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Bioelectricity generation in an integrated system combining microbial fuel cell and tubular membrane reactor: Effects of operation parameters performing a microbial fuel cell-based biosensor for tubular membrane bioreactor

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ABSTRACT

A bio-cathode microbial fuel cell (MFC) with tubular membrane was integrated to construct a microbial fuel cell-tubular membrane bioreactor (MFC-TMBR) system, in which the bio-cathode MFC was developed as a biosensor for COD real-time monitoring in TMBR and the performance was analyzed in terms of its current variation caused by operation parameters. With a constant anode potential, the effect of HRT demonstrated that higher rate of mass transport increased the response of the system. The system was further explored an inverse relationship between TMP and current peak by using EPS concentration under the different MLSS concentration. The sensor output had a linear relationship with COD up to 1000mg/L (regression coefficient, R^2=0.97) and MLSS (regression coefficient, R^2=0.94). The simple and compact bio-cathode MFC biosensor for TMBR using MFC-TMBR integrated system showed promising potential for direct and economical COD online monitoring, and provided an opportunity to widen the application of MFC-based biosensor.

Keywords: bio-cathode microbial fuel cell; COD; biosensor; membrane reactor.

1. Introduction

Microbial fuel cell (MFC) is a bio-electrochemical device which use microorganisms as catalyst for converting chemical energy into electrical energy (Logan, 2008). MFC consists of an anode exposed to an electron donor, and a cathode exposed to a terminal electron accepted. The two chambers are typically separated by a permeable membrane. As current can be monitored easily on line, MFC can act as an inexpensive online biosensor which can be operated steady (Chang et al., 2004, 2005; Kim et al., 2003a,b) with naturally-occurring bacteria and constructed with low-cost materials. In the general scheme of a biosensor, the biological recognition element responds to the target chemicals and the transducer converts the biological response to a detectable signal, which can be measured electrochemically, mechanically, acoustically, or optically (Su et al., 2011). Such an online MFC-based biosensor measured with an electrical current as the signal, which does not need a mediation to read the signal or convert it to an electrical signal. Various types of MFC-based biosensors have been reported (Di Lorenzo et al., 2009; Stein et al., 2010; Feng et al., 2013), showing that it has a major advantage over many other types of biosensors (Hyun et al., 1993; Chee et al., 2005).

A number of researchers have used biosensors to monitor water quality (e.g. Lee et al., 2005, 2007; Kim et al., 2007; Di Lorenzo et al., 2009). Online MFC-based biosensors are widely used to monitor water quality of water flows like food wastewater,

drinking water or processing water, or used to be integrated with artificial neural networks (ANNs) to identify specific chemicals present in water samples. The relationship between water quality and MFC signals depends on the physical patameters of the MFC, operating conditions (e.g. pH, temperature, organic loading rate and electrical load), as well as the ecology of the biofilm. There are some direct evidences that MFC-based biosensor can be used to monitor water quality in real time. For example, Di Lorenzo et al. found out a linear relationship between chemical oxygen demand (COD) concentration and MFC current output (Di Lorenzo et al., 2009), demonstrating the applicability of this system to real-time COD monitoring. Feng et al. demonstrated that the peak area generated by the electrical signals correlated well with the chemical oxygen demand (COD) present in water samples (Feng et al., 2011). Kumlanghan et al. developed a biosensor based on a single-chamber microbial fuel cell, and the current study showed the development of a MFC sensor system for fast estimation of easily biodegradable organic matter in which glucose was used as the only preliminary substrate (Kumlanghan et al. 2007). Zhang and Angelidaki developed a submersible microbial fuel cell (SBMFC) as a biosensor for real-time monitoring of dissolved oxygen (DO) in environment waters (Zhang and Angelidaki, 2012). Tront et al. explored a MFC sensor to in suit monitoring of substrate concentration, showing that current generation was mirrored by acetate concentration, and a correlation (R^2=0.92) was developed (Tront et al., 2008). Similar results have been retrieved for other MFC-based biosensor researches (Chang et al., 2004, 2005; Shen et al., 2012; Modin

and Wilen, 2012). However, most previous studies of MFC-based biosensor have not discussed the practical application in detail.

Di Lorenzo et al. suggested that the MFC-based biosensor could be installed between the clarifier and the aeration tank to determine the quality of the effluent in terms of COD content after the primary clarifier in a wastewater treatment plant (Di Lorenzo et al., 2009). In this study, compared with this design, a MFC-based biosensor for membrane bioreactor (MBR) was developed, in which the aeration tank of a MBR was directly used as cathode chamber. Using bio-cathode MFC combined with tubular membrane, a combined system of microbial fuel cell and tubular membrane bioreactor (MFC-TMBR) for biosensor and wastewater treatment appeared to be more attractive in terms of costs and the practical application (Wang et al., 2013). The electrical signals (e.g. electrical current) generated by the bio-cathode MFC were thus a direct linear measure for metabolism of the electrochemically active microorganisms under the condition of the stability of anode potential. The aim of the series of tests in this study is to investigate the interrelationship between MFC electricity generation and tubular membrane bioreactor (TMBR) operation parameters under different operation conditions. The bioelectricity performance of MFC-TMBR system was evaluated in terms of its chemical oxygen demand (COD) range, loading rate, mixed liquor suspended solids (MLSS) concentration, extracellular polymeric substances (EPS) concentration and transmembrane pressure (TMP). A microbial fuel cell-based biosensor for monitoring COD in tubular membrane bioreactor was also investigated,

which could be potentially useful for a wider COD concentration range. In this paper, we demonstrate the new type of COD sensor for on-line monitoring TMBR operation using a bio-cathode MFC-based biosensor. The development of MFC-TMBR system will provide an advantageous sensor design for COD monitoring and expand the application of the MFC technology.

2. Materials and methods

2.1. Integrated MFC-TMBR system

The MFC-TMBR system was constructed with a bio-cathode MFC and single tubular membrane, as shown in Fig.1a. The ultrafiltration membrane (PES: MWCO=30k; Shanghai SINAP Membrane Tech Co., Ltd, China) separated the anode and the bio-cathode. The two chambers (2.5L, 10cm*10cm*25cm) were filled with 2.2L liquid. The anode and cathode electrode each was a piece of carbon felt (126cm^2, Beijing Honghaitian Tech Co., China) without any pretreatment. The cathode chamber was directly used as the aeration tank. The anode and cathode were connected through a 1000Ω resistor. The cell voltage and electrode potential were recorded automatically every 5 min using a data acquisition system (USB-FS1208, Measurement Computing^{TM}, America). For the TMBR section, the single tubular membrane (10cm, polyvinglidene fluoride with an average pore size of 0.1μm, Tianjin Motimo Membrane Tech Co., China), as shown in Fig.1b, with a filtration area of 37.68cm^2 was placed out of the aeration tank. Aeration unit was placed at the bottom of the chamber and the aeration

flow rate was 78L/h. Peristaltic pumps (BT100-2J, Baoding Langer pump company, China) rotating at different revolutions per minute with different flux were used to conduct the control of constant flow for drawing out effluents, and the hydraulic retention time (HRT) had a corresponding change. The TMP was measured by pressure sensors (Danfoss, MBS 3000, Denmark) for monitoring membrane fouling. Tubular membrane was washed with sodium hypochlorite (0.5%) for 1h and back-flushed with tap water for 3h when TMP reached -50kpa.

2.2 Operating conditions

4.4g/L KH_2PO_4, 3.4g/L K_2HPO_4, 0.5g/L NaCl, 0.1g/L NH_4Cl, 0.05g/L $MgCl_2$, and 0.05g/L $CaCl_2$ were dissolved in tap water to synthesize simulative influent wastewater for the whole experiment (Shan et al., 2011). The COD concentration of the artificial water in the cathode chamber was controlled by adding an appropriate amount of glucose, and the COD concentration of the artificial water in the anode chamber was 1000mg/L consistently. The aerobic active sludge was taken from Jizhuangzi Wastewater Treatment Plant (Tianjin, China). A 1000ml bacterial suspension collected from laboratory bioreactors was injected as inoculum into the anodic zone. Copper wire was used to connect the cathode and anode electrode, respectively. After reaching a stable status for about 200 days, the MFC finished executing and the coupled system began to work. To achieve the constant anode potential, the MFC-TMBR system was operated at a room temperature of 25±3℃, a pH of 7 and a substrate of glucose (1g/L in

anode chamber).

During the tests, the MLSS concentration of the aeration tank was varied from 3400mg/L to 12240mg/L. Due to the cultivation of the sludge, the MLSS concentration was increased step by step. The method of maintaining the MLSS concentration at each stage test was sludge wasting, which meaned that about 100ml mixed sludge liquor was discharged from aeration tank every day.

2.3 Electrochemical and chemical measurements

The polarization curves of MFC were obtained by varying the circuit external resistance from 10 to 10,000Ω when the cell voltage of the MFC was relatively stable. The working potential of the electrodes was measured against a reference electrode (type of 232, 0.2244V vs SHE, Shanghai Leici, China) connected to the data acquisition system, which was set in the corner of reactor at distances from anode and cathode 3cm and 3cm, respectively. The coulombic efficiency (CE), at the steady state was calculated with Formula (1) :

$$CE=C_p/C_t *100\% \quad (1)$$

Where C_p is the total coulombs calculated by integrating the current over time, and C_t is the theoretical amount of coulombs available based on the COD removed in the MFC.

The COD was determined by the standard method using chromate as the oxidant as previously described (APHA, 1998). The COD consumption rate was calculated when the steady state was reached with Formula (2) :

Loading rate = Q * (COD_{IN} - COD_{OUT}) (2)

Where Q ($dm^3 h^{-1}$) is the fuel flow rate, and COD_{IN} and COD_{OUT} (mg dm^{-3}) are the COD of the influent and the effluent, at steady-state, respectively (Di Lorenzo et al., 2009).

HRT was the ratio of the solution volume in the reactor (V_S, 2.2L) to the flow rate (V, L/h):

$HRT = V_S/V$ (3)

EPS was obtained using the procedure with centrifugation at 4000 rpm for 10 min followed by filtration through a 0.22-μm filter, and then using heating method at 80□ for 40 min in a water bath (Huang et al., 2011). The total EPS was normalized as the sum of proteins and carbohydrates. Proteins were quantified using the Lowry method (Lowry et al., 1956) with bovine serum albumin (BSA) as standard, and carbohydrates were analyzed by the phenol–sulfuric acid method using glucose as standard (Dubois et al., 1956). The loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS) were extracted by two step heating methods and analyzed for the contents of proteins and carbohydrates (Li and Yang, 2007, Su et al., 2013).

3. Results and discussion

3.1. Electricity generation performance of MFC-TMBR

The MFC was incubated continuously for more than 200 days at an external resistance of 1000Ω. Fig.2a shows the current generation for 60 days after the MFC

became stable. The current curve of the MFC was measured to determine the operational range with a constant anode potential (-0.4V). The current produced by the MFC in the system was 0.7-0.75mA at pH 7. The COD concentrations in two chambers were 1000mg/L and the temperature was 25±3℃. Good repeatability was exhibited for consecutive multiple cycles.

The variation on cathode potential was a key evaluation parameter in determining whether bio-cathode can be applied for biosensor. Biofilm on the cathode could produce proton and electron via direct contact, shuttling compounds and nano-wire structures to catalyze the synthesis of water molecules. It can be seen that microorganisms on the cathode could transform the chemical energy into the electrical energy and cause variety of current. In order to access the biosensing behaviour of the cathode potential from MFC, a constant anode potential was applied during the whole process of operation. To achieve the current of the bio-cathode MFC-based biosensor it was thus important to keep anode potential constant to assure a constant energy supply. Microorganisms gained energy from electron donor, and in this case glucose, is the electron donor. The reaction taking place at the anode is:

$C_6H_{12}O_6+6H_2O \rightarrow 6CO_2+24H^++24e^-$.

The theoretical value of the electron donor potential can be determined by the Nernst equation.

$$E_{eletron\_donor} = E_0 + \frac{RT}{nF} \ln \frac{[H^+]^{24}}{[glu\cos e]} \quad (4)$$

In which

$E_{electron\_donor}$ = electron donor potential under the present conditions (V)

R = Gas constant ($8.314 Jmol^{-1}K^{-1}$)

T = Temperature (K)

n = Number of electron involved in the half reaction (-)

F = Faradays constant ($96485.3 Cmol^{-1}$)

E_0 = 0.2244V vs SHE for glucose.

As Nernst equation shows, anode potential control implies control of concentration and type of substrate, pH and temperature. These factors can be controlled during the whole process of operation.

The power generation potential of MFC-TMBR was indicated by power density and polarization curves (Fig.2b). With the situation of modest MLSS (4500±120mg/L), the peak of power density was $0.060 W/m^2$ (normalized to the anode area) and the open circuit voltage was 0.93V. The internal resistance calculated by the slope of polarization curve was 500±15Ω. The power output achieved in this test was comparable with other MFC (You et al., 2007; Aldrovandi et al., 2009) or MFC integrated with activated sludge systems (Liu et al., 2011).

3.2. Effect of loading rate

The MFC-TMBR biosensor system was investigated in a continuous mode. Table 1 reports the changes in current response on increasing the artificial water flow rate to decrease the HRT. Artificial water was fed into the bio-cathode chamber at different flow rates and the current monitored. The MFC was fed at a specific flow rate until a

stable current was gained and then the feeding rate was increased. The influent COD was fixed at 1000mg/L. The MLSS concentration was controlled between 4000-5000 mg/L during the operation. Loading rate referred to the reactor effective volume (2.2L). Effluent COD mean data from at least three replicates. When stable current was generated, it would stop recording the TMP. TMP increase rate was used to characterize the filtration behavior.

The steady-state current was increased with the flow rate in steps of 0.2-0.35L/h, varying from 0.68mA for a flow rate of 0.2L/h up to a value of 0.76mA for a flow rate of 0.35L/h. No further increase in current was observed at flow rates above 0.35L/h. The increase in current with flow rate indicated a response of MFC-TMBR system in terms of biosensor. An enrichment of electrochemical microbial in the cathode chamber was achieved by an increase in the rate of mass transport. A peak current was observed at higher feeding rate.

Table 1 also describes the changes in COD effluent, coulombic efficiencies and TMP for each HRT. By increasing the flow rate and decreasing the HRT, the effluent COD and COD removal rate increased. For the first step, the effluent COD accounted for 6% of the influent, whilst for the last step, it was approximately 10%. The coulombic efficiencies (5%-6.5%) were close in the cell. The TMP increase rate was increased with each step in flow rate, doubled from -2.3kpa/h for a flow rate of 0.2L/h to -4.6kpa/h for a flow rate of 0.35L/h. The increase in TMP was mainly caused by the increased permeate flow. The increasing effluent COD might also have some effect on

TMP variation, at least not serious. Therefore it was decided to perform all the following tests at a flow rate 0.3L/h and HRT 7.3h which gave the higher steady-state current and coulombic efficiency.

3.3. Effect of MLSS

The effect of MLSS on the system response was investigated as shown in Fig.3a. Different MLSS seemed to provide serious impacts on electricity generation in a bio-cathode MFC. A series of tests was therefore performed in which the MLSS concentration was varied from 3400mg/L to 12240mg/L at a constant inlet COD concentration of 1000mg/L to explore the effect of MLSS on the sensor of performance. With other operating conditions unchanged, when MLSS increased from 3400mg/L to 4340mg/L, the current stable peak increased 19% from 0.64mA to 0.76mA while the anode potential was kept constant at -0.40V and the dissolved oxygen (DO) was above 5mg/L. However, when MLSS increased from 5870mg/L to 12240mg/L, the current stable peak was dropped step by step as well as the DO. MLSS (5870-12240mg/L) gave a decrease of current accounting for 48%. The DO decreased to 2.5mg/L from 6.8mg/L. So change in MLSS led to a change in current under a constant aeration. From the experiment it has become clear that changes in MLSS might be the results of a serious change in current. It has been shown that changes in DO can also give current changes in the same order of magnitude. This shows the necessity of a good control of these variables.

A linear relationship between current and MLSS concentration was observed with

a constant aeration (Fig.3b). The linear regression coefficient was 0.941. The current were almost perfectly inversely proportional to MLSS concentration. The results indicated that the MLSS concentration was important for the bio-cathode MFC biosensor. The operations of TMBR were required to be taken into account for choosing an appropriate MLSS concentration and an appropriate aeration. The lower MLSS the higher current, and thus, the higher oxygen would be consumed at the cathode. Therefore, using of relative higher MLSS concentration could lower the impact of oxygen consumption by electro-microorganism on the monitoring activities.

Sludge loading rate was one of the most important parameters during the TMBR operation. With the increasing level of the sludge concentration, a variation on sludge loading rate was taken place, which led to different treating efficiency. The sludge loading rate was calculated by Formular (5):

$$Ns = F/M = QS/VX \quad (5)$$

Where Ns is the sludge loading rate (kgCOD/kgMLSS·d), Q is the daily flow rate (m^3/d), S is the COD concentration (mg/L), V is the solution volume (m^3) and X is the sludge concentration (mg/L). The sludge loading rate was investigated under different MLSS concentration as shown in Table 2. The lower MLSS concentration resulted in a considerably better sludge loading rate and a higher current peak of the system. In particular, in the case of an up-shift to MLSS, the sludge loading rate was falling step by step as well as the steady-state current. When MLSS concentration increased from 4300mg/L to 5870mg/L, the sludge loading rate ranged from 0.754kgCOD/kgMLSS·d

to 0.558kgCOD/kgMLSS·d. In general sludge loading rate between 0.5-0.9kgCOD/kgMLSS·d could perform a better sludge adsorption and precipitation. Therefore, 4340±140mg/L MLSS concentration gave the highest current peak and the optimal sludge loading rate. Considering the above, 4340±140mg/L MLSS concentration was used in the following experiments.

3.4. Effect of EPS on electricity generation and membrane fouling variation

TMP is a critical parameter for operating performance of TMBR. In order to investigate its effect factors, the average TMP was calculated every 6 hour interval and was plotted as shown in Fig4a. The TMP variation indicated the membrane fouling characteristics in MFC-TMBR system. The system was operated 30 days continuously and the MLSS concentrations were 3400±189mg/L, 4340±140mg/L, 5870±117mg/L, 6780±85mg/L, 8550±125mg/L, 10090±150mg/L, respectively. The line expresses the slope of TMP increasing rate under different MLSS concentration. The TMP and the average current outputs were observed at all the tested MLSS concentration. It was found that the higher MLSS concentration resulted in higher slope, and the difference was visible, but the average current was decreased simultaneously, which indicated that the TMP and the current had an inverse relationship with an increasing MLSS concentration. To better understand the relationship between membrane fouling mechanism and current variation, EPS was a controlling factor of membrane fouling in MBR, which need to be conducted.

EPS played a significant role in membrane fouling during MBR operation. The

concentration of EPS including lower proteins (EPS_P) and higher carbohydrates (EPS_C) under different MLSS concentration were observed as shown in Table 3. At low MLSS level, EPS was relatively low. The higher MLSS resulted in higher EPS. The concentration of EPS secreted by microorganisms reflected the degree of activity in general aerobic process and metabolism. EPS could be used by bacteria as carbon and energy sources, and it would be released seriously when there was a substrate shortage (Sheng et al., 2010). Higher EPS indicated that lower electro-microorganisms operated in electricity generation, meaning that the changes in current would be taken place. In addition, according to Lin et al. (Lin et al., 2009), higher EPS would have higher stickiness to favor the development of cake layer formation, which aggravated the membrane fouling. Therefore, the concentration of EPS in the bio-cathode chamber affected the long-term stability of the sensor and the operation of MFC-TMBR. These results underline that the sensor needs calibration by taking the concentration of EPS into account.

3.5. Sensor response to COD concentration

The bio-cathode MFC biosensor was tested with external resistance of 1000Ω. Fig.5a shows the dynamic response of the biosensor to different COD levels (100-3000mg/L). The cell was continuously fed with a specific COD until a steady current was generated. The current increased stepwise as the COD increased from 100mg/L to 1000mg/L. When the bio-cathode was fed with COD concentration of more than 1000mg/L, only a small increase in the current was observed. The arrows show the

moments when we injected the bio-cathode MFC with substrate. After each change of COD levels, response time was observed for biosensor to reach a new steady-state current (Fig.5a), indicating the good sensor sensitivity. As the special character of the bio-cathode microorganism such as certain adaptation, rapid propagate and metabolize, the current was dropped at first and then rose sharply when changing the COD level. For a fixed inlet COD, a stable current was obtained with a coefficient of variation of 0.1%. Fig.5b shows the variation in current with COD concentration. The correlation between current and COD concentration was established as shown in Fig.5c and Fig5d. It is clear shown that the current (0.3±0.005-0.75±0.003mA) increased linearly (regression coefficient, R^2=0.97) with COD up to 1000mg/L (Fig.5c), which presented a good reproducibility. Due to a better oxygen supply at the cathode and a larger area of the cathode electrode, the dynamic range of COD concentration detected by biosensor was increased. Nevertheless, the increase was not significant by further increasing COD concentration, which suggested that the current generation was nearly saturated. The relative standard deviation of the current at each COD level was less than 3%. Fig.5d provides correlations between the influent COD (100-3000mg/L) and the peak current. The model of Michaelis-Menten-type law was introduced to express the variation of the current with COD:

$$J = \frac{J_{\max} COD}{K_{COD} + COD} \quad , \tag{6}$$

Where J_{max} (mA) is the maximum current that could be provided by the bio-cathode at the applied potential in optimal COD condition, and K_{COD} the Michaelis-Menten

equivalent constant in terms of COD (mg/L). Fitting was done with J_{max} = 0.906 and K_{COD} = 267.609 for reactor (Fig.5d). The regression coefficient was 0.89. The model revealed that organic matter degradation reaction by microorganisms is a first order reaction at low COD inlet, and mixed order reaction was obtained when substrate concentration was up to an intermediate level. However, with the increasing of substrate concentration continuously, biodegradation reaction was in transition from first order reaction to zero-order reaction. The degradation reaction model fitted the experimental COD and a surprisingly high electrochemical COD abatement was obtained at inlet COD of 1000mg/L. In addition, the model was fitted better at high COD level as shown in Fig.5d.

The above results suggest that the bio-cathode MFC has the potential to be a simple and rapid COD sensor and applied a model to predict higher COD concentration. Compared with conventional COD sensors or measurement methods, the bio-cathode MFC-based biosensor for TMBR has its own advantages. Firstly, there is no need of external power sources. The sole fuel to power the MFC is wastewater, which make the sensor suitable for long-term monitoring. Secondly, Bio-cathode MFC biosensor made an intelligent use of the electrical energy. The electrical current as a direct, real time measure of COD can be easily measured. The biosensor can be connected with various data logging system for online monitoring. Lastly, bio-cathode MFC can be applied in suit to tubular membrane reactor using MFC-TMBR system without extra construction. In addition, the development in bio-cathode MFC also provided an opportunity to widen

the application of the MFC-based biosensor. For TMBR part, a combination of TMBR and bio-cathode MFC-based biosensor was a novel way to realize the on-line TMBR operation monitoring embedded in the better control of loading rate, MLSS and COD, which made TMBR become a more attractive, promising technology. The MFC-TMBR system has the potential to dash towards integration of wastewater treatment, energy recovery, biosensing and real time on-line monitoring.

To further insight into the reason for the current variation caused by bio-cathode, the mass balances of COD were analyzed. With the inlet COD concentration of 1000mg/L, the mass balances of COD in bio-cathode MFC are shown in Fig.6. Bio-cathode chamber contained electricity generation process. The COD consumption related to electricity process might include COD recovery in electrogenesis and COD metabolized by microbes. COD abatement related to the electrochemical reactions was calculated from the electrical charge extracted from the system by the bio-cathode (Ketep et al., 2013):

$$e\Delta COD_{\exp} = \frac{A}{V_s}\frac{32}{4F}\int_t^{t+\Delta t} Jdt \qquad (7)$$

Where A is the electrode surface area (m^2), V_s is the solution volume (m^3), 32 is the molar mass of oxygen (g/mol), n = 4 is the number of electrons exchange per mol of oxygen oxidized (mol^{-1}), F = 96485 is the Faraday constant (C/mol), J is the current density (A/m^2) and t is the time (s). Based on the equation mentioned above, the current over time in the form of ΔCOD could be calculated as 38 mg/d, account for 1.7% COD translating into electricity.

4. Conclusion

A new type of bio-cathode MFC-based biosensor for TMBR was developed as a practical application instance. The objective of the work was to investigate the effects of operation parameters on MFC-TMBR system and assess the performance of the biosensor for COD monitoring. Strict control of anode potential was important to obtain a stable baseline current. Higher loading rate and MLSS concentration had much effect on current generation. Linearity was observed for COD and MLSS, and the coefficients of determination (i.e. R^2) were generally higher. The increased EPS predicted the falling tendency in current and the rising tendency in TMP.

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Figure Captions

Fig.1. Schematic of the MFC-TMBR integrated system.

Fig.2. (a) Variation of current with time electrochemically-active microorganism of MFC-TMBR; (b)Polarization and power density curves for the MFC.

Fig.3. MFC-TMBR response to MLSS concentration. (a) Current generation under different MLSS concentration; (b) Calibration curve.

Fig.4. Profile of TMP increases in MFC-TMBR system.

Fig.5. MFC-TMBR response to COD concentration. (a) Current generation under different COD concentration; (b) Steady-state current in relation to the inlet COD; (c) Calibration curve; (d) Sigmoidal calibration curve.

Fig.6. The mass balances of COD in the MFC-TMBR system.

Table 1. Effect of loading rate on current generated and TMP variation

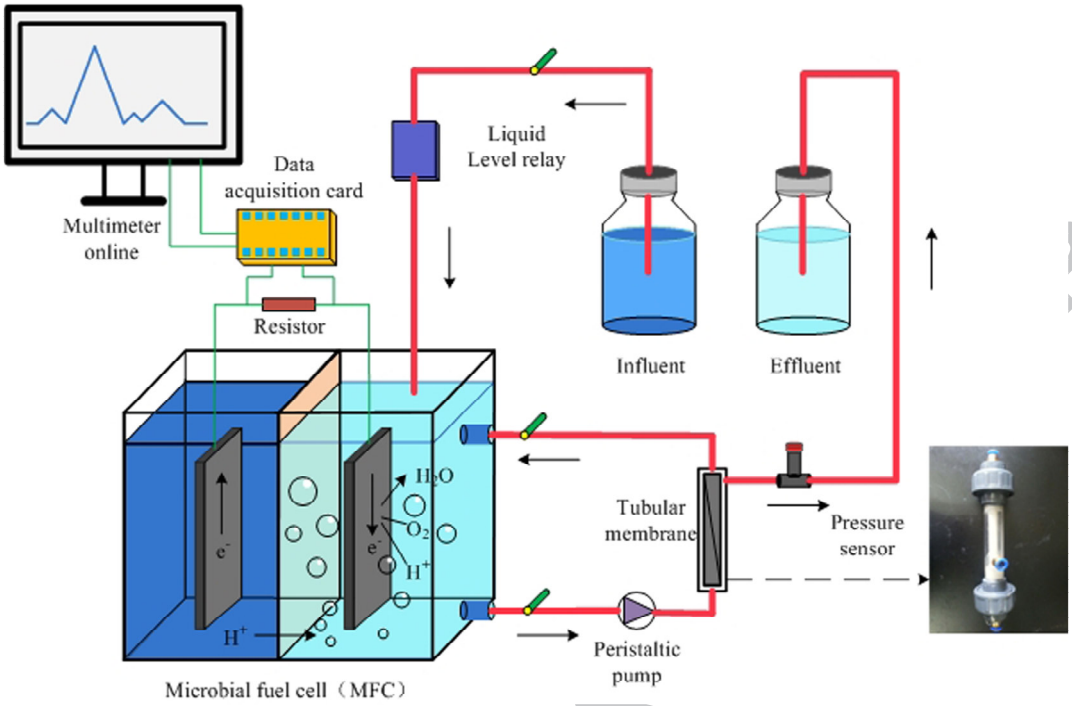
Flow rate (L/h)	Loading rate (mgCOD/h·m^3)	Steady-state current (mA)	HRT (h)	COD effluent (mg/L)	COD removal rate (mgCOD/h)	Coulombic efficiency (%)	TMP increase rate (kpa/h)
0.2	0.091	0.48±0.02	11	60±5.0	85.50±0.5	5.5±0.1	-2.3±0.1
0.25	0.114	0.62±0.05	8.8	75±2.7	105.10±0.3	6.0±0.4	-3.5±0.1
0.3	0.137	0.73±0.03	7.3	80±3.5	126.00±0.5	6.5±0.3	-4.2±0.3
0.35	0.159	0.76±0.01	6.3	100±1.6	142.85±0.3	5.8±0.8	-4.6±0.2

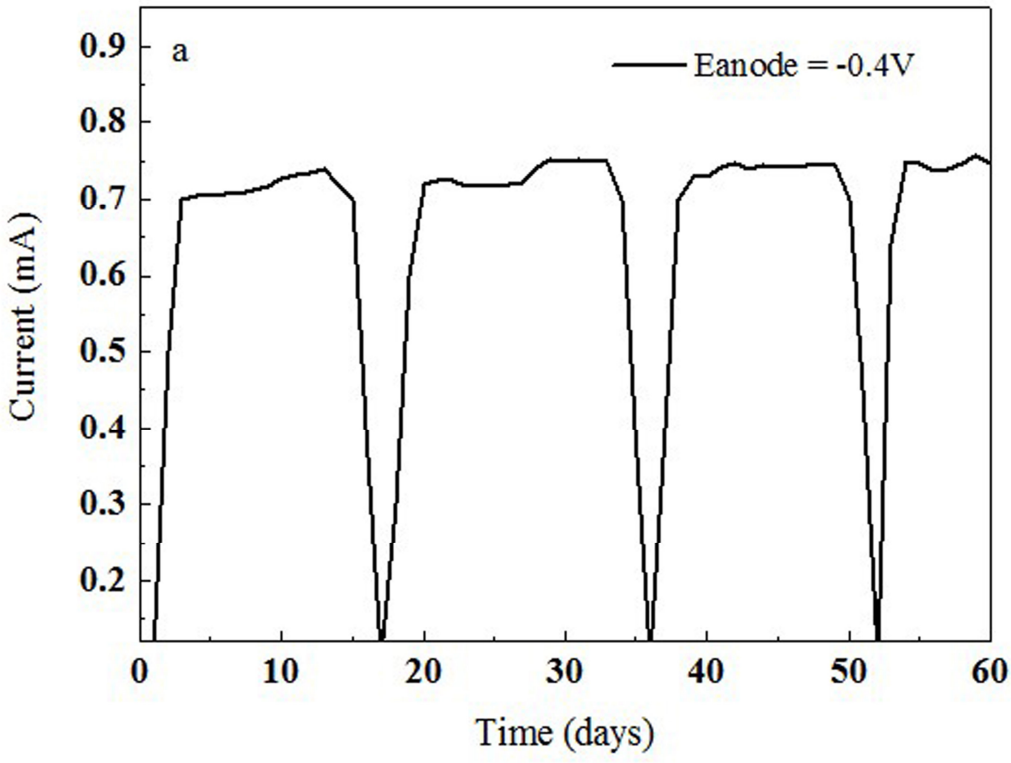
Table 2. Sludge loading rate in relation to MLSS concentration

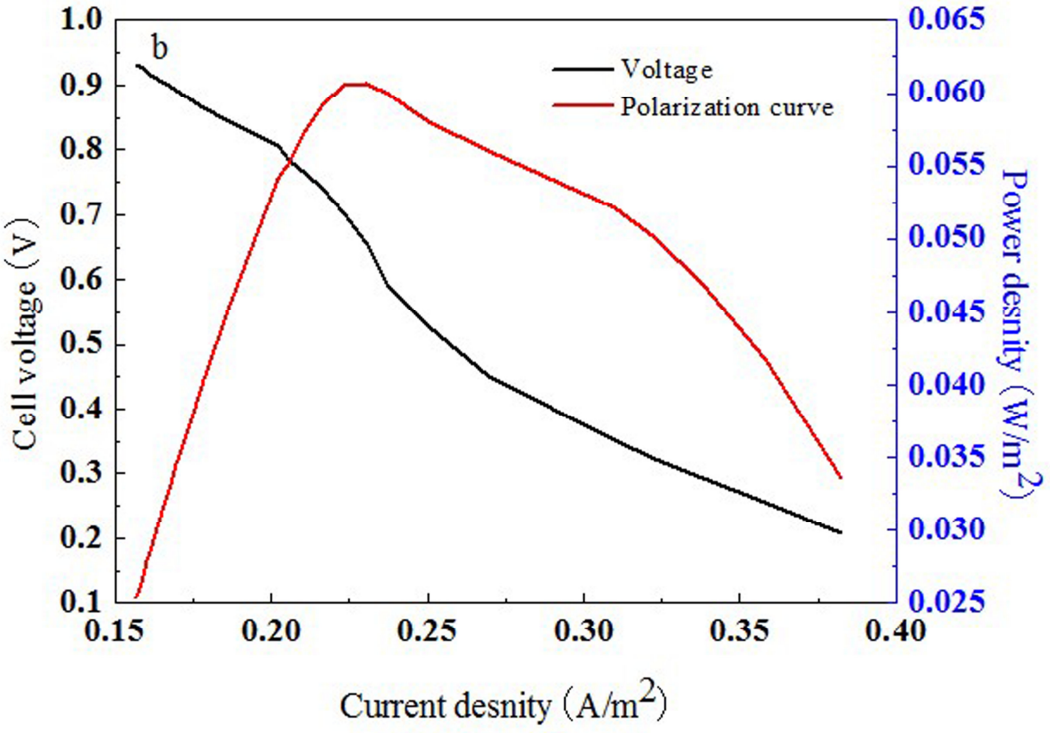
MLSS (mg/L)	Sludge loading rate (kgCOD/kgMLSS·d)	Steady-state current (mA)
3400±189	0.963	0.66±0.02
4340±140	0.754	0.76±0.03
5870±117	0.558	0.64±0.02
6780±85	0.483	0.56±0.03
8550±125	0.383	0.45±0.04
10090±150	0.324	0.35±0.03
12240±72	0.267	0.28±0.02

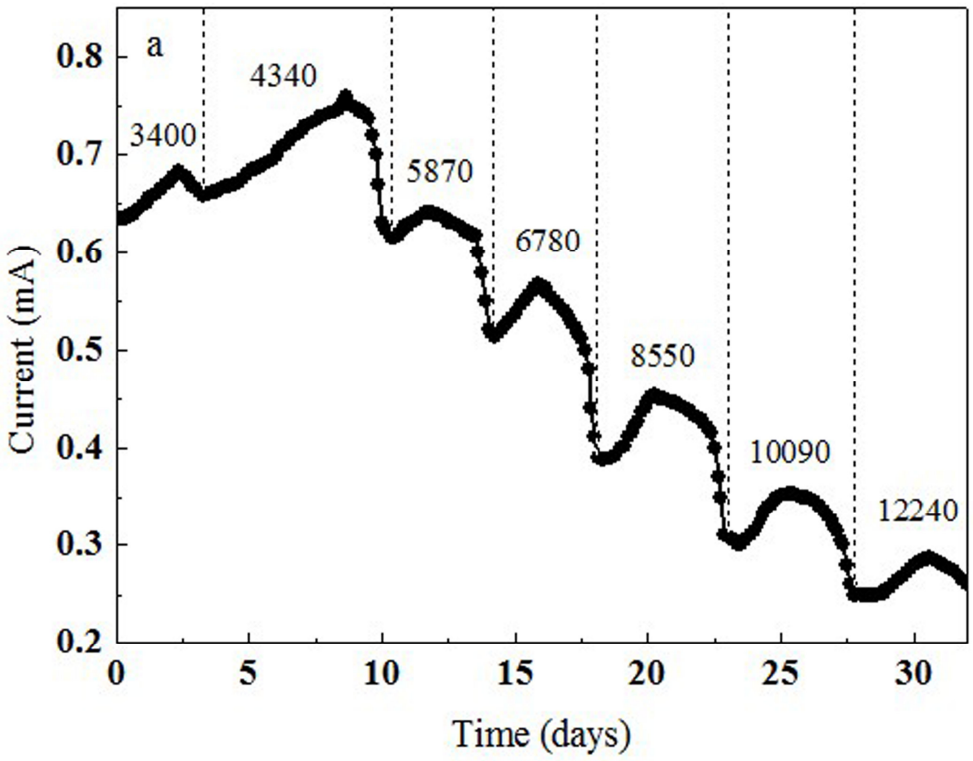
Table 3. Effect of sludge characteristics on current generated

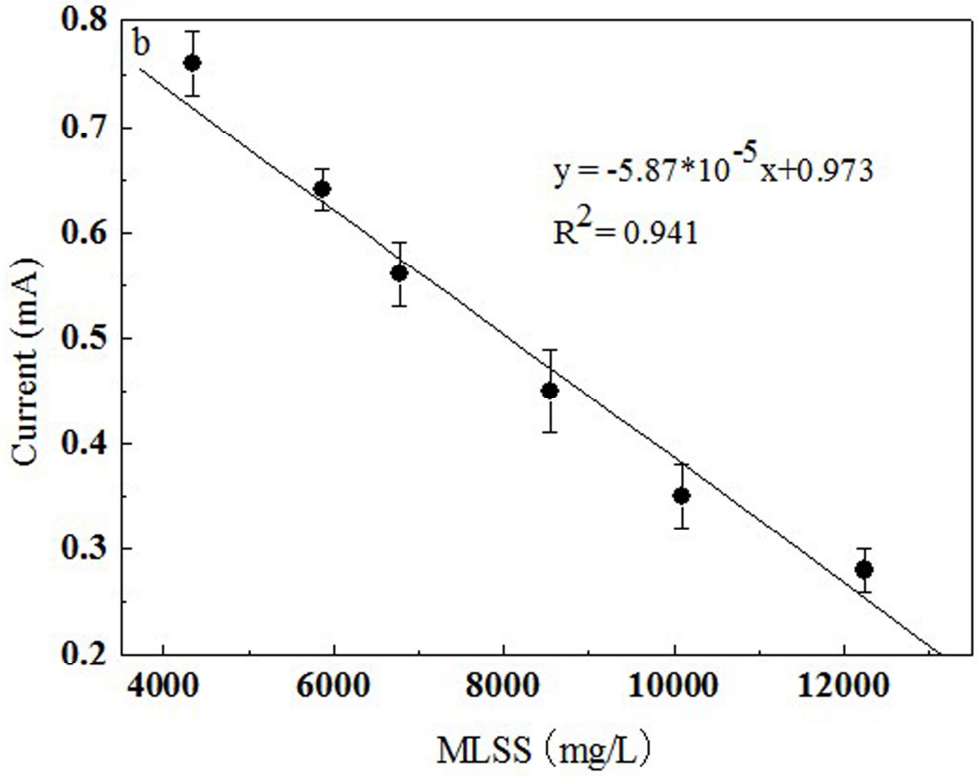
MLSS (mg/L)	EPS (mg/gMLSS)	EPS_P (mg/gMLSS)	EPS_C (mg/gMLSS)	Steady-state current (mA)
3400±189	84.92±1.5	32.94±0.8	51.98±0.5	0.66±0.02
4340±140	89.41±1.3	35.56±0.7	53.85±0.6	0.76±0.03
5870±117	93.30±0.9	37.88±0.5	55.42±0.4	0.64±0.02
6780±85	98.56±2.1	40.12±0.5	58.44±1.5	0.56±0.03
8550±125	109.22±1.9	44.65±0.9	64.57±1.2	0.45±0.04
10090±150	123.49±1.0	50.83±0.4	72.66±0.6	0.35±0.03

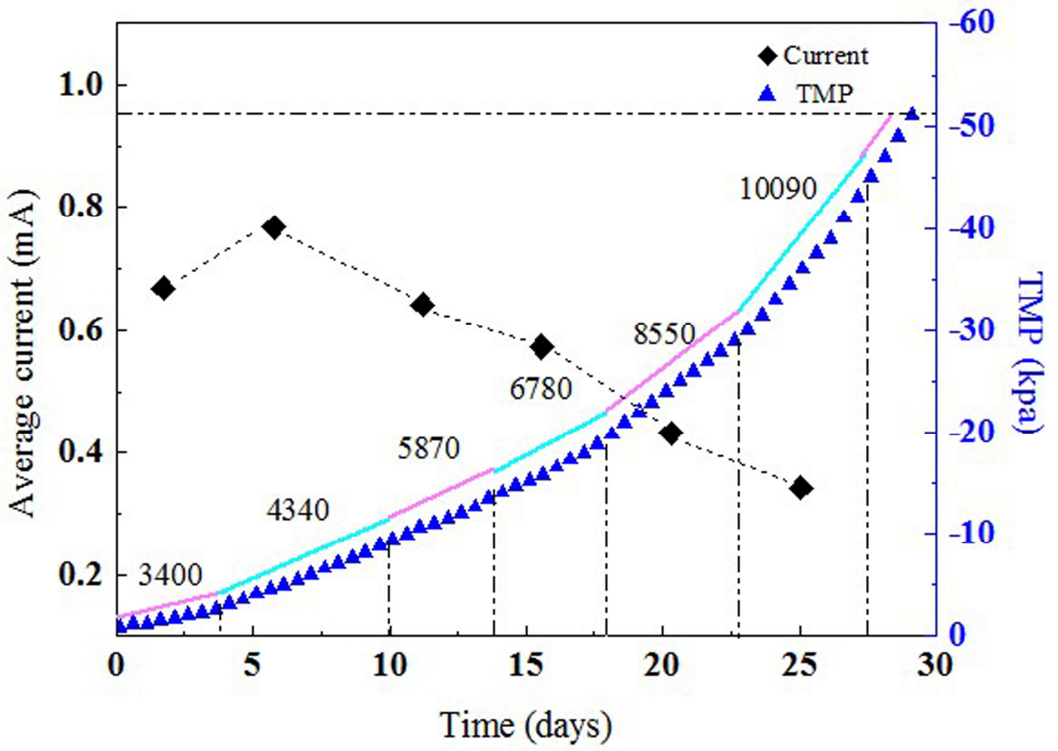


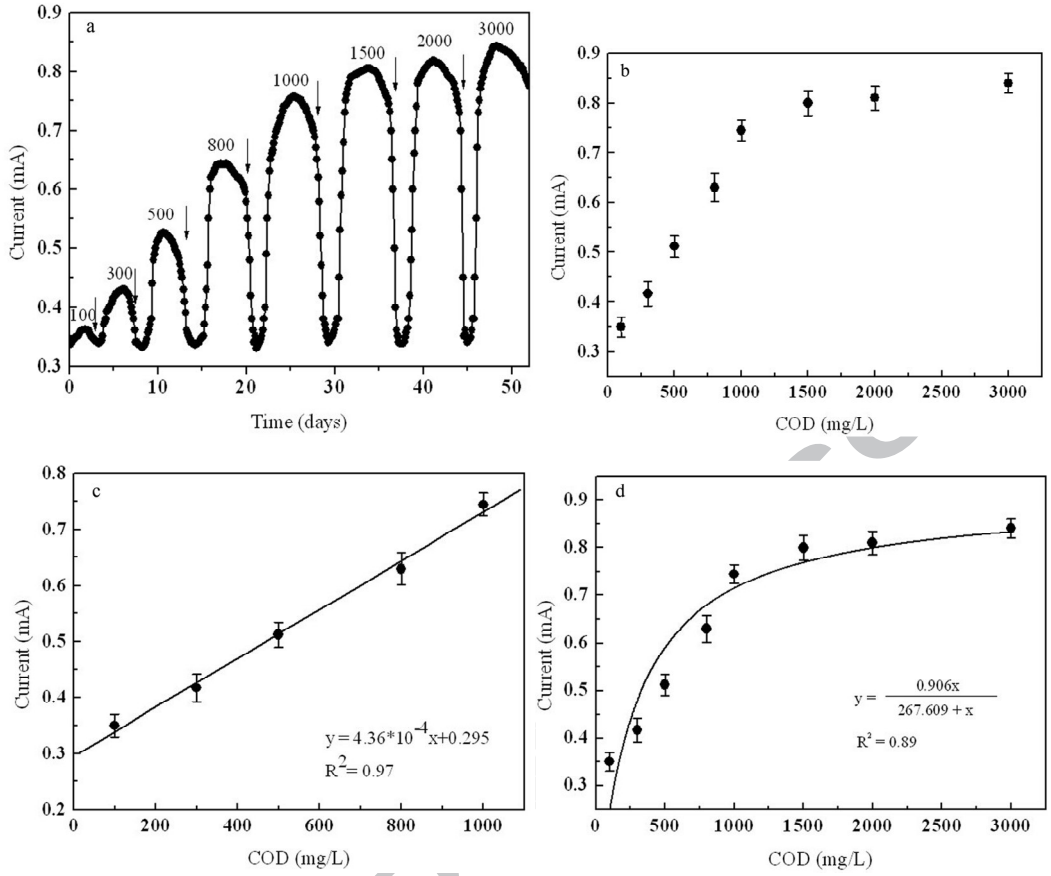


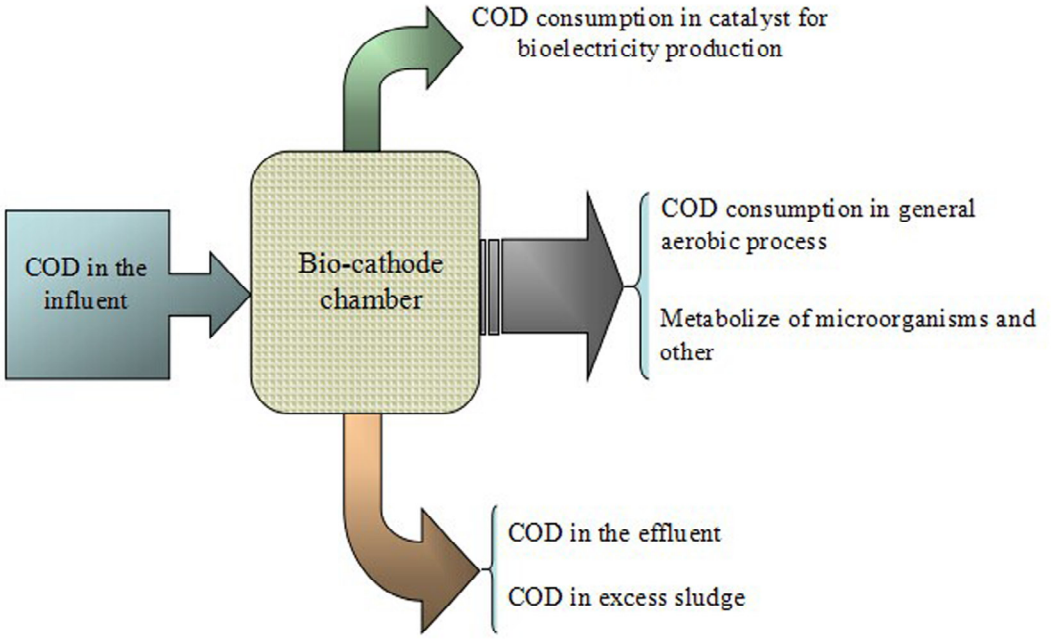












Highlights:

1. A new type of bio-cathode MFC-based biosensor was developed for COD monitoring.

2. The performance of bio-cathode MFC-based biosensor was affected by HRT, MLSS and COD.

3. The range of COD concentrations detected by biosensor was increased.

4. The MFC-TMBR system produced electricity for biosensing while organic was degraded.