing. Thereafter, the recently emerged, relatively larger scale BES (i.e. constructed wetland-microbial fuel cell, CW-MFC) was specifically examined in this study. The biocathode formation and the influence of anodic material on sensor performance were systematically evaluated. The system with metal-based anode was found to produce a more stable and quicker response (low NST) than that with carbon-based anode. Significantly, the continuous loading mode was found to greatly reduce the NMDR compared to the batch mode, and the hydraulic residence time (HRT) is the critical factor determining the NMDR. Furthermore, it was found that the electrical signals generated from the CW-MFC system were insignificantly influenced by some specific chemical disturbances, such as Cu^{2+} and herbicide. Therefore, normalized toxicity (NT) is suggested to be considered in BES based biosensor. However, for chemicals with higher reduction potentials (NO_3^- in this work), the system presented a high response, enabling its potential for monitoring NO_3^- in effluents or groundwater. This study can hopefully contribute to further development of the sustainable BES based biosensors in CW.

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https://doi.org/10.1016/j.chemosphere.2020.128532
0045-6535/

1. Introduction

Self-sustained technologies can be worked independently without reliance on power supply, and therefore play a significant role in future sustainable society development (Wang, 2013; Xu et al., 2016; Conzuelo et al., 2018). Among these, bio-electrochemical system (BES, including microbial fuel cell (MFC) and microbial electrolysis cell (MEC)) for organic sensing comes up as a strong competitor to traditional cumbersome methodologies, for example, the dichromate colorimetric method (Greenberg et al., 1992; Xu et al., 2017). Related publications show that there is an increasing popularity of trying BES as the biosensor for organic sensing in recent years (Fig. 1a, Table S1). (Abrevaya et al., 2015a, 2015b; Jiang et al., 2018) The principle of BES based biosensor can normally be expressed as: Current (or coulomb) ∝ Substrate concentration (biodegradable substrate). Therefore, the level of biodegradable organics in water samples can be directly transferred into digital signals, which is much convenient for *in-situ* monitoring. During the organic sensing process, the electrode (usually the anode) is the key component in BES as the solid electron acceptor. Different materials were utilized before (Fig. 1b, Table S1), however, no systematic work has been conducted to investigate the influence of electrode material on organic sensing performance of a BES based biosensor and this will be specifically studied here.

Generally, the detection range and response time of BES based biosensor are two of the main parameters to judge its feasibility in a practical application. It can be speculated that these two factors could be influenced by the system scale. However, the plot of the maximum detection range (MDR) or sensing time (ST) *versus* sensing chamber volume indicates no correlation between either of them (Figures S1a and S1c). Therefore, unveiling or establishing some criteria, to evaluate the performance or guide the fabrication of BES based biosensors, is indispensable. Herein, the normalized MDR (NMDR) and sensing time (NST) (normalized to the sensing electrode chamber volume, normally the anodic chamber volume (chamber volume for short)) are proposed, in order to obtain the relationship between either of them to the system scale:

$$Normalized\ MDR = MDR / Chamber\ volume$$

$$Normalized\ Sensing\ Time = Sensing\ time / Chamber\ volume$$

Replotting of the normalized data showed that the NMDR correlates to the sensing chamber volume (continuous mode: R^2 (Xu et al., 2016) = 0.7568, batch mode: R^2 (Xu et al., 2016) = 0.4512, batch and continuous modes together: R^2 (Xu et al., 2016) = 0.6547) (Fig. 1c and S1b, the plots being discussed are a graphical summarization of the data in the publications indicated in Table S1). In

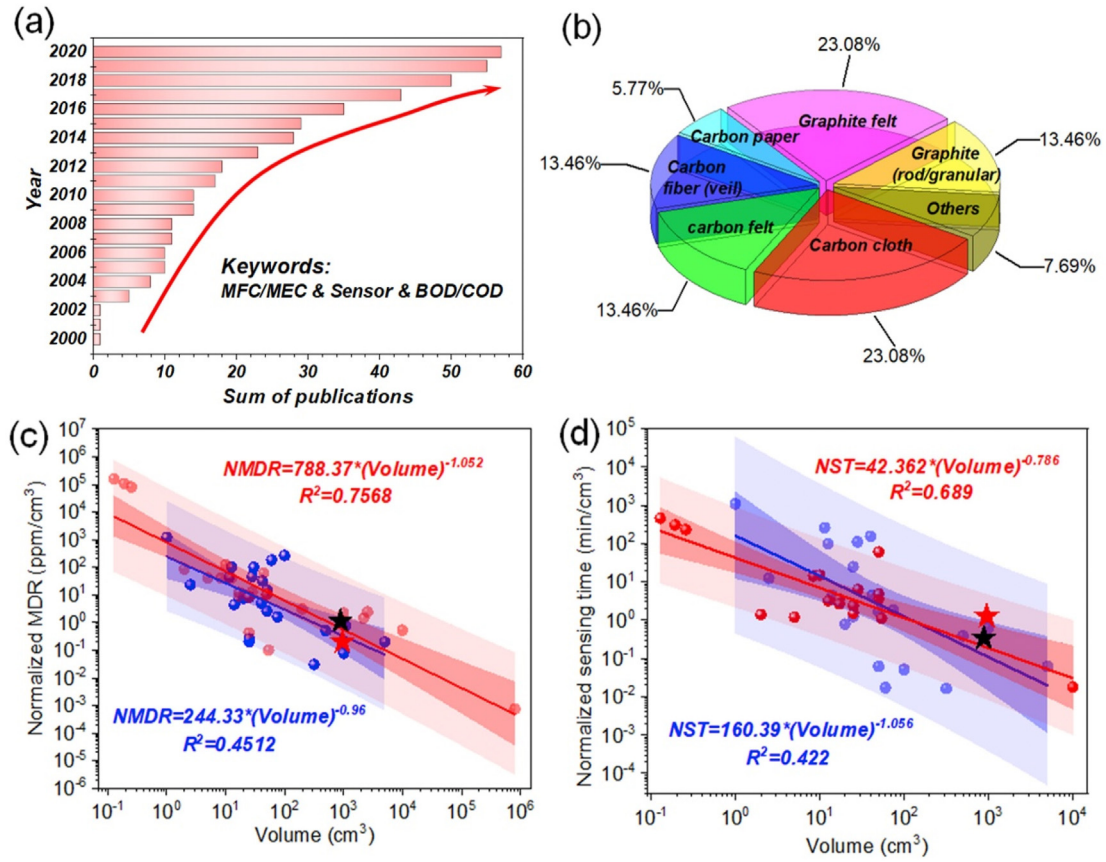

Fig. 1. (a) The number of publications concerning BES based COD/BOD biosensors since 2000 (publication data was accessed on August 8th, 2020, with "Keywords = (microbial fuel cell OR microbial electrolysis cell AND sensor AND BOD OR COD)" in Web of Science, unrelated and review papers were manually excluded); (b) relative use (%) of different anodic materials described in the publications listed in Table S1; (c, d) variation of the normalized maximum detection value of COD/BOD (c) and the normalized response time (d) of the BES based biosensor, with chamber volume, as described in the publications listed in Table S1 (Red and blue color represent continuous and batch loading mode, respectively; the light and dark shadows represent 95% prediction and 95% confidence bands, respectively; the black (Xu et al., 2017) and red (Corbella et al., 2019) stars represent the data derived from the published works on CW-MFC. It can be seen that the black star performs better than the red star regarding its higher NMDR and lower NST. In addition, it can also be observed that NMDR of the black star is above the prediction level while the red star is below the prediction level. In terms of the NST, both of them have higher NST than the prediction level, indicating their performance should be further optimized regarding the sensing time). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

terms of the NST, a similar trend can be obtained as well (Fig. 1d and S1d). Additionally, it is also noteworthy that none or weak correlation was observed when the MDR or ST normalized to the sensing electrode surface area, indicating this kind of relationship (the correlation between NMDR/NST and chamber volume) is not arbitrary (Figure S2). Hence, it is reasonable to consider the NMDR and NST as the potential criteria to evaluate the performance of the BES based biosensors for organic sensing, especially for the continuous loading system.

With these considerations in mind, the recently emerged, relatively larger scale BES (i.e. constructed wetland-microbial fuel cell, CW-MFC (Yadav et al., 2012; Zhao et al., 2013)) was specifically examined in this study. For CWs, they also belong to green sustainable facilities and are receiving increasing attention as a low impact development (LID) technique for wastewater treatment (Vymazal, 2013; Zhang et al., 2014), especially in China due to the initiative of "sponge city" concept. The integration between CW and MFC greatly broadened the potential application of BES-CW for future sustainable wastewater treatment (Xu et al., 2019). Other than the improved treatment efficiency, the prospect of applying CW-MFC for organic sensing will be specifically investigated in this study. Previous work has verified the viability of CW-MFC as a biosensor for organic sensing (Xu et al., 2017; Corbella et al., 2019). Therefore, this won't be the aim of this study. Two practical points will be investigated here: 1) Influence of the material of the solid electron acceptor (i.e. the anode) on the performance of CW-MFC for organic sensing, and 2) Impact of the operation conditions (e.g. HRT or chemical disturbances) on the biosignal production of CW-MFC during organic sensing. It is believed that this work provides further, valuable insights into the potential sensing application of BES based biosensor in CW, i.e. to develop a mini CW-MFC and possibly apply for a large CW system for remote monitoring its performance without any chemicals involved.

2. Materials and methods

2.1. Bench-scale batch mode CW-MFC system

A batch reactor was employed based on a cylindrical bucket with the dimensions of φ 600 × 400 mm (Figure S3). Three parallel systems with the same anodic chamber volume but different anodic materials were examined to investigate the influence of electrode material on the electrical signal production. Detailed descriptions for the arrangement of the system can be found in the Supplementary Information (SI). Before the operation, both the anode and cathode were inoculated with activated sludge sourced from Malahide Wastewater Treatment Plant, Dublin. The composition of the synthetic wastewater fed to the reactor in each batch was similar to that used and reported in our previous study (Xu et al., 2017), while the COD of the anolyte was 1000 mg/L (sodium acetate (NaAc) as the carbon source). The duration for the batch mode operation is around two months.

2.2. Bench-scale continuous flow mode CW-MFC system

For the continuous sensing trials, the reactor was adapted from one of our previous works (Xu et al., 2017). The synthetic wastewater (using the same composition as described above) with targeted COD concentration or chemical disturbance (for herbicide, details can be found in Table S2, SI) was fed to the reactor via an upflow regime. The HRT of the system was controlled via peristaltic pumps. The duration for the continuous flow mode operation is around one month.

All the experiments were conducted in the laboratory at room temperature (20 ± 2 °C).

2.3. Data measurement and analysis

During the sensing tests, the COD concentration was determined using the COD kit with HACH DR/2400 spectrophotometer according to its standard operating procedures. The electrical signal produced from either batch or continuous mode was recorded via a data acquisition system (USB-6000, National Instrument, USA) in terms of the voltage drop (U, in units of V) across the external resistor (R = 1000 Ω). Power densities ($P = U^2$ (Xu et al., 2016)/ RV_{aev}, mW/m^3) were determined through basic electrical calculations, where V_{aev} is the anodic chamber volume (m^3). To obtain the polarization curve, the external resistance was varied over a range from 20 Ω to 580 KΩ and the steady-state voltage across the resistors was measured. The electrode potentials were determined against a saturated Ag/AgCl electrode (Mettler Toledo, +0.197 V vs Standard Hydrogen Electrode (SHE)). OriginPro 2018 (OriginLab, Northampton, Massachusetts, USA) was used for all statistics.

3. Results and discussion

3.1. Biocathode formation and the role of electrode material in CW-MFC during batch-mode organic sensing

To obtain reliable sensing results, stable cathodic performance is extremely important during the organic sensing process. After the inoculation, the cathodic potential (V_{ca}) was continuously monitored throughout the experiment and the results showed that the process of biocathode formation is highly consistent with the microbial growth curve (Fig. 2a), indicating the microbial governed oxygen reduction process. A recent study showed that microbial growth is a thermodynamic process and its equation was found relying on an explicit theoretical ground sustained by Boltzmann statistics (Desmond-Le Quemener and Bouchez, 2014). Herein, the curve ($V_{ca}(T)$) was constructed by fitting experiment data points with a modified Boltzmann equation (Fig. 2a, R^2 (Xu et al., 2016) = 0.977 and Equation S1) and the equilibrium cathodic potential (V_{max}) was found to be 322.21 mV, with $V_{T_{1/2}}$ = 143.03 mV and $S_{T_{1/2}}$ = 37.33, respectively (see SI), after around 1 month operation. The stable equilibrium potential provides a reliable reference to investigate the influence of different anodic materials on biosignal production.

Sharing the same cathode, it can be seen that the circuit with SSM based anode produced the highest average voltage (364.3 mV on day 1–348.83 mV on day 5), followed by the GF based anode and then the CFB based anode (Fig. 2b to d). Polarization curves also showed the same trend (Fig. 2e) and the electrode potential measurements of each system further revealed that the differences were ascribed to the anode (Fig. 2f). The system with the SSM as the anode had the lowest anodic potential losses, while CFB presented the highest energy losses.

From the results of the residual COD concentration in the respective anodic chamber (at the end of each batch test) (Figure S4) and the continuous monitoring of the anodic potential (Figure S5), it can be understood that the oxidative kinetic for organics directly influenced the bioelectricity generation. As indicated in our previous work, the reduction of organic concentration can increase the mass transfer energy losses, limiting the rate of the anodic oxidation reaction and therefore elevate the anodic electrode potential (Xu et al., 2017). Though the three parallel systems have the same anodic chamber volume, for the CFB, its higher specific surface area enables the exoelectrogens which acclimated on the anode having a greater removal efficiency of organic substances than SSM, and which therefore presented the lowest anodic potential after a particular period of organic degradation.

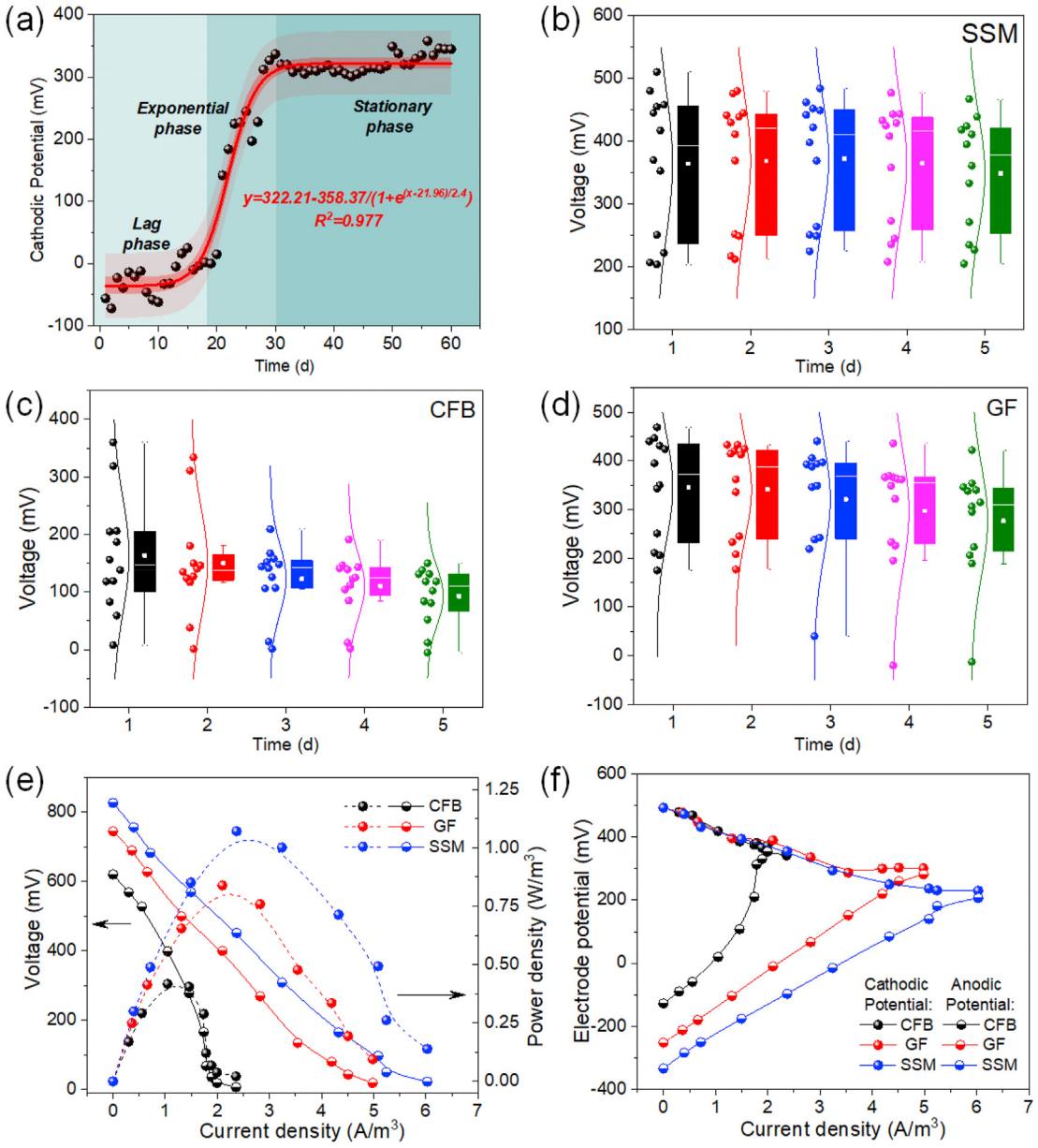

Fig. 2. (a) The evolution of the cathodic potential with the period of system operation (the overall period can be divided into three phases: lag phase, exponential phase, and stationary phase). (b–d) The output voltage of each circuit with different anodic materials throughout the 12 batches, where each batch operated for 5 days and each figure shows the values from day 1 to day 5; (e, f) polarization test (i.e. changes in power density (e) and electrode potential (f)) of each circuit with different anodic materials at the end of the operation (SSM: stainless steel mesh; CFB: carbon fiber brush; GF: graphite felt).

Therefore, it is believed that the electrode material can significantly influence the NMDR and NST, and the performance evaluations between different systems should keep this in mind.

Metal-based anodic materials have been shown to be high-performing alternatives to carbon-based materials in BES (Baudler et al., 2015). However, most previous studies of BES based biosensors for organics in wastewaters employed graphite or carbon-based anodic materials (over 90%, Fig. 1b). Compared to the carbon-based materials, metal-based electrode materials could sustain a longer stable electrical output due to the slow oxidative kinetic for organics (the slow oxidative kinetic for organics only relates to the signal duration rather than the sensor sensitivity). Furthermore, it was observed that the system with SSM as the anode had a much faster response (representing lower NST) compared to systems using CFB or GF as the anodic material (Figure S5). The prospect of utilizing metal-based anodic materials in a CW-MFC system for organic sensing is encouraging and therefore further evaluation is recommended in the future.

3.2. Continuous loading CW-MFC system for organic sensing: influence of HRT and chemical disturbances

The performance of the CW-MFC system for organic sensing was further evaluated under continuous loading mode. Significantly, compared to the batch mode, the system operated under the continuous loading mode has a much lower NMDR (decreased from 1.13 to 0.11 ppm/cm^3 at HRT of 5 h and further decreased to 0.06 ppm/cm^3 at HRT of 2.5 h). More specifically, at an HRT of 5 h, the system has a saturated COD concentration of 100 ppm (above which the anodic potential will keep constant, red and blue parts,

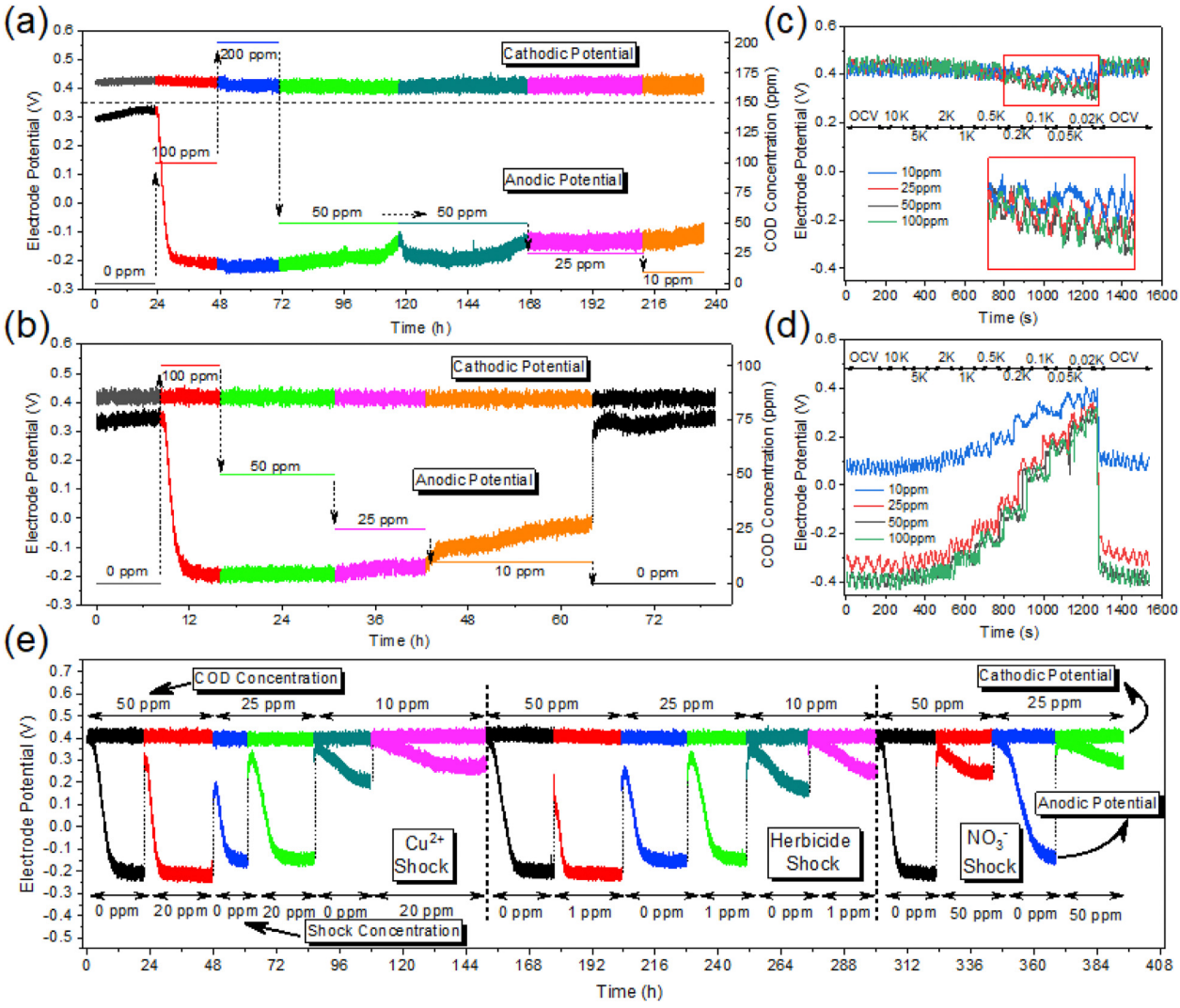

Fig. 3. CW-MFC system for organic sensing under continuous loading mode: (a) electrode potential changes at different influent COD concentrations, HRT = 5 h (the sharp decrease of anodic potential after around 2 day's operation (at about the 120th h) with the feeding COD concentration of 50 ppm could be ascribed to the autolysis and degradation of the stocked feeding solution and once the influent was renewed, the anodic potential gradually recovered to its original level); (b) electrode potential changes at different influent COD concentrations, HRT = 2.5 h; (c, d) the corresponding polarization test with different influent COD concentrations at HRT of 2.5 h (inset in c, magnified version of the region highlighted with a red square); (e) the influence of different chemical disturbances (Cu^{2+}, herbicide, and NO_3^-) on CW-MFC based biosensor for organic sensing at different COD concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3a), with a stable anodic potential of around −220 mV. Reducing the influent COD to 50 ppm tended to decrease the anodic potential with increasing operation time (green and dark cyan parts, Fig. 3a), and with the further reduction of COD to 25 ppm, the average anodic potential declined to approximately −135 mV (magenta part, Fig. 3a). Further decrease of the influent COD to 10 ppm, led to a gradual declining trend in the average anodic potential from about −130 to around −105 mV within 24 h (orange part, Fig. 3a).

When the HRT decreased to 2.5 h (Fig. 3b), the response of the system was found to be different. At a COD concentration of 50 ppm, the anodic potential showed a comparatively stable average value of around −193 mV. A reduction in the COD to 25 ppm only slightly reduced the anodic potential to an average value of −175 mV. However, when the influent COD decreased to 10 ppm, the average anodic potential sharply decreased from about −145 to only around −20 mV within 22 h. The electrode potentials during the polarization tests indicated that the disparity of cathodic potentials only appeared when the external resistance was lower than 200 Ω at a COD concentration of 10 ppm, which could be ascribed largely to the elevated anodic potential at the low COD concentration (Fig. 3c and d). In terms of the anodic potential, it can be seen that when the COD concentration was lower than 50 ppm, its value gradually decreased as revealed by the output voltage, especially at COD concentrations lower than 25 ppm (Fig. 3d). Therefore, given these results, it can be concluded that a shorter HRT can give a quicker response (low NST). However, a higher flow rate will provide the anodic exoelectrogens more organics within a certain time and therefore narrow the NMDR of the system.

The response of the CW-MFC system to three different chemical disturbances (i.e. heavy metal ion: Cu^{2+}, herbicide (Table S2) and NO_3^-) was investigated at an HRT of 2.5 h to examine its stability (Fig. 3e). It can be seen that the disturbances of Cu^{2+} (20 ppm) and herbicide (1 ppm) didn't have a significant influence on anodic potential when the influent COD was higher than 25 ppm, and only slightly reduced the anodic potential when the COD concentration declined to 10 ppm. These results are in contrast to some previously

published studies (Feng et al., 2013; Shen et al., 2013), where for example, Shen et al. revealed that 7 ppm of Cu^{2+} induced an inhibition ratio of 85% (for the voltage output) at a low flow rate (1.3 mL/min, background COD: 300–400 ppm) (Shen et al., 2013). In addition, Jiang et al. reported that Cu^{2+} inhibited the biocurrent generation with a background NaAc concentration of 5.0 mM (COD of approximately 320 ppm) (Jiang et al., 2016). Furthermore, the presence of an herbicide (atrazine as the effective component) at 1 ppm was also found to inhibit around 10% of the current production even when the background KAc concentration was as high as 100 mM (Chouler and Di Lorenzo, 2019). The different responses to Cu^{2+} and herbicide between our tests and previously published studies could result from the system scale. In the studies conducted by Shen et al. and Chouler and Di Lorenzo, the reactor volume was 28 mL and 128 μL, respectively (Shen et al., 2013; Chouler and Di Lorenzo, 2019). It is possible that the higher normalized toxicity (NT, concentration of disturbance/sensing chamber volume) makes the small scale system more sensitive to the disturbances (in the two aforementioned cases, the NT were 0.18 and 7.81 ppm/cm (Conzuelo et al., 2018), respectively, and the NT were only 0.02 and 0.001 ppm/cm^3 for Cu^{2+} and herbicide in this study). Therefore, the larger anodic volume of CW-MFC could make it more resistant to the toxic disturbances.

In the case of a NO_3^- chemical disturbance, it can drastically reduce the anodic potential (over 400 mV) at a COD concentration of either 50 or 25 ppm. A previous study conducted by Wang et al. revealed that at a low NaAc concentration (1 mM), the nitrate would result in a substantial voltage drop (Wang et al., 2018). However, an increased NaAc concentration (5 mM) could reduce the corresponding response in an open-circuit condition and fully mask the response when the circuit is closed, which could be ascribed to the provision of electrons from the oxidation of organics via exoelectrogens (details from the reduction potential perspective will be discussed later). This could also be a partial reason for the negligible effect of NO_3^- on voltage production observed from a single chamber cubic MFC biosensor (with NO_3^- concentration from 1 to 48 mg/L, 200 mg/L NaAc) (Liu et al., 2014).

3.3. Implications and future perspectives

The potential of applying CW-MFC for organic sensing opens a new scope for the development of CW-MFC system. However, due to its comparatively larger dimension, the electrical signal generated could be different from those of a small scale BES. Here, for the first time, the NMDR and NST of the BES based biosensors for organics were proposed and they were found to be correlated to the scale. Based on which, the NMDR and NST of a BES based biosensor with a designed scale for organic sensing can be roughly predicted, and for different systems, it can tell whether their performance is above or below the prediction level (as shown in Fig. 1 and S1), which is of great significance.

The characteristic of the continuous CW-MFC system makes it a suitable method of detecting excessive organic matter in the natural environment or secondary effluents from wastewater treatment plants (lower NMDR). For example, in China, the First Grade A standards for the quality of discharges from municipal wastewater treatment plants require COD $\leq$50 ppm, and the Grade I to V of Environmental quality standards for surface water require COD $\leq$15–40 ppm (China. and Discharge st, 2002a; China. and Environmenta, 2002b). Therefore, with the adjustment of the HRT, the CW-MFC could be applied as a sensor for different COD levels, which will also be of significant environmental benefit.

The air biocathode was verified to be viable both in batch and continuous modes, and therefore this could be the most favorable option for a CW-MFC based biosensor. With regard to the anodic material, metal-based anodic materials in CW-MFC based biosensors are recommended for further investigation in the future due to their production of relatively stable electrical signals and quicker response (lower NST), which is vital for a reliable biosensor.

It was found that the CW-MFC was not able to sense some specific toxic disturbances, such as Cu^{2+} and the herbicide investigated in this study, probably due to its relatively larger scale and therefore lower NT. In addition, the lower reduction potential of Cu^{2+} (compared to the O_2 reduction potential (Equations (1) and (2); E^0: standard reduction potential; $E_0^{'}$: at pH 7, T = 25 °C) and the cathodic potential (Fig. 3e)) could be another reason for the weak response.

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^0 = 0.3419\ V \tag{1}$$

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E_0' = 0.82\ V \tag{2}$$

In another case, for chemicals with higher reduction potential, such as NO_3^- studied in this work (Equations (3) and (4)), CW-MFC can present a strong response, which enables CW-MFC to be a potential biosensor for NO_3^- (or equivalent substances with higher reduction potentials) monitoring, or even quantification.

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \quad E_0' = 0.42\ V \tag{3}$$

$$NO_3^- + 6H^+ + 5e^- \rightarrow 1/2N_2 + 3H_2O \quad E_0' = 0.74\ V \tag{4}$$

This could be a significant development/direction in effluent water quality monitoring of CW treatment systems or for groundwater quality monitoring. Overall, the CW-MFC based biosensor is a very attractive and promising approach for the further development of CW-MFC technology, and the utilization of "normalized concept" can further contribute to its practical application.

4. Conclusions

In this study, the system scale (i.e. sensing chamber volume) was shown to be a critical factor determining the performance of BES based biosensor for organic sensing. Therefore, for the first time, NMDR and NST were proposed to be the criteria for BES based biosensor. Subsequently, CW-MFC based biosensor was specifically examined. Anodic material, operation mode, and HRT were all found to significantly influence the NMDR and NST of the CW-MFC based sensing system. Furthermore, chemical disturbance with higher reduction potential was revealed to exert a strong influence on the biosignal produced from CW-MFC. However, for other toxic disturbances, like Cu^{2+} and herbicide, NT is suggested to be considered. This work can overall contribute to further development of BES-CW based biosensor, which would be valuable to protecting and maintaining the terrestrial-aquatic environment.

Credit Author Statement

Lei Xu and Wenzheng Yu designed the experiment; Lei Xu completed the main experiment and wrote the draft; all authors contributed to the final version of this manuscript.

Declaration of competing interest

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.

Acknowledgements

This research was supported by a Marie Curie International Incoming Fellowship (FP7-PEOPLE-2012-IIF-328867) within the 7th European Community Framework Programme. This work was also supported by National Natural Science Foundation of China (Grants No. 51908537 and 51108444).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.128532.

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