Journal of Environmental Management 252 (2019) 109682

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: http://www.elsevier.com/locate/jenvman

Research article

Enhancement of biological oxygen demand detection with a microbial fuel cell using potassium permanganate as cathodic electron acceptor

Siqi Wang, Shuai Tian, Panyue Zhang *, Junpei Ye, Xue Tao, Fan Li, Zeyan Zhou, Mohammad Nabi

Beijing Key Lab for Source Control Technology of Water Pollution, Beijing Forestry University, Beijing, 100083, China

ARTICLE INFO

Keywords:
Biochemical oxygen demand
Microbial fuel cell
$KMnO_4$
Detection limit
Response time

ABSTRACT

When dual-chamber microbial fuel cell (MFC) is used to detect biochemical oxygen demand (BOD), dissolved oxygen is traditionally used as cathodic electron acceptor. The detection limit of this MFC-based BOD biosensor is usually lower than 200 mg/L. In this paper, the startup of MFC-based BOD biosensor was researched and the external resistor of MFC was optimized. Results showed that the MFC started up with the dissolved oxygen as cathodic electron acceptor within 10 d, and the external resistor was optimized as 500 Ω to ensure the maximum output power of MFC. Dissolved oxygen and potassium permanganate ($KMnO_4$) were used as cathodic electron acceptor to run MFC for detection of wastewater BOD, and the performances of two kinds of BOD biosensors were compared. The MFC-based BOD biosensor using $KMnO_4$ (10 mmol/L) as cathodic electron acceptor exhibited an excellent performance, compared with that using dissolved oxygen. The upper limit of BOD detection was greatly broadened to 500 mg/L, the response time was shortened by 50% for artificial wastewater with a BOD of 100 mg/L, and the relative error of BOD detection was reduced to less than 10%. The MFC-based BOD biosensor using $KMnO_4$ as cathodic electron acceptor showed a better linear relationship ($R^2 > 0.992$) between the electric charge and BOD concentration within a BOD range of 25–500 mg/L. The MFC-based BOD biosensor using the $KMnO_4$ as cathodic electron acceptor is promising with a better application prospect.

1. Introduction

Biochemical oxygen demand (BOD) is the amount of oxygen needed by aerobic biological organisms to degrade organic materials in water or wastewater samples at a certain temperature over a specific time, which is an important index for evaluating organic contamination of water or wastewater (Lotfi et al., 2019; Wang et al., 2018). At present, the 5-day biochemical oxygen demand (BOD_5) test is widely used to evaluate the organic pollution of water or wastewater (Li et al., 2016; Ibrahimoglu and Yilmazoglu, 2018). However, this method is time-consuming, and requires accurate control and complicated procedure, making on-line monitoring and fast detection be difficult to be realized in biological wastewater treatment (Jouanneau et al., 2014). Therefore, fast BOD detection based on biosensor has attracted extensive attention in recent years (Jouanneau et al., 2014; Li et al., 2016).

BOD biosensors based on microbial fuel cell (MFC) have been developed with the advantage of no oxygen limitation in the biodegradation reaction. MFC is a device that turns chemical energy into electrical energy with the aid of electrochemically-active microbes (Feng et al., 2010; Han et al., 2010). MFC usually consists of an anode chamber and a cathode chamber, which are usually separated by a proton exchange membrane (Estrada-Arriaga et al., 2018; Yu et al., 2006). The electrochemically-active microorganisms decompose organics in the anode chamber and generate electrons and protons (Islam et al., 2018). The electrons are transferred from the anode to cathode through an external electric circuit, and the protons migrate from the anode chamber to cathode chamber through proton exchange membrane (Islam et al., 2018; Kumlanghan et al., 2007). In the cathode chamber, generated electrons and protons react with oxidant. With this closed circuit the current is produced. Karube et al. (1977) firstly constructed a MFC with *hydrogenogens* to detect the wastewater BOD. Striling et al. (1983) and Thurston et al. (1985) developed MFC-based BOD biosensors containing redox mediators. However, the life of these MFCs was short and could not steadily operate for a long time. Catterall

* Corresponding author. College of Environmental Science and Engineering, Beijing Forestry University, Qinghua East Road 35, Haidian District, Beijing, 100083, China.

E-mail address: panyue_zhang@bjfu.edu.cn (P. Zhang).

https://doi.org/10.1016/j.jenvman.2019.109682
Received 15 March 2019; Received in revised form 20 September 2019; Accepted 5 October 2019
Available online 11 October 2019

et al., 2003 demonstrated that the mixed consortium exhibited a higher extent and rate of biodegradation compared to the individual pure microbial, and markedly improved correlation to the BOD_5 from standard method. Therefore, mixed strains (Catterall et al., 2003) and activated sludge (Chang et al., 2004) were used to replace single strain for enrichment of electrochemically-active microbes in MFC system, and enhancement of BOD detection.

The traditional MFC-based BOD biosensors use dissolved oxygen as cathodic electron acceptor, and the BOD measurement range is between 0.1 and 200 mg/L (Jouanneau et al., 2014). However, the dissolved oxygen in water is limited even under aeration, and lack of oxidant leads to accumulation of protons in the anode chamber, causing acidification when detecting a wastewater sample with a high BOD concentration (Kim et al., 2003). The pH reduction weakens the activity of microbes and then the coulomb quantity generated by the MFC becomes lower than expected. Therefore, when the dissolved oxygen was as cathodic electron acceptor of MFC, the upper detection limit of MFC-based BOD biosensors is usually lower than 200 mg/L (Kim et al., 2006), and the detection time lasts about 20 h (Peixoto et al., 2011). The narrow detection range and long detection time restricts the applicability of MFC-based BOD biosensors.

For improving the electricity production of MFC, some redox-mediators, such as sodium bromate (Dai et al., 2016), persulfate (Wang et al., 2011), ferricyanide (Nakamura et al., 2007; Oota et al., 2010; Wei et al., 2012), potassium dichromate (Sindhuja et al., 2018) and potassium permanganate ($KMnO_4$) (Cai et al., 2016; Jafary et al., 2013) etc., were used as electron acceptor in the cathode chamber instead of oxygen. The main advantage of adding these redox-mediators was that the biodegradation reaction did not depend on oxygen, the electricity generation is obviously enhanced, and the samples dilution was not necessary in order to decrease organic load (Jouanneau et al., 2014). Pandit et al. (2011) investigated the performances of cathodic electron viz. Potassium ferricyanide (K_3 [$Fe(CN)_6$]), potassium dichromate ($K_2Cr_2O_7$), potassium persulfate ($K_2S_2O_8$) and $KMnO_4$ to determine the most suitable electron acceptor in terms of power density, and found the following order: $KMnO_4$ (116.2 mW/m^2) > $K_2S_2O_8$ (101.7 mW/m^2) > $K_2Cr_2O_7$ (45.9 mW/m^2) > (K_3 [$Fe(CN)_6$]) (40.6 mW/m^2). It was reported that the $KMnO_4$ as the cathodic solution of MFC led to a higher power density than K_3 [$Fe(CN)_6$] because of its higher redox potential of 1.68 V (Jafary et al., 2013). Similar results were demonstrated by other studies (Cai et al., 2016; Sathishkumar et al., 2018). Therefore, the $KMnO_4$ as cathodic electron acceptor of MFC may be promising in broadening detection range, shortening response time, improve accuracy and sensitivity, even maintaining repeatability and stability of MFC-based BOD biosensor through producing higher power density. However, few researches applied $KMnO_4$ as cathodic electron acceptor to improve BOD detection performances of MFC-based BOD biosensor. The study on $KMnO_4$ as cathodic electron acceptor in MFC-based BOD biosensor is of great significance.

In this study, a novel MFC-based BOD biosensor was constructed with $KMnO_4$ as cathodic electron acceptor. The performances of BOD biosensor were evaluated through comparison with an MFC-based BOD biosensor using dissolved oxygen as cathodic electron acceptor. Moreover, the response time, detection range, repeatability and stability of MFC-based BOD biosensors were investigated.

2. Material and methods

2.1. MFC system

MFC was constructed with an anode chamber and a cathode chamber (Fig. S1), with the volume of 30 ml (5 cm × 5 cm × 1.2 cm) for each chamber. The two chambers were separated by a proton exchange membrane (Nafion 117, USA). Before operation of MFC, the proton exchange membrane was activated by immersing it in a 3% H_2O_2 solution at 80 °C for 1 h and successively in a 10% HNO_3 solution at 80 °C for 1 h. Graphite felts were used as anode and cathode, which were connected with titanium wire through a variable resistance. The current and voltage of MFC were measured with a multimeter, which was connected with a computer to record the data.

2.2. Materials

Artificial wastewater was used as substrate to evaluate the performances of MFC-based BOD biosensor. Glucose was used as organics to adjust the BOD of artificial wastewater. Besides, the artificial wastewater contained 0.56 g/L $(NH_4)_2SO_4$, 0.42 g/L $NaHCO_3$, 0.2 g/L $MgSO_4{\cdot}7H_2O$, 15 mg/L $CaCl_2$, 1 mg/L $FeCl_3{\cdot}6H_2O$, 20 mg/L $MnSO_4{\cdot}H_2O$, 50 ml/L phosphate buffer solution (1 mol/L, pH = 7.0), and 20 mg/L L-cysteine (as oxygen absorbent). All chemicals were of analytical grade and the water used was deionized water in this study. Cleaning solution for the anode chamber contained the same constituents of artificial wastewater except glucose.

2.3. Startup of MFC

Electrochemically-active microbes were enriched from anaerobic sludge (Wang et al., 2009), which was collected from sludge digester of a local sewage treatment plant with anaerobic-anoxic-oxic (A^2O) process in Beijing, China. The seed sludge with a solid content of 5% and artificial wastewater with a BOD concentration of 1000 mg/L were mixed at a volume ratio of 1:1 (Eliato et al., 2016). After being oscillated at 37 °C for 10 h, the mixture was injected into the anode chamber to enrich the electrochemically-active microbes. The external resistance was set as 1000 Ω during the startup period (Wang et al., 2009). Dissolved oxygen was used as cathodic electron acceptor through continuously pumping the aerated tap water into the cathode chamber with a flow rate of 10 ml/min. The mixture was replaced every day until enough microgrames were enriched in the anode, the MFC system reached a stable operating state, and the current pattern of MFC system changed insignificantly. When the MFC-based BOD biosensor stably ran, the external resistance was set from 100 to 1000 Ω to select the external resistance of MFC-based BOD biosensor for high potential output power and accurate BOD detection (Kumlanghan et al., 2007).

2.4. BOD detection with MFC-based BOD biosensors

In this study, dissolved oxygen and $KMnO_4$ were applied as electron acceptor of MFC in the cathode chamber, and the flow rate of aerated water was 10 ml/min and the $KMnO_4$ concentration was 1, 5 and 10 mmol/L, respectively. After the MFC operated stably, the anode chamber was cleaned 3 times with cleaning solution before BOD detection to ensure the same initial conditions of MFC system, thus to reduce the system errors. When the current was lower than 10 μA, the wastewater sample with a BOD concentration up to 1000 mg/L was injected into the anode chamber for BOD detection with the aerated water of 10 ml/min or $KMnO_4$ solution of 1, 5 and 10 mmol/L as electron acceptor in the cathode chamber. The detection time, also called response time, started from injecting the wastewater sample and ended when the current dropped to 5% of the maximum current (Kim et al., 2003; Gil et al., 2003). After the current dropped to 5% of the maximum current, the current generation became insignificant, moreover, the reaction rate became very slow. Voltage (U, mV) of external resistance was recorded every 10 s by using a data acquisition system (MPS-010602, Morpheus Electronics Technology Co (Beijing)., Ltd., China). Current (I, μA), MFC power density (P, mW/m^2), and electric charge (Q, C) generated by MFC was calculated by Eqs. (1)–(3), respectively (Peixoto et al., 2011).

$$I = U/R_{ext} \quad (1)$$

$$P = UI/A \quad (2)$$

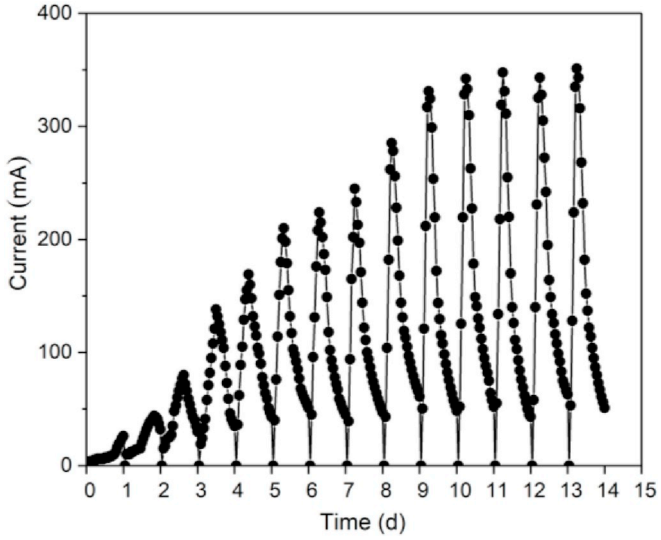

Fig. 1. Current generation by MFC for every operation cycle (flow rate of aerated tap water of 10 ml/min, and external resistance of 1000 Ω).

$$Q = \int_0^t I\,dt \tag{3}$$

where R_{ext} is the external resistance (Ω), A is the surface area of electrode (m^2) and t is the response time (s).

Each sample was detected in triplicate and the average value was used as the result. Wastewater samples with BOD concentration from 10 to 1000 mg/L were analyzed, and the correlation between electric charge and wastewater BOD concentration were regressed within the linear range as the standard curve for BOD detection.

2.5. Repeatability of MFC-based BOD biosensor

After determining the BOD detection range according to the linear correlation between the electric charge and wastewater BOD concentration, artificial wastewater samples with a BOD concentration from 100 to 500 mg/L were prepared to test the repeatability of MFC-based BOD biosensor with dissolved oxygen of 10 ml/min or $KMnO_4$ of 10 mmol/L as cathodic electron acceptor. Each wastewater sample was detected 5 times, and the voltage and response time were recorded to calculate electric charge. The BOD concentration was calculated by the corresponding correlation curve.

2.6. Stability of MFC-based BOD biosensor

After the MFC-based BOD biosensor ran for 6 months, series of wastewater samples with known BOD concentration were measured to test the stability of MFC-based BOD biosensor with dissolved oxygen of 10 ml/min or $KMnO_4$ of 10 mmol/L as cathodic electron acceptor. The measured BOD value was calculated by the corresponding correlation curve and compared with the corresponding true BOD value. The relative errors were determined to evaluate the stability of MFC-based BOD biosensor.

2.7. Statistical analysis

All experiments were carried out in triplicates. To compare the average detection performances of two MFC-based BOD biosensors, an analysis of Student's unpaired *t*-test was used, and $P < 0.05$ was considered to be statistically significant.

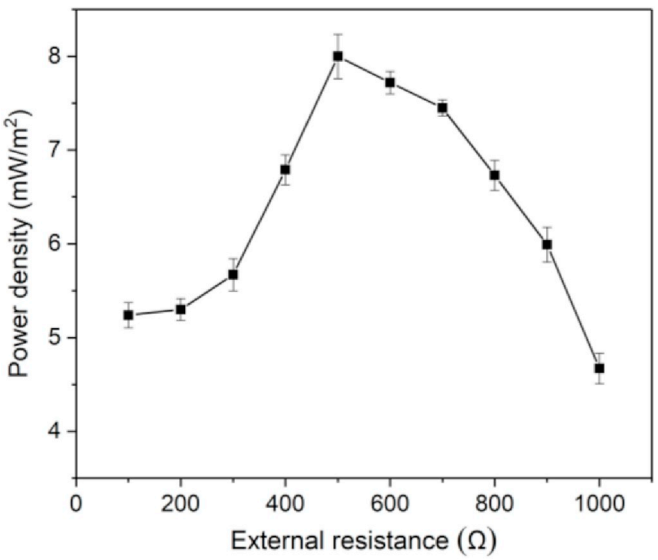

Fig. 2. Effect of external resistance on output power density of MFC (flow rate of aerated tap water of 10 ml/min).

3. Results and discussion

3.1. Startup and optimization of MFC system

After the MFC was inoculated with activated sludge and fed with the artificial wastewater as substrate, the maximum current generated every day increased with the time prolonging, indicating that the electrochemically-active microbes were gradually enriched on the anode, as shown in Fig. 1. After 10-day culturing and enrichment, the maximum current kept stable at about 350 μA, showing that a stable microbe system was formed on the anode. When the substrate was provided every day, the current first increased rapidly, which might be attributed to that the abundant food for microbe growth and rapid degradation of organics by microbes resulted in a quick increase within 5 h. Then the current gradually dropped due to the lack of food and the accumulation of some metabolites in the anode chamber (Lorenzo et al., 2009). When the organics were depleted, the current returned to baseline (Lorenzo et al., 2009; Wang et al., 2018). After 15-day culturing, the MFC-based BOD biosensor was suitable for detecting the BOD concentration of wastewater.

Effect of external resistance on output power density of MFC is shown in Fig. 2. The output power density increased with the increase of external resistance from 100 to 500 Ω, and reached a maximum of 8 mW/m^2 when the external resistance was up to 500 Ω, then started to decrease with further increasing the external resistance. The high external resistance probably limited the electron uptake through electric circuit (Gil et al., 2003; Hsieh and Chung, 2014). Therefore, the external resistance was selected as 500 Ω to ensure the maximum output power density of MFC.

3.2. Performances of MFC-based BOD biosensor with dissolved oxygen as cathodic electron acceptor

The change of response time with BOD concentration is shown in Fig. 3a. The response time obviously increased with the increase of BOD concentration. When the BOD concentration was higher than 100 mg/L, the response time was longer than 10 h, because longer time was required for biodegradation of more organics. The response time is usually selected to be shorter than 10 h, since longer response time may limit the application of BOD biosensor in fast BOD detection of wastewater (Peixoto et al., 2011; Wang et al., 2018). Thus, the upper detection limit of BOD with dissolved oxygen as cathodic electron acceptor should

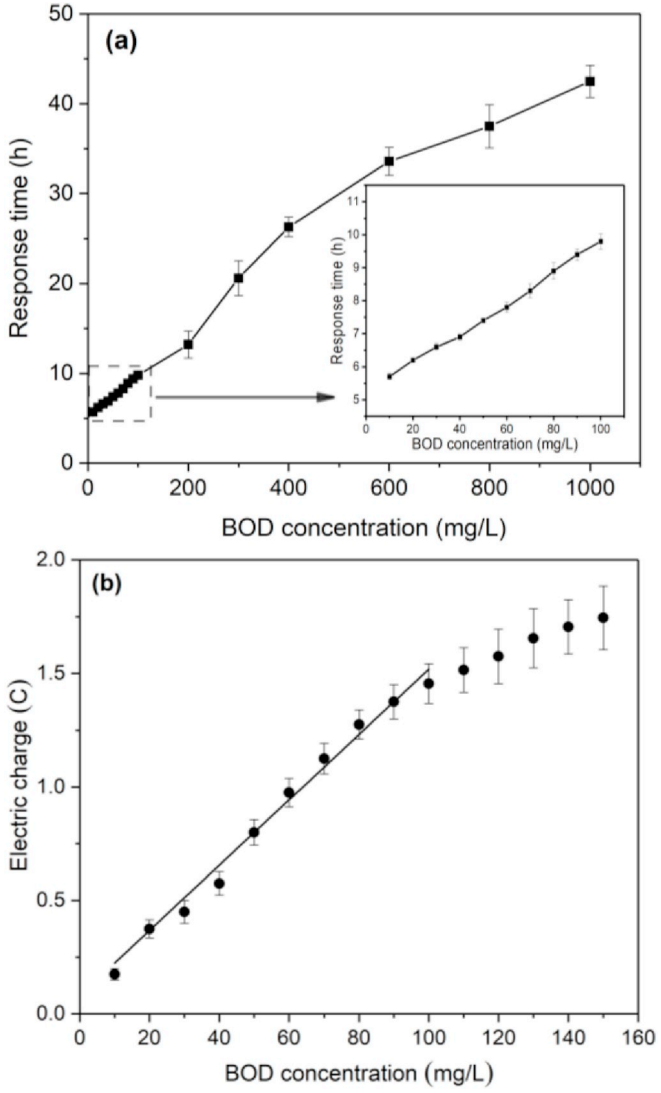

Fig. 3. Performances of MFC-based BOD biosensor using dissolved oxygen as cathodic electron acceptor: (a) response time, and (b) electric charge.

not be higher than 100 mg/L, which agrees with other researches (Kim et al., 2006; Moon et al., 2004).

The currents and the electric charges of MFC according to Eq. (3) with different BOD concentrations are shown in Fig. 3b. The electric charge linearly increased with increasing the wastewater BOD concentration up to 100 mg/L, as Eq. (4):

$$Q = 0.014\ BOD + 0.048 \qquad (R^2 = 0.987) \tag{4}$$

$R^2 = 0.987$ indicated the excellent linearity between the electric charge and wastewater BOD concentration, which was mainly attributed to the stable microbes in the form of biofilm in MFC system and the stable wastewater sample with a certain concentration. The linear range was similar to results reported by Chang et al. (2004) and Peixoto et al. (2011). When the BOD concentration was higher than 100 mg/L, the electric charge deviated from the linearity to a lower value, which was probably due to the acidification in the anode chamber, moreover, the response time was longer than 10 h (Fig. 3a). Therefore, the upper detection limit of MFC-based BOD biosensor with dissolved oxygen as cathodic electron acceptor was 100 mg/L. The MFC-based BOD biosensor had a small relative standard deviation below ±15% during the BOD detection, which was comparable with that of conventional 5-day BOD test (Liu et al., 2000).

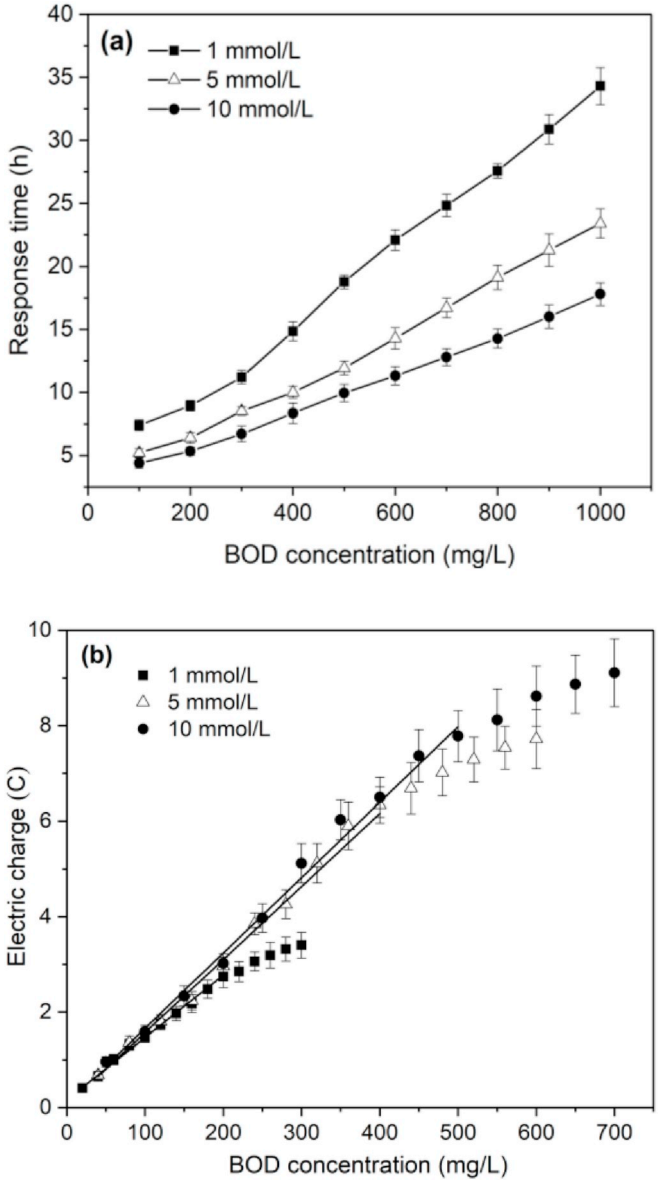

Fig. 4. Performances of MFC-based BOD biosensor using $KMnO_4$ as cathodic electron acceptor: (a) response time, and (b) electric charge.

3.3. *Performances of MFC-based BOD biosensor with $KMnO_4$ as cathodic electron acceptor*

For enhancing the performances of MFC-based BOD biosensor, the $KMnO_4$ replaced dissolved oxygen as the cathodic electron acceptor. Fig. 4a shows the effect of BOD concentration on the response time of MFC-based BOD biosensor with $KMnO_4$ solution of 1, 5 and 10 mmol/L, respectively. Similarly, the response time increased with the increase of BOD concentration. Furthermore, higher $KMnO_4$ concentration exhibited a shorter response time for the same wastewater sample. For the wastewater sample with a BOD concentration of 100 mg/L, the response time was 5, 6 and 8 h when the $KMnO_4$ concentration was 10, 5 and 1 mmol/L, respectively, which reduced by 50%, 40% and 20%, compared with that with dissolved oxygen as cathodic electron acceptor. $KMnO_4$ has a higher redox potential of 1.68 V (Eq. (5)) than dissolved oxygen (1.229 V) (Eq. (6)) (Eliato et al., 2016), resulting in that $KMnO_4$ has stronger ability to react with protons and electrons transferred from the anode chamber (Karthikeyan et al., 2012).

$$MnO_4^- + 4H^+ + 3_e^- \rightarrow MnO_2(s) + \qquad (E^0 = 1.68\ V) \tag{5}$$

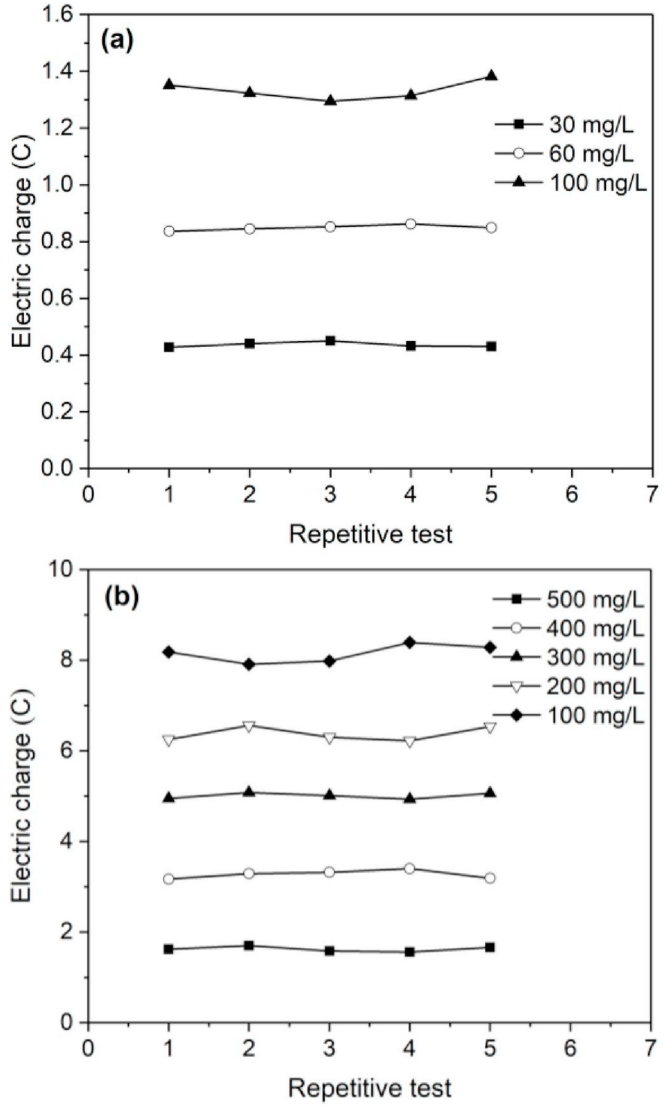

Fig. 5. Repeatability of MFC-based BOD biosensors: (a) dissolved oxygen, and (b) $KMnO_4$ as cathodic electron acceptor.

$$O_2+4H^++4e^- \rightarrow 2H_2O \qquad (E^0 = 1.229\ V) \tag{6}$$

On the other hand, when 10 h was considered as the accepted response time, the upper limit of wastewater BOD detection greatly expanded. Meanwhile, delay of electricity production was eased with the $KMnO_4$ as cathodic electron acceptor.

The relationship between electric charge and wastewater BOD concentration for the MFC-based BOD biosensor using $KMnO_4$ as cathodic electron acceptor is shown in Fig. 4b. Excellent linearities between the electric charge and wastewater BOD concentration were observed with three $KMnO_4$ concentrations within different BOD ranges. The upper limit of linear range significantly increased with the increase of $KMnO_4$ concentration, which was 200, 400 and 500 mg/L with a $KMnO_4$ concentration of 1, 5 and 10 mmol/L, respectively. The linear relationship can be described as Eqs. (7)–(9) with a $KMnO_4$ concentration of 1, 5 and 10 mmol/L, respectively:

$$Q = 0.012\ BOD + 0.215 \qquad (R^2 = 0.994) \tag{7}$$

$$Q = 0.016\ BOD + 0.088 \qquad (R^2 = 0.994) \tag{8}$$

Table 1
Relative errors of BOD detection with MFC-based BOD biosensors using dissolved oxygen and 10 mmol/L $KMnO_4$ solution as cathodic electron acceptor.

Dissolved oxygen			$KMnO_4$		
True BOD (mg/L)	Measured BOD (mg/L)	Relative error	True BOD (mg/L)	Measured BOD (mg/L)	Relative error
5	3.88	22.4%	25	22.6	9.6%
15	17.63	17.5%	75	68.78	8.3%
25	21.85	12.6%	125	132.13	5.7%
35	30.94	11.6%	175	167.65	4.2%
45	39.10	13.1%	225	238.05	5.8%
55	50.10	8.90%	275	283.80	3.2%
65	60.65	6.70%	325	305.83	5.9%
75	72.38	3.50%	375	358.86	4.3%
85	81.86	3.70%	425	413.10	2.8%
95	89.59	5.70%	475	487.33	2.5%
–	–	–	500	486.26	2.7%

$$Q = 0.016\ BOD + 0.040 \qquad (R^2 = 0.992) \tag{9}$$

when the BOD concentration exceeded the linear range, the electric charge was lower than expected, just like the MFC-based BOD biosensor with dissolved oxygen as cathodic electron acceptor. This might be due to that the manganese dioxide (MnO_2), a reduction product of $KMnO_4$, increased the internal resistance of MFC system (Eliato et al., 2016). Broadening the linear range with increasing the $KMnO_4$ concentration meant that the upper limit of BOD detection for wastewater BOD concentration was greatly broadened. Moreover, the upper limit of BOD detection with $KMnO_4$ as cathodic electron acceptor can be controlled through regulating the $KMnO_4$ concentration.

3.4. Repeatability of MFC-based BOD biosensors

The repeatability of MFC-based BOD biosensor with dissolved oxygen and 10 mmol/L $KMnO_4$ as cathodic electron acceptor is shown in Fig. 5. The relative standard deviation of MFC-based BOD biosensor with dissolved oxygen was ±3.8%, ±2.9% and ±4.3% for artificial wastewater with a BOD concentration of 30, 60 and 100 mg/L, respectively. And the relative standard deviation of MFC-based BOD biosensor with $KMnO_4$ as cathodic electron acceptor was ±2.5%, ±2.9%, ±1.3%, ±2.6% and ±2.8% for artificial wastewater with a BOD concentration of 100, 200, 300, 400 and 500 mg/L, respectively. Overall, the relative standard deviation of MFC-based BOD biosensor with $KMnO_4$ as cathodic electron acceptor was lower than that with dissolved oxygen. The repeatability of MFC-based BOD biosensors in this study was better than that in previous studies with about ±7.2% relative standard deviation (Kumlanghan et al., 2007), and also better than that of biofilm-type BOD biosensors in general (Liu and Mattiasson, 2002).

3.5. Stability of MFC-based BOD biosensors

A stable performance over a desired operational period is essential for a reliable biosensor system (Kumlanghan et al., 2007; Hsieh and Chung, 2014). After the MFC-based BOD biosensor running for 6 months, the stability of MFC-based BOD biosensors with dissolved oxygen and 10 mmol/L $KMnO_4$ as cathodic electron acceptor for detecting series artificial wastewater with known BOD concentration is shown in Table 1. Comparing the measured BOD values with the true BOD values, the maximal relative error for MFC-based BOD biosensor with dissolved oxygen as cathodic electron acceptor was 22.4% when the true BOD concentration was 5 mg/L, and the relative error decreased with the increase of true BOD value. The measured BOD value was almost lower than the true BOD value, which was probably due to the limit of proton flux caused by pollution of proton exchange membrane, resulting in a

Table 2
Performance comparison of different MFC-based BOD biosensors.

MFC system classification	Electron donor	Electron acceptor	Startup time (d)	Maximum detection Concentration (mg/L)	Reference
1-chamber	Real wastewater	Dissolved oxygen	18	350	Lorenzo et al. (2009)
1-chamber	Real wastewater	Dissolved oxygen	21	78	Peixoto et al. (2011)
2-chamber	Glucose and glutamate	Dissolved oxygen	56	200	Kim et al. (2006)
2-chamber	Glucose	10 mmol/L $KMnO_4$ solution	10	500	Present study

decrease of current (Pandit et al., 2011). For MFC-based BOD biosensor with $KMnO_4$ as cathodic electron acceptor, the relative errors reduced below 10%, for example, it was in a range of 6%–10% when the wastewater BOD was between 25 and 75 mg/L, and further decreased below 6% when the wastewater BOD was in a range of 125–500 mg/L. Hsieh et al. (2015) measured the BOD concentration of artificial wastewater using a mediator-less MFC, and the relative error was 6.9%–7.6% when wastewater BOD was 320–580 mg/L, which was relatively higher than that in this study (2.5%–5.9%). Moreover, Kumlanghan et al. (2008) measured the BOD concentration of food wastewater (25–560 mg/L) using a BOD cell-based biosensor, and the relative error was 5.4%–22.0%. A biosensor based on immobilized microbial cell was used to determine the BOD concentration of municipal wastewater (24.1–129.6 mg/L), and the relative error was 4.0%–10.4% (Wang et al., 2010). Therefore, the MFC-based BOD biosensor with $KMnO_4$ as cathodic electron acceptor showed a better stability than that with dissolve oxygen, and also better than that of other kinds of BOD biosensors.

Table 2 shows the performance comparison of MFC-based BOD biosensor in this study and other researches. Compared with other MFC-based BOD biosensors using dissolved oxygen as cathodic electron acceptor, the novel MFC-based BOD sensor using a 10 mmol/L $KMnO_4$ solution as cathodic electron acceptor showed an obviously broader limit of BOD detection of 25–500 mg/L within the same response time of 10 h. This was mainly due to that the $KMnO_4$ had higher redox potential than dissolved oxygen, resulting in a stronger ability and a quicker speed of $KMnO_4$ to react with protons and electrons from the anode chamber (Pandit et al., 2011), which was advantageous for the degradation of organic matters in the anode chamber (Jouanneau et al., 2014). In addition, the dissolved oxygen in water was limited even using aeration, and the lack of oxidant might lead to accumulation of protons and further acidification in the anode chamber when detecting a wastewater sample with a high BOD concentration (Kim et al., 2003).

Although the high concentration of $KMnO_4$ solution significantly expanded the upper limit of BOD detection, the proton exchange membrane and electrodes may be corroded, and the life of biosensor may be shortened. Therefore, optimization of cathodic electron acceptor, development of pollution-resistant proton exchange membrane, shortening of startup time, broadening of limit of BOD detection, extension of biosensor life and application of the MFC-based BOD biosensor on real wastewater analysis should be further studied. In addition, complete sets of MFC-based BOD biosensor should be developed for continuous and online monitoring of water and wastewater.

4. Conclusions

A novel MFC-based BOD biosensor with $KMnO_4$ as cathodic electron acceptor showed a better performances of shorter response time, broader detection limit and better stability, compared with that using dissolved oxygen as cathodic electron acceptor. With an external resistance of 500 Ω, excellent linear relationships ($R^2 > 0.992$) between the electric charge and BOD concentration were observed. The BOD detection range with a 10 mmol/L $KMnO_4$ solution was 25–500 mg/L with a response time shorter than 10 h. Within the BOD detection range, the data repeatability was excellent.

Acknowledgements

This research was funded by the National Natural Science Foundation of China (51578068) and Specialized Research Fund for the Doctoral Program of Higher Education of China (20130161110013).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.109682.

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