Enhancement of Emerging Contaminants Removal Using Fenton Reaction Driven by H₂O₂-producing Microbial Fuel Cells

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Abstract

The discharge of emerging contaminants (ECs) into the environment has raised great concerns due to their negative effects on the ecosystem. Intensive research efforts have been undertaken in order to find effective methods to treat these compounds. In this study, the removal of four ECs including Bisphenol A (BPA), Estrone (E1), Sulfamethazine (SM2), Triclocarban (TCC) was investigated in the microbial fuel cell (MFC)-Fenton system. Glucose and graphite rod with stacked graphite granules were used as the substrate and electrode, respectively since they improved current density of MFCs system and increased cathodic H₂O₂ synthesis. Both batch and continuous flow modes of MFCs were compared and the operational parameters for higher H₂O₂ yield were also studied. The results showed that for both batch and continuous flow modes, initially the H₂O₂ production had a rising trend and arrived at the highest level but subsequently it decreased. We later

demonstrated that controlling pH at 3 would promote H₂O₂ accumulation. Integrating the in-situ H₂O₂ synthesis and Fe²⁺ addition in the cathodic chamber, production of hydroxyl radicals was evidenced through salicylic acid degradation and formation of its hydroxyl products. The MFC-Fenton system could effectively remove E1, BPA, TCC and SM2. Our results showed that the removal of ECs was attributed to the oxidation by •OH and the adsorption on graphite materials. The contribution of the two removal mechanisms to the overall removal will vary with different ECs depending on the ECs reactivity in Fenton reaction. This study demonstrates the application of the MFC-Fenton technology to effectively remove E1, BPA, TCC and SM2, which provides a promising and cost-effective alternative for future ECs removal.

Key words:

Microbial fuel cell (MFC); emerging contaminants (ECs); Fenton; hydrogen peroxide synthesis

1. Introduction

The release of emerging contaminants (ECs) into the aquatic environment has attracted great concern, as a number of endocrine disruptors and antibiotic resistance in different organisms were observed from the long-term contact of ECs [1-3]. Wastewater treatment plants (WWTPs) are primary sources for ECs discharge into the aquatic environment [4, 5]. Therefore, the effective removal of ECs from wastewater is essential to prevent aquatic environment from contamination of ECs. Due to the increasing awareness of the risks resulting from emerging contaminants, public health officials and researchers are questioning the ability of current treatment processes for effectively removing these chemicals from water and wastewater to levels that do not pose a public health risk [6]. Conventional WWTPs with biological treatment processes are reported to remove varying extent of ECs from wastewater [7-10]. However, the remaining ECs in the WWTPs effluent are still a major concern for the receiving environment and downstream users [11]. It is challenging to develop effective and environmentally friendly approaches for ECs removal.

Hydrogen peroxide (H_2O_2) is a commonly used compound in different areas; especially it is the major component in the Fenton process, which is one of the most effective advanced oxidation agents and has been widely applied to clean up recalcitrant chemicals / contaminants. It is attractive to achieve H_2O_2 generation in-situ without transport and storage of H_2O_2 and immediately use for contaminants removal. For this purpose, in-situ H_2O_2 synthesis can be achieved in the electrochemical cell with external power supply [12]. Bio-electrochemical systems, e.g. microbial fuel cells (MFCs), have been successfully developed for wastewater treatment and could recover energy directly from the wastewater [13-15]. Microorganisms can produce electricity in the system by oxidizing organic matters in the wastewater [16, 17]. Recently, several studies have proven the concept that cathodic H_2O_2 could be synthesized on the surfaces of carbon materials through biological electrons generated in MFC system without the need for external power supply (Eq. 1) [18-20]. As reported earlier [18, 21], a two-electron oxygen reduction could be controlled for H_2O_2 production by using a spectrographically pure graphite electrode with a relatively low energy consumption. The electrode material is considered as an important factor for H_2O_2 production. For example, Li et al. (2016) developed a carbon black and graphite hybrid air-cathode MFC for H_2O_2 production. The optimal mass ratio of carbon black to graphite is 1:5 with the maximum H_2O_2 yield of $11.9 \text{ mg/L/h /cm}^2$ [22]. Several other factors were demonstrated to have influence on the H_2O_2 production in a bioelectrochemical system, such as the resistance value. For instance, it was pointed out that the amount of H_2O_2 production increased along with the decrease in external resistance [18]. Thus far, there is still limited study on operational parameters effect on the H_2O_2 synthesis, such as the substrate types, and operating mode (batch or continuous).

Furthermore, several reports have shown the feasibility of utilizing the similar principle of E-Fenton process in the MFC for contaminant removal or sustainable environmental remediation,

which is named as the Bio-E-Fenton or MFC-Fenton process [19, 21, 23, 24]. These reports have demonstrated the utilization of H_2O_2 produced in MFC with Fe^{2+} as the Fenton reagent for the production of $\bullet\text{OH}$ (Eq. 2 and 3) to remove recalcitrant pollutants (RP) (Eq. 4), including azo dyes [21, 23, 25] and p-nitrophenol [26]. However, only limited study focused on the removal of ECs using the MFC-Fenton system.

The goal of this study was to provide insight into in-situ H_2O_2 production in the MFC-Fenton system under varying operational conditions, including different substrates and electrodes. Afterwards, we tested the capability of MFC-Fenton process to treat different ECs under both batch and continuous operations. The ECs used in this study included Bisphenol A (BPA), Estrone (E1), Sulfamethazine (SM2) and Triclocarban (TCC) due to their frequent detection in the wastewater. The performance and parameters influencing the degradation of ECs in the MFC-Fenton system were evaluated.

2 Materials and Methods

2.1 Reagents and Chemicals

The ECs used in this study included E1 (99%, Sigma-Aldrich, USA), BPA (99%, Sigma-Aldrich, USA), SM2 (99%, Aladdin Chemistry Co Ltd., China) and TCC (98%, Adamas Reagent Co, Ltd., China). The chemicals used for the mobile phase of high performance liquid chromatography (HPLC) detection included HPLC grade acetonitrile (CH_3CN , Burdick and Jackson, Muskegon, MI) and methanol which was purchased from Mailinckrodt chemical company

(St. Louis, MO). Salicylic acid, catechol, 2,3-dihydroxybenzoic acid (2,3-DHBA, 99%), 2,5-dihydroxybenzoic acid (2,5-DHBA, 99%) were purchased from Sigma-Aldrich (USA). All other reagents were commercial products of the highest grade available.

2.2 MFC system construction and operation

The MFC reactor was comprised of plexiglass dual chambers physically separated by a proton exchange membrane (Qianqiu, Zhejiang, China). Each chamber had a net volume of 125 mL ($5 \times 5 \times 5 \text{ cm}^3$). The anodic and cathodic catholyte were 64 mL. All the MFCs were inoculated and operated with acclimated anaerobic activated sludge and pre-acclimated under $1 \text{ k}\Omega$ of external resistance for 3 months before downstream study of H_2O_2 generation and ECs degradation. The anode solution contained glucose (12 mM), NH_4Cl (2 mM), KCl (5 mM), $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (0.2 M), and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (0.2 M). The trace elements were prepared according to previous study [14]. The cathode chamber was filled with Na_2SO_4 (0.1 M) with four ECs (E1, BPA, SM2 and TCC) and aerated with air [18].

To assess the H_2O_2 generation and ECs degradation, the MFCs were operated in batch or continuous flow modes in the anodic chamber (Table 1). According to the reported study [18], the amount of H_2O_2 production dropped along with the increase of external resistance. Thus, in this study $10 \text{ }\Omega$ of resistance was used to achieve higher yield of H_2O_2 for ECs degradation. Carbon cloth or graphite were purchased from Qianqiu Company (Zhejiang, China) and used as the electrodes. The MFCs with electrodes of graphite rods or graphite granules were referred as RB. The graphite granules (Qianqiu, Zhejiang, China) were 0.5 cm in diameter and 0.6 cm in length. Two graphite rods (diameter 1 cm and length 8 cm) were used for both electrodes. Within batch mode, the anodic and cathodic solutions was replaced every 48 h for batch test. Meanwhile, different substrates (glucose and acetate) and their concentration effects were studied. To compare

the operational mode effect on H_2O_2 generation, in the continuous flow experiment, the anodic solution was fed into the anodic chamber with a flow rate of 0.21 mL/min (HRT= 5.1 h). The MFC systems conducted under continuous flow were referred as RC. To test the effect of pH, the pH of cathodic solution was then controlled at 3 by manually adding 0.1 M H_2SO_4 in continuous flow mode and the corresponding MFCs were referred to as RC3 and RC4. The pH was monitored by a probe meter (Denver instrument UB-7, US).

Afterwards, the optimum condition for H_2O_2 synthesis was applied to study ECs degradation. To verify that degradation took place partly due to absorption, controls were run in parallel with open circuit. To produce $\bullet\text{OH}$, the catholyte was adjusted to pH 3.0 and added 1.25 mM of FeSO_4 [27].

2.3 Chemical analytical methods

Samples containing four ECs were taken from the cathodic chamber at different time intervals and then extracted using ether for HPLC - UV (Dionex Ultimate 3000, USA) analysis. The initial concentration of ECs was 1 mg/L. The pollutants were detected by HPLC equipped with the C18 column (150 × 4.6mm, 5 μm , Lachrom, Japan) and the mobile phase was composed of acetonitrile (35%) and Milli-Q water (65%) at a flow rate of 0.3 mL/min and the absorbance wavelengths were 256 and 220 nm. All of the analysis was conducted in triplicate with relative errors less than 10% at room temperature and atmospheric pressure.

H_2O_2 concentration was determined at 0, 2, 6, 8, 12, 24, 36, and 48 h through the I_3^- Method and by KMnO_4 Titration [28]. The production of $\bullet\text{OH}$ was further confirmed using the trapping reagent salicylic acid and reaction products including 2,3-DHBA, 2,5-DHBA, and catechol [29]. The concentration of salicylic acid, 2,3-DHBA and 2,5-DHBA were measured by HPLC equipped with the C18 column (250×4.6 mm, 5 μm , Thermo, USA). For salicylic acid analysis, the mobile

phase contained 25% acetonitrile and 75% KH_2PO_4 solution (2.55g/L) with the absorbance wavelength at 236 nm [30]. In terms of the analysis of catechol, 2,3-DHBA and 2,5-DHBA, the mobile phase was composed of acetonitrile (10%), methanol (10%), citric acid (0.03M), acetic acid (0.3M) with the absorbance wavelengths at 326 and 275 nm, respectively. The flow rate for the mobile phase was 1 mL/min.

2.4 Electrochemical measurements

Cell voltage (U) was recorded online every 10 min via a data acquisition system (USB7660-B, ZTIC, China) which was connected to a personal computer. The current (I) was calculated from the external resistance and cell voltage (U) according to Ohm's law ($I = U/R$). The power densities (P) were normalized to the liquid volume of the anodic chamber. P was calculated by using $P \text{ (mW/m}^3\text{)} = 10^3 U^2 / (RV)$, where U (mV) was the output voltage, V (cm^3) was the volume of the anodic chamber, and R (Ω) was the external resistance [14, 31].

3 Results and discussion

3.1 Optimization of process performance for in-situ cathodic H_2O_2 synthesis MFC systems

3.1.1 The effects of different substrates and electrodes on cathodic H_2O_2 production

The anodic substrate is significant for the MFC, because it influences not only the bacterial community in the anodic biofilm, but the reactor performance including the power density and coulombic efficiency [32, 33]. However, a H_2O_2 -producing MFC should be used for H_2O_2 generation rather than producing voltage [18], since the process of H_2O_2 production in MFCs requires the two-electron pathway for oxygen reduction rather than four-electron pathway in the cathode. With these respects, it is necessary to investigate the substrate effect on H_2O_2 synthesis, including carbon

sources and their concentration. The initial chemical oxygen demand (COD) concentration was approximately 700 mg/L for both glucose- and acetate-fed MFC systems. According to Fig. S1 in Supporting Information (SI), in glucose-fed MFC system the maximum H_2O_2 concentration was 0.36 mg/L using graphite rod as the electrode. In contrast, the corresponding H_2O_2 concentration in the acetate-fed MFC system was 0.08 mg/L. This could be likely attributed to the widest community diversity in glucose-fed MFCs [32, 34]. It was pointed out that the presence of more complex mixed consortia of diverse exoelectrogens or the syntrophic bacteria due to the production of diverse glucose fermentation byproducts such as acetate and butyrate, resulting in the rapid generation of current without lag time [32]. Therefore, higher current density was achieved in glucose-fed MFC in our study (Table 2).

Furthermore, H_2O_2 production can be further improved by adding graphite granules into the anodic and cathodic chambers. According to Table 2, H_2O_2 production in reactors RB-2 to RB-6 gradually increased from 0.36 to 0.8 mg/L with the increase of graphite granules in the anodic and cathodic chambers. In addition, when compared with reactors RB-6 and RB-8, it was found that the maximum concentration of H_2O_2 increased from 0.80 to 2.06 mg/L when the glucose concentration increased by three times with the graphite rod and graphite granules as the electrode. As shown in Table 2, adding graphite granules and increasing glucose concentration effectively boost current and current density of the MFC system, which contributes to the enhanced H_2O_2 production. For example, when the current density was 4.4 A/m^3 , the maximum H_2O_2 concentration was only 0.25 mg /L. However, 2.06 mg/L H_2O_2 was produced under 32.8 A/m^3 current density. This provides a potential method to enhance the production of H_2O_2 by increasing the current density.

3.1.2 In-situ H₂O₂ production in batch and continuous flow mode MFCs

Through comparing different carbon substrates and electrodes, glucose and graphite rod with 100 graphite granules were chosen for further experiments. Fig. 1a exhibits concentration of H₂O₂ in the cathodic chambers of MFC system with close and open circuit (RB1 and RB2) in batch mode. The concentration of H₂O₂ in the cathodic chamber of RB1 fluctuated over 24 h. More specifically, in the beginning, the H₂O₂ production had a rising trend, increasing from 0 mg/L at 0 h to 2.1 mg/L at 8 h, which was equivalent to a volumetric H₂O₂ production rate of 6.3 g H₂O₂/m³/d. After that, the concentration of H₂O₂ declined. Finally, H₂O₂ concentration dropped to 0.8 mg/L at 24 h. However, almost no H₂O₂ was detected during the whole 24 h in RB2.

As shown in Fig. 1b, generally, the corresponding H₂O₂ concentration in the continuously-fed MFC witnessed a similar trend to that in batch MFC. During the first 8 h, the H₂O₂ production arrived at the highest level (1.8 mg/L at 8 h) and subsequently it decreased. The final concentration of H₂O₂ was approximately 0.3 mg/L at 48 h. The H₂O₂ concentration of RC1 (1.19 mg/L) at 24 h was higher than that in the RB1 (0.8 mg/L). The H₂O₂ concentration in continuous mode RC1 dropped at a slower rate than that in batch-mode RB1, implying the positive effect of continuous feeding to the anodic chamber. However, the original purpose for the continuously-fed MFCs was to achieve the accumulation of H₂O₂, but the result was not as high as expected and we were surprised to see the rapid decline of the H₂O₂ concentration as in the fed-batch MFCs. The findings led to the question: What could be the possible factor affecting the stable H₂O₂ generation? The reason for the unstable status of H₂O₂ in MFCs is discussed below in Section 3.1.3.

3.1.3 pH effect on H₂O₂ generation in continuous MFCs

Fig. 1c indicates the variation of pH in the cathode of MFC systems under batch and continuous flow operation. Generally, the operation mode showed less influence on pH variation. More exactly, the initial pH was controlled at 3. The pH consistently rose in the next 48 h and eventually the pH mounted to approximately 9. Whereas the corresponding pH in the open circuit (RC2 and RB2) was kept stable level, due to no power generation in the cathode.

Since the optimal pH for Fenton reaction is generally in the range of 2.5-3.5 [35], the increasing pH in the cathode would inhibit the H₂O₂ generation and •OH occurrence. The H₂O₂ production with pH control is described in the Fig. 1c. After 6 h, the average concentration of H₂O₂ was above 1.5 mg/L. The maximum value reached 2.75 mg/L, which was 1.6 folds of that in RC1 without pH control, indicating that pH was a critical parameter for H₂O₂ generation. Therefore, controlling catholyte pH was an effective approach to enhance H₂O₂ production, and should be considered as an important measure for future application of the MFC-Fenton technology.

3.2 The performance of electricity generation and organic matter reduction in MFC systems

Fig. 2 illustrates the removal rate of COD and output voltage. The initial COD concentration in RB1 and RB2 was 2172 ± 85 mg/L. The results showed that about 88% of COD was biodegraded within 48 h in both RB1 and RB2, and the difference of COD removal between MFCs with closed circuit and open circuit was negligible. While in RC1 and RC2, small fraction of COD (12%) was degraded because of the short HRT (5.1 h) in the anodic compartment.

The change of output voltage with different operating modes is depicted in the Fig. 2, indicating that the glucose was utilized for power generation by exoelectrogens growing on the

anode. The batch RB1 and continuous flow RC1 with 10 Ω were capable of producing currents of 2.0 and 2.2 mA, respectively, which were similar to the value reported by the previous study [21]. Current density of H₂O₂-producing MFC RB1 and RC1 was 31 and 35 A/m², respectively. The power densities achieved in RB1 and RC1 were 625 and 784 mW/m², respectively. The open circuit voltage of the RB1 can be as high as 410 mV, which was 15% higher than the control reactor RB2 (350 mV). In fact, a H₂O₂-producing MFC is used for H₂O₂ generation rather than producing electricity [18]. The amount of H₂O₂ production dropped along with the increase in external resistance. Thus, in this study 10 Ω of resistance was used to achieve higher yield of H₂O₂, leading to a relatively lower power density compared with other studies [33, 36].

3.3 Proof of the hydroxyl radicals occurrence in MFC-Fenton system

According to the previous introduction, two reactions could be involved in the cathodic chamber of RC1 (Eq. 2 and 3). In order to confirm the downstream •OH production during the Fenton process, we tracked salicylic acid degradation and formation of its hydroxyl products in the batch test. Salicylic acid (0.35 mM) together with ferrous sulfate (1.25 mM) were added into the cathodic chamber of RB1 and RB2. Salicylic acid could be oxidized by •OH to form three products, i.e. 2,3-DHBA, 2,5-DHBA and Catechol [35]. As shown in Fig. 3, these hydroxyl products as well as salicylic acid were analyzed every 12 h. In Fig. 3a, the removal rate of salicylic acid in RB1 was much faster than that in RB2. There was almost no salicylic acid found in the cathodic chamber of RB1 whereas 30% of salicylic acid remained in the cathodic chamber of RB2 after 24 h. Salicylic acid concentration decreased in the cathodic chamber of RB2, implying that salicylic acid was slowly absorbed by the graphite. As shown in Fig. 3b, the formation of the three hydroxyl products,

2,3-DHBA, 2,5-DHBA and Catechol, in RB1 could be detected within the period of 72 h. The result supported the formation of $\bullet\text{OH}$. We further compared the concentrations of H_2O_2 in RB1 with and without the addition of Fe^{2+} in the cathodic chamber (Fig. 3c). Apparently, with the addition of Fe^{2+} (MFC-Fenton), the maximum concentration of H_2O_2 dropped to approximately 50% of that without the addition of Fe^{2+} , implying the reaction between H_2O_2 and Fe^{2+} and the generation of $\bullet\text{OH}$. Overall, in addition to the absorption by graphite material, salicylic acid was degraded through the reaction with $\bullet\text{OH}$ in RB1 (with Fe^{2+}), and therefore, RB1 could achieve a faster degradation rate of salicylic acid than that in RB2.

3.4 Degradation of four emerging contaminants in batch and continuous operating modes

MFC-Fenton system

The ECs i.e., E1, BPA, TCC, and SM2 were introduced into the cathode of MFC-Fenton system with an initial concentration of 1 mg/L. The residual pollutant concentration was measured in the close and open circuit until the end of the experiment at the following times: 0, 2, 6, 8, 12 and 24 h. Fig. 4 exhibits the removal of four ECs in batch and continuous flow operating modes. In agreement with previous studies of degradation of organic pollutants in traditional E-Fenton system [23, 37], the reduction of emerging contaminants was observed in the MFC-Fenton process. Generally, RB1, RC1 and RC3 with closed circuit showed significantly higher capacity to degrade the ECs than RB2, RC2 and RC4 (open circuit). In batch mode, the removal efficiencies for E1, BPA, TCC and SM2 were 100%, 73%, 99% and 100% within the 24 h in RB1; while the corresponding data were 90%, 65%, 93%, 58% and 56% in RB2. In continuous flow MFC, the concentrations of E1, BPA, TCC, SM2 in RC1 decreased by 100%, 75%, 98% and 97%, respectively; whereas the data in RC2 represented 94%, 64%, 62% and 62%, respectively. Among the contaminants, the removal efficiency of BPA was the lowest compared with others. These

results clearly suggest that MFC-Fenton system is capable of efficiently removing the contaminants from the aqueous phase but show distinct removal effects towards different ECs. According to previous $\bullet\text{OH}$ generation (Section 3.3), the ECs' decrease was attributed to the Fenton reaction of in-situ generated H_2O_2 and addition of Fe^{2+} in the cathodic chamber to form $\bullet\text{OH}$ [23, 25] that is effective oxidizers to degrade organic pollutants [25, 38]. In addition, the data in RB2, RC2 and RC4 indicated that the adsorption by electrode material (graphite rod and graphite granules) under the open circuit condition was also significant. Compared with previous studies, the graphite electrode material seemed to have greater capacity to absorb organic pollutants than other electrode materials [23]. Thus, the mechanism underlying ECs removal in MFC-Fenton system may attribute to two major factors: the adsorption of electrode materials and the oxidation by $\bullet\text{OH}$.

The experimental data in Fig. 4a, b, c, and d were fitted by the apparent first-order logarithmic decay model (Eq. 5). The apparent rate constant values with different ECs were determined as shown in Table 3. It was found that removal of the four ECs followed the pseudo first-order kinetics. In comparison with control groups (MFCs with open circuit), the removal rate constants of most ECs in MFCs with close circuit (RB1, RC1 and RC3) were dramatically higher regardless of the operation modes or pH control. The results implied that Fenton process significantly boosted the removal rate of ECs. The removal rate can also be used to explain the contribution of MFC-Fenton oxidation and absorption for different ECs removal. For example, in batch MFCs, it was found that the MFC-Fenton process significantly improved the removal rate constant of E1 compared with solely absorption (i.e. 0.238 h^{-1} v.s. 0.097 h^{-1}), although the removal rate constant of BPA did not increase much with MFC-Fenton process (i.e. 0.049 h^{-1} v.s. 0.044 h^{-1}). This is because different ECs have different reactivity towards chemical oxidation. As shown in the previous literature [39], for $\text{pH} < 5$, rate constant for the E1 with ozone is about 10-fold that of BPA with ozone (i.e. 1.53×10^5 v.s. $1.68 \times 10^4\text{ M}^{-1}\text{ s}^{-1}$). Therefore, the contribution of MFC-Fenton process to the overall removal will vary with different ECs depending on the ECs reactivity in Fenton reaction. To some extent, it reflects the capacity of MFC-Fenton system for removal of ECs under different conditions.

$$\ln \frac{C_t}{C_0} = -K_{app} t \quad (5)$$

Where C_t and C_0 are the concentration of ECs at time t and time zero, respectively, and t is the reaction time. i represents different emerging contaminants. K_{app} is apparent rate constant.

4. Conclusions

The optimization of cathodic H_2O_2 synthesis was investigated in MFC systems. The results demonstrated that the optimum substrate and electrodes will improve the current density and increase the yield of H_2O_2 . Afterwards, the removal of E1, BPA, TCC and SM2 was studied in the MFC-Fenton system. The MFC-Fenton system could achieve effective removal of E1, BPA, TCC and SM2 respectively within 24 h in batch and continuous modes. The removal was due to the adsorption onto the graphite electrodes and the degradation by $\bullet OH$ from Fenton reaction. The contribution of the two removal mechanism to the overall removal will vary with different ECs depending on the ECs reactivity in Fenton reaction. Continuous flow MFC with pH control of cathodic electrolyte showed improvement on in-situ production of H_2O_2 and should be considered in future application of MFC-Fenton system.

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Abbreviations

MFC Microbial fuel cell;

ECs	Emerging contaminants
BPA	Bisphenol A
E1	Estrone
SM2	Sulfamethazine
TCC	Triclocarban
•OH	Hydroxyl radicals
HPLC	High performance liquid chromatography
COD	Chemical oxygen demand
H ₂ O ₂	Hydrogen peroxide
WWTP	Wastewater treatment plant

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Table Captions

Table 1 The experimental design of MFC system for H₂O₂ generation or ECs degradation

Table 2 The H₂O₂ generation based on batch MFC systems under different conditions

Table 3 Kinetic parameters (K_{app}) of the emerging contaminants degradation by MFC-Fenton process

Table 1 The experimental design of MFC system for H₂O₂ generation or ECs degradation

Operating mode	Batch		Continuous			
MFCs	RB1	RB2	RC1	RC2	RC3	RC4
Resistance (Ω)	10	/	10	/	10	/
Circuit	Close	Open	Close	Open	Close	Open
Electrode	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
	rod	rod	rod	rod	rod	rod
Graphite granules	100	100	100	100	100	100
pH control	/	/	/	/	yes	yes

Table 2 The H₂O₂ generation based on batch MFC systems under different conditions

Reactors	RB-1	RB-2	RB-3	RB-4	RB-5	RB-6	RB-7	RB-8
Substrates	Acetate	Glucose	Glucose	Glucose	Glucose	Glucose	Glucose	Glucose
Original COD (mg/L)	700 ± 34	700 ± 34	700 ± 34	700 ± 34	700 ± 34	700 ± 34	700 ± 34	2172 ± 85
Electrode materials	Graphite rod	Graphite rod	Graphite rod	Graphite rod	Graphite rod	Graphite rod	Graphite rod	Graphite rod
Graphite granules No. in the anode	0	0	0	0	50	100	100	100
Graphite granules No. in the cathode	0	0	60	100	100	100	100	100
Resistance (Ω)	10	10	10	10	10	10	880	10
<i>U</i> _{max} (mV)	11.9	13.7	14.9	16	17	20	250	21
<i>I</i> _{max} (mA)	1.19	1.37	1.49	1.6	1.7	2	0.28	2.1
<i>P</i> _{max} (W/m ³)	0.22	0.29	0.35	0.40	0.45	0.63	1.11	0.69
<i>J</i> _{max} (A/m ³)	18.59	21.41	23.28	25.00	26.56	31.25	4.44	32.81
H ₂ O ₂ concentration (mg/L)	0.08	0.36	0.55	0.65	0.73	0.80	0.25	2.06

RB: The graphite-MFCs with close circuit in batch mode; *U*_{max}: Maximum voltage; *I*_{max}: Maximum current; *P*_{max}: Maximum power density; *J*_{max}: Current density.

Table 3 Kinetic parameters (K_{app}) of the emerging contaminants degradation by MFC-Fenton process

MFCs	E1		BPA		TCC		SM2	
	K_{app} (h ⁻¹)	R ²	K_{app} (h ⁻¹)	R ²	K_{app} (h ⁻¹)	R ²	K_{app} (h ⁻¹)	R ²
RB1	0.2382	0.9526	0.0489	0.9514	0.1695	0.9915	0.1937	0.9218
RB2	0.0969	0.9797	0.0436	0.9965	0.0368	0.9886	0.0323	0.6945
RC1	0.2494	0.9692	0.0496	0.8242	0.1602	0.8558	0.1432	0.9408
RC2	0.1101	0.9662	0.0376	0.9000	0.0396	0.9494	0.0398	0.9617
RC3	0.1796	0.9443	0.0529	0.9522	0.1366	0.9993	0.1607	0.9676
RC4	0.0670	0.9809	0.0325	0.9749	0.0495	0.9928	0.0327	0.9062

Figure Captions

Fig. 1 The profile of H₂O₂ concentration and pH in the cathodic chamber of MFC systems in (a) batch, (b) continuous operation mode without pH control, and (c) continuous operation mode with pH control at 3. The glucose was fed into the anodic chamber, with an initial COD concentration of 2172 ± 85 mg/L. The graphite rod with 100 graphite granules was used as the electrode in both anodic and cathodic chambers.

Fig. 2 The profile of COD concentration and output voltage of the studied MFC systems in batch and continuous operation mode.

Fig. 3 Detection of the (a) removal of salicylic acid, (b) formation of three hydroxyl products (2,3-DHBA, 2,3-DHBA, 2,5-DHBA and Catechol) and (c) H₂O₂ production at pH 3, 1.25 mM Fe²⁺, 0.35 mM salicylic acid.

Fig. 4 The degradation of four ECs ($C_0 = 1$ mg/L) (a) E1, (b) BPA, (c) TCC and (d) SM2 in batch and continuous operation MFCs. RB1: batch MFC operated with close circuit; RB2: batch MFC operated with open circuit; RC1: continuous MFC operated with close circuit; RC2: continuous MFC operated with open circuit; RC3: continuous MFC operated with close circuit with control of pH in the cathodic electrolyte at 3.0; RC4: continuous MFC operated with open circuit with control of pH in the cathodic electrolyte at 3.0. The data point shown represents the average on triplicate measurements $\pm$ standards deviations obtained from three independent experiments.

Fig. 1 The profile of H_2O_2 concentration and pH in the cathodic chamber of MFC systems in (a) batch, (b) continuous operation mode without pH control, and (c) continuous operation mode with pH control at 3. The glucose was fed into the anodic chamber, with an initial COD concentration of 2172 ± 85 mg/L. The graphite rod with 100 graphite granules was used as the electrode in both anodic and cathodic chambers.

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Graphic abstract

The evidence of $\cdot\text{OH}$ production by detecting three hydroxyl products

The degradation of emerging contaminants