



Enhanced recalcitrant pollutant degradation using hydroxyl radicals generated using ozone and bioelectricity-driven cathodic hydrogen peroxide production: Bio-E-Peroxone process

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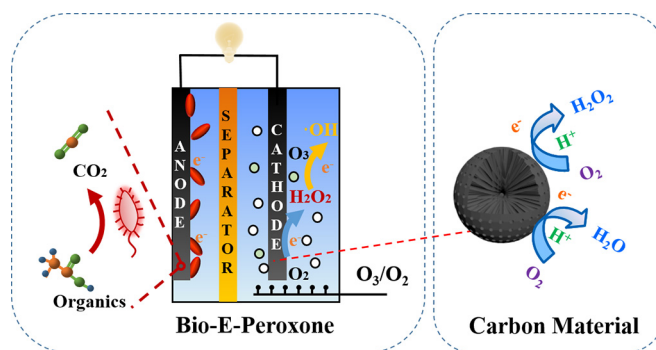
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HIGHLIGHTS

- Bio-E-Peroxone (BEP) process combined H₂O₂ produced in MFC with O₃-enriched air.
- BEP achieved refractory organics degradation and simultaneous electricity generation.
- BEP outperformed pure ozonation and MFC-driven electrolysis on MB degradation.
- CB XC-72 exhibited the best electrochemical H₂O₂ generation among CB, CMK and CNT.

GRAPHICAL ABSTRACT



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ABSTRACT

Accelerated pollutant degradation was examined using a new combined chemical and bioelectrochemical system, called a Bio-E-Peroxone process, based on generating ·OH from H₂O₂ produced on the cathode of a microbial fuel cell (MFC) and using ozone-enriched air. To optimize H₂O₂ formation, different carbon materials were examined and the highest H₂O₂ rates were obtained using XC-72 carbon black cathode. In E-Peroxone tests using the XC-72 cathode, methylene blue (a model pollutant) degradation rates followed first-order kinetics, with a rate constant of 0.237 min⁻¹, 6 times higher than that obtained using only ozonation (0.032 min⁻¹), 15 times of electrolysis+O₂ system (0.015 min⁻¹) and 46 times greater than electrolysis (0.005 min⁻¹). In MFC tests when using the complete Bio-E-Peroxone system, the removal rate constant for methylene blue was 2.05 h⁻¹, compared to 1.86 h⁻¹ using only ozone and 0.41 h⁻¹ using only MFC. Adding ozone to the air in cathode also increased power production by 47% to 170 mW m⁻³. The results demonstrated that this Bio-E-Peroxone system could be a feasible method for both refractory compounds degradation and wastewater electricity generation.

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1. Introduction

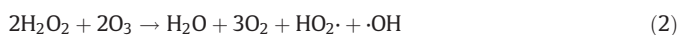
Greater emphasis is being placed on resource recovery from used water, for example capturing energy from the organic matter, and

recovering nutrients in the wastewater (Logan et al., 2015). Microbial fuel cells (MFCs) are an example of one of these technologies being examined for simultaneous wastewater treatment and electricity production (Ge et al., 2014; Li et al., 2019; Logan et al., 2019; Rossi et al., 2019; Tang et al., 2019; Yang et al., 2014). However, many pollutants are very recalcitrant, and therefore they are not removed from the wastewater during MFC treatment. An alternate approach to removing such recalcitrant compounds is to further treat the wastewater in the MFC catholyte chamber. Oxygen is one of the most common electron acceptors in MFCs (Hong and Logan, 2004; Zhang et al., 2013), with a 4-electron transfer pathway usually preferred for the oxygen reduction reaction (ORR) due to a higher cathode potential than that obtained with a 2-electron transfer pathway into hydrogen peroxide (H_2O_2) (Logan and Rabaey, 2013; Wang et al., 2017). However, H_2O_2 produced in the cathode is a valuable product that could be used for further treatment, especially in advanced oxidation processes (AOP) (Feng et al., 2010), in order to obtain a higher effluent quality (Asghar et al., 2017).

H_2O_2 can be formed on an MFC cathode. Efficient in-situ production (Eq. (1)) and utilization of H_2O_2 in the cathode could enable an MFC to not only accomplish removal of conventional pollutants but also achieve treatment of refractory wastewater. Inexpensive carbon-based catalysts could achieve relatively high $2e^-$ ORR performance (Dong et al., 2018). Proper selection of the cathode catalyst is needed to improve H_2O_2 production.



A key factor in achieving effective wastewater treatment is the efficient utilization of H_2O_2 (Guo et al., 2019). The E-Peroxone (EP) system was developed to degrade recalcitrant chemicals by the production of hydroxyl radicals ($\cdot\text{OH}$) using in-situ electrochemically generated H_2O_2 (through cathodic ORR) and gas sparging with ozone via (Esplugas et al., 2002; Li et al., 2014; Qu et al., 2020; Wang et al., 2015; Wang, 2018; Yao et al., 2019):



Electro-generation of H_2O_2 avoids the challenges of traditional methods, such as requiring extra addition of a mass dosage of H_2O_2 that results in risks during storage, transportation and usage (Bakheet et al., 2013; Barazesh et al., 2015; Li et al., 2014). This approach also overcomes the disadvantages of ozone such as relatively low mineralization and toxic organic by-products formation, improves mass transfer and utilization of ozone, and inhibits production of undesirable formation of bromate (Katsoyiannis et al., 2011; Rosenfeldt et al., 2006; Wu et al., 2019).

In this study, a Bio-E-Peroxone system was developed based on using the self-sustaining energy in wastewater, H_2O_2 produced at the cathode in an MFC, and by using catholyte aeration with ozone. Using this in situ generated H_2O_2 eliminated the need for its production using an external energy source, thus achieving the dual purpose of efficient degradation of organic matter and low external energy consumption. To examine the overall efficiency of this process, eight types of carbon materials were tested for their efficiency of H_2O_2 generation, with the optimal material used in E-Peroxone system and Bio-E-Peroxone system.

2. Materials and methods

2.1. Materials

In order to maximize the production of H_2O_2 from the cathode, eight types of carbon materials were initially screened as cathode catalysts: three kinds of carbon black (Vulcan XC-72R, Vulcan XC-72 and Black Pearls 2000, Cabot Corp., USA), three types of carbon nanotubes (CNT, OH-CNT and N-CNT, Timesnano, Chengdu Organic Chemicals Co. Ltd.),

and two mesoporous carbon materials (CMK-3 and N-CMK, Nanjing XFNANO Materials Tech Co., Ltd). The cathodes were prepared with a loading of 7.4 mg cm^{-2} catalyst, $23.5 \mu\text{L cm}^{-2}$ deionized water, and $10.4 \mu\text{L cm}^{-2}$ 60 wt% PTFE (poly tetra fluoroethylene), and pressed onto a stainless steel mesh (current collector) (Dong et al., 2018).

An abiotic electrochemical reactor with a 28 mL-volume anode chamber and 14 mL-volume cathode chamber, separated by a cation exchange membrane, was employed to measure the electrochemical catalytic performance of the different carbon catalysts via cyclic voltammetry (CV), liner sweep voltammetry (LSV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The CA tests were conducted at -0.4 V , -0.3 V , -0.2 V , -0.1 V , 0 V , and 0.1 V vs a saturated calomel electrode, (SCE, 0.241 V versus a standard hydrogen electrode). LSV and CV tests were conducted at a scan rate of 10 mV s^{-1} from -0.4 V to 0.1 V (vs SCE). EIS tests were processed from 100 kHz to 0.01 Hz at an amplitude of 10 mV. H_2O_2 production was measured by titanium potassium oxalate spectrophotometry after 15, 30, 45, and 60 min at the wavelength of 402 nm in the chronoamperometry tests and chronopotentiometry tests. Additional details are given in the Supporting Information.

2.2. E-Peroxone experiments

E-Peroxone experiments were conducted in an epoxy glass resin reactor that contained a 400 mL anode chamber and a 600 mL cathode chamber separated by a cation exchange membrane (Fig. S1). An aerator was placed in the cathode chamber. The E-Peroxone treatment used Pt electrode as anode, SCE as reference electrode, and carbon-PTFE electrode as cathode. A 50 mM phosphate buffer solution (PBS) was utilized as anolyte with E-Peroxone treatment of 600 mL methylene blue (MB) solution (5 mg L^{-1}) in the cathode chamber, while 50 mM Na_2SO_4 was used as the catholyte. MB is used here since MB is difficult to be degraded by H_2O_2 , it is more easily degraded by $\cdot\text{OH}$, and it is commonly used in Fenton and electro-Fenton processes (AOPs) as a model pollutant (Li et al., 2017; Yang et al., 2009; Zhou et al., 2014). The ozone generator (Tianmin Technology Ozone Corp. 500 mg h^{-1}) was used to provide ozonated air. Air was bubbled into the cathode to demonstrate that ozone is essential for the system, which is marked as electrolysis+ O_2 . To identify the existence of $\cdot\text{OH}$, 320 μM tert-Butyl alcohol (t-BuOH) as scavenger was used in control tests for validation.

E-Peroxone treatment was initiated using a potentiostat (CHI600E, CH Instruments, Inc., Shanghai) that provided a constant potential for electrodes. An ozone generator was turned on at the same time to produce ozone using the air. The ozonized air was bubbled into the cathode chamber at a steady rate of 0.5 L min^{-1} , and the gas O_3 concentration is 0.5 mg L^{-1} . The treatment lasted for 2 h. The removal rate of MB was measured by spectrophotometry at the wavelength of 664 nm.

2.3. Bio-E-Peroxone experiments

The Bio-E-Peroxone experiments were conducted in an MFC reactor that had the same structure as the EP reactor (Fig. S2). The cathode chamber was filled with 50 mM Na_2SO_4 electrolyte and 20 mg L^{-1} MB, and aerated with O_3 -enriched air. Activated carbon granules (2 mm diameter, thickness of 3–5 mm) were used as the anode, and were acclimated to simulated wastewater. The organic matter used in the anode is sodium acetate and the details of anolyte are described in SI. The voltage was measured across a resistor, with the data collected using a data acquisition system (Keithley Series 2700). Polarization curves and power density curves were determined to measure power output with the external resistance varied from 5000Ω to 10Ω at 20 min intervals. The Bio-E-Peroxone treatment was conducted with an external resistance of 10Ω , and lasted for 3 h.

3. Results and discussion

3.1. Carbon material selection based on electrochemical tests

To obtain more H_2O_2 in the E-Peroxone and Bio-E-Peroxone systems, eight types of carbon electrocatalysts were investigated for H_2O_2 production in an abiotic 3-electrode electrochemical reactor. Carbon black XC-72 cathode had the best performance in H_2O_2 electro-generation based on chronoamperometry and chronopotentiometry tests (Figs. 1a, S3–S4). XC-72 exhibited the best 2-electron transfer pathway for the ORR among all CB materials, CMK performed the best among the mesoporous carbon materials, and OH-CNT produced the most H_2O_2 for the CNTs materials. At -0.4 V (vs SCE) in chronoamperometry tests, XC-72 produced the most H_2O_2 with a production rate of $121 \text{ mg L}^{-1} \text{ h}^{-1}$, which was 22% higher than OH-CNT cathode ($102 \text{ mg L}^{-1} \text{ h}^{-1}$), and 32% higher than the CMK cathode ($94 \text{ mg L}^{-1} \text{ h}^{-1}$). At a current density of 1.43 mA cm^{-2} in chronopotentiometry tests, the XC-72 cathode had the highest yield of $62 \text{ mg L}^{-1} \text{ h}^{-1}$, which was 45% higher than CMK cathode ($43 \text{ mg L}^{-1} \text{ h}^{-1}$), and 70% higher than OH-CNT cathode ($36 \text{ mg L}^{-1} \text{ h}^{-1}$). Carbon black performed the best among three types of carbon materials. Furthermore,

functional groups of the electrocatalysts played a crucial role in ORR. The oxygen-doped carbon material OH-CNT had a better production of H_2O_2 than plain CNT. However, nitrogen-doped carbon materials, like N-CNT and N-CMK, had a lower production of H_2O_2 , and facilitated a 4-electron transfer pathway ORR, consistent with previous studies (Guo et al., 2016; Rao et al., 2010).

The XC-72 cathode displayed the highest H_2O_2 production, and thus, leading to the lowest current intensity, consistent with the results of CA, CV and LSV tests (Figs. 1b, S5–S8). As expected, oxygen captured fewer electrons via the 2-electron pathway instead of the 4-electron pathway. In the CA tests, the XC-72 cathode delivered the lowest current density of -9.8 A m^{-2} at -0.4 V (vs SCE), 61% lower than BP2000 cathode (-24.8 A m^{-2}), and 52% lower than CMK cathode (-20.7 A m^{-2}). In LSV tests, the XC-72 cathode material had the lowest current density among 8 materials. At -0.4 V (vs SCE), XC-72 cathode had a current density of -8.7 A m^{-2} , lower than BP2000 (-17.7 A m^{-2}) and CMK cathodes (20.0 A m^{-2}). The results suggest that XC-72 was a reliable carbon electrocatalyst for 2-electron pathway ORR, and thus XC-72 cathode was chosen for subsequent studies.

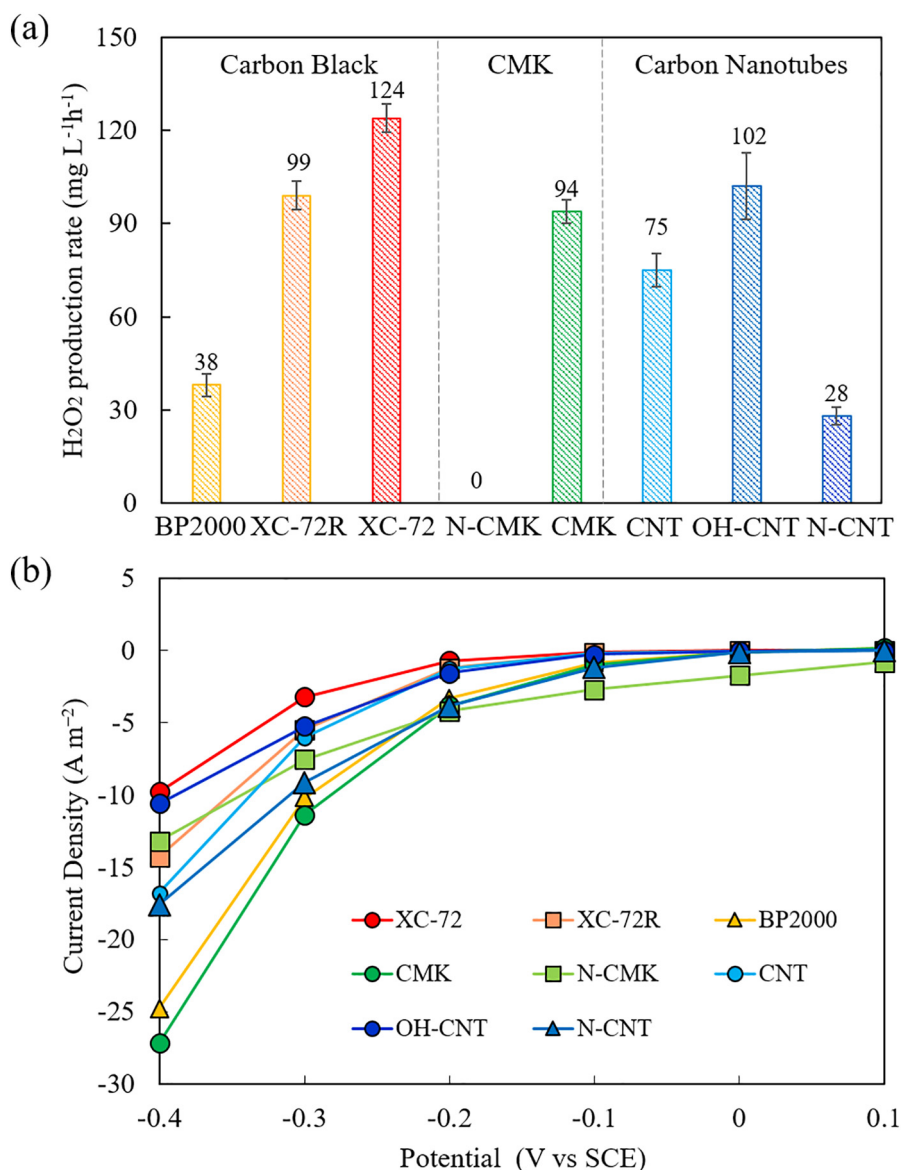


Fig. 1. (a) H_2O_2 production of 8 carbon materials in chronoamperometry tests; (b) CA tests of 8 carbon materials.

3.2. E-Peroxone tests

To evaluate performance of the E-Peroxone system utilizing the CB XC-72 cathode, degradation tests of the model pollutant MB were examined in E-Peroxone, ozonation, electrolysis and electrolysis+O₂ systems (Fig. 2a). The results showed that E-Peroxone system was far superior to ozonation, electrolysis and electrolysis+O₂ with respect to removal of 5 mg L⁻¹ of MB. After 15 min, there was 98% MB removal in the E-Peroxone system compared with 61% removal with only ozone, 30% with electrolysis+O₂, and 26% with only electrolysis (Fig. 2c). Kinetic analysis showed that the MB degradation was in line with first order kinetics in all processes. The rate constant of E-Peroxone was 0.237 ± 0.02 min⁻¹, 6 times higher than ozonation ($k = 0.032 \pm 0.007 \text{ min}^{-1}$), 15 times of electrolysis+O₂ ($k = 0.015 \pm 0.001 \text{ min}^{-1}$), and 46 times higher than electrolysis ($k = 0.005 \pm 0.001 \text{ min}^{-1}$) (Fig. 2d). To further validate the effect of ·OH in the E-Peroxone system, 320 μM t-BuOH was added in E-Peroxone system to scavenge ·OH in the bulk solution, and the results revealed that the rate of MB removal decreased when adding t-BuOH, and the first order rate constant was only 0.017 ± 0.001 min⁻¹. The lowered reaction kinetics in the presence of t-BuOH supported the view that ·OH could play a key role in MB degradation in the E-Peroxone system.

In the E-Peroxone process, H₂O₂ is electro-generated from oxygen via a 2-electron pathway ORR in the cathode (Eq. (1)), and then reacted with ozone to yield ·OH (Eqs. (2), (S3)–(S7)). ·OH can also be produced in the approach of ozone-electrolysis process (Eqs. (S6)–(S9)) (Fischbacher et al., 2013).



Due to that ·OH could oxidize most of the organics, the E-Peroxone system had the highest MB removals in these three processes. Additionally, degradation of MB by ozone was attributed to destruction of unsaturated bond and heterocyclic ring (Tehrani-Bagha et al., 2010).

In order to gain more insights into the E-Peroxone process, additional tests were conducted using different MB concentrations, applied potentials, and ozone dosages (Li et al., 2014; Wang et al., 2015). At a higher MB concentration of 20 mg L⁻¹, the first order rate constant of E-Peroxone was 0.232 ± 0.03 min⁻¹, which was much larger than that obtained by ozonation (0.031 ± 0.002 min⁻¹) or electrolysis+O₂ (0.009 ± 0.0005 min⁻¹). The rate constants of E-Peroxone, ozonation and electrolysis+O₂ were similar to those obtained at the lower initial MB concentration of 5 mg L⁻¹ (Fig. S11). Notably, first-order rate constants should not change with the initial pollutant concentration. The results further implied that the removal of MB conformed to first-order kinetics.

More negative applied potentials contributed to higher H₂O₂ production rates, which enhanced ·OH generation and led to faster pollutant degradation. The E-Peroxone system removed 98% of the MB in 15 min at -0.4 V (vs SCE), higher than that of -0.3 V (81%) and -0.2 V (41%) in 15 min. At -0.4 V, the rate constant was 0.237 min⁻¹, larger than those of -0.3 V (0.115 min⁻¹) and -0.2 V (0.047 min⁻¹) (Fig. S12). The CA tests of E-Peroxone system showed that the more negative potential applied, the higher current densities achieved (Fig. S13a). Thus more H₂O₂ was produced (Fig. S13b), and the removal of MB in E-Peroxone system was increased. Overall, the increased H₂O₂ generation at more negative potentials enhanced ·OH formation in E-Peroxone system, leading to faster MB removal.

To evaluate the influence of ozone dosage on E-Peroxone, its value was altered from 0.3 mg L⁻¹ (gas) to 0.5 mg L⁻¹ (gas). Previous studies have shown that a higher ozone dosage effectively enhanced pollutant removal, and hence ozone dosage was another crucial factor for E-Peroxone system performance (Wang et al., 2018; Wang, 2017). The result obtained in this study confirmed that higher ozone dosage would improve the removal of MB (Fig. S14). The first-order rate constant was calculated to be 0.237 min⁻¹ using 0.5 mg L⁻¹ ozone, 10 times that obtained at an ozone dosage of 0.3 mg L⁻¹ (0.022 min⁻¹), and 82% higher than that obtained at 0.4 mg L⁻¹ (0.126 min⁻¹). In principle, the higher ozone concentration in the gas phase would enhance ozone

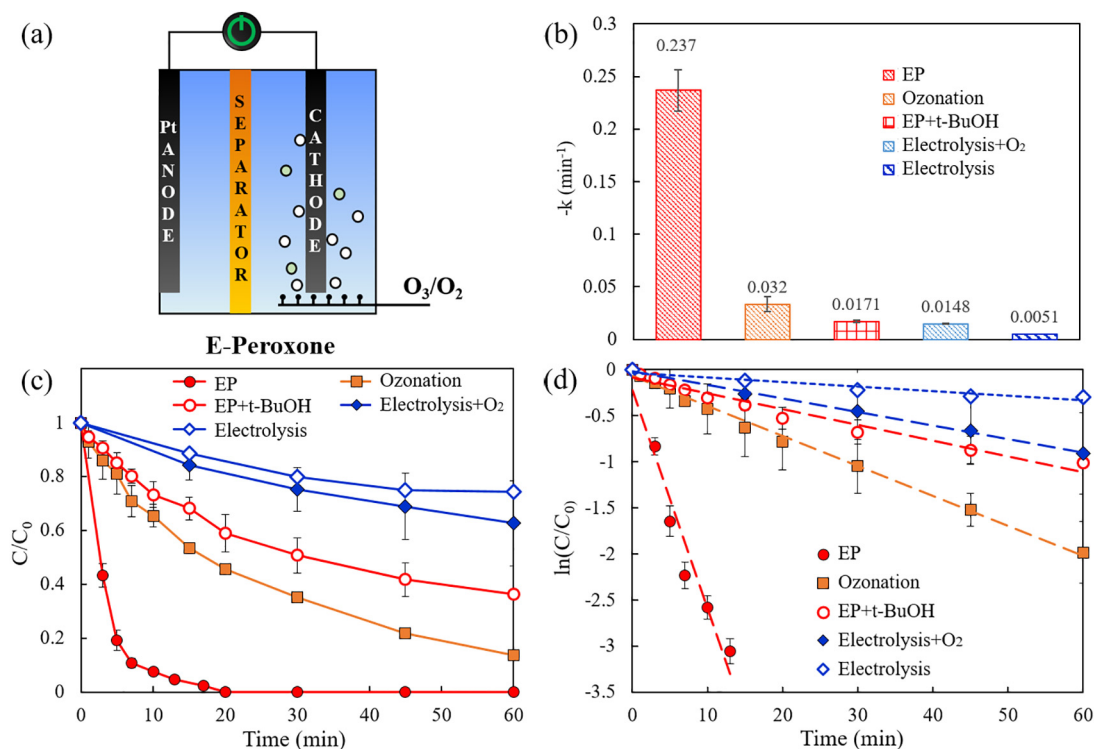


Fig. 2. (a) Schematic of the E-Peroxone system; (b) Degradation constants by ozonation, electrolysis, electrolysis+O₂, E-Peroxone and E-Peroxone + t-BuOH; (c) Removal of MB by ozonation, electrolysis, electrolysis+O₂, E-Peroxone and E-Peroxone + t-BuOH; (d) First order kinetics of ozonation, electrolysis, electrolysis+O₂, E-Peroxone and E-Peroxone + t-BuOH.

mass transfer into the liquid phase, thereby increasing the production of $\cdot\text{OH}$ in the aqueous solution.

3.3. Bio-E-Peroxone system

To evaluate performance of the Bio-E-Peroxone system using the CB XC-72 cathode, degradation tests of the model pollutant MB were examined in Bio-E-Peroxone, ozonation, MFC systems (Fig. 3a). The rate of MB (20 mg L^{-1}) degradation in the Bio-E-Peroxone system surpassed that of MFC alone (Fig. 3b). Bio-E-Peroxone had the highest removal of 83% in 30 min, higher than ozonation (76%) and MFC (31%). Kinetic analysis also showed that the degradation rates were in line with first order kinetics. The rate constant of the Bio-E-Peroxone system was $2.05 \pm 0.19 \text{ h}^{-1}$, larger than those of ozonation ($1.86 \pm 0.09 \text{ h}^{-1}$) and MFC ($0.41 \pm 0.05 \text{ h}^{-1}$). The main reason for high removal of MB by Bio-E-Peroxone could be ascribed to $\cdot\text{OH}$ produced by the reactions between cathodic H_2O_2 generated via a 2-electron transfer pathway ORR, and bubbled ozone (Eqs. (1)–(3)). Additionally, other reactions also took place during the Bio-E-Peroxone process. O_3 would be reduced into $\text{O}_3^{\cdot-}$ and then transformed into $\cdot\text{OH}$ (Eqs. (S1)–(S6)), while O_2 reduction is not inhibited or replaced by O_3 reduction in the mixed atmosphere (Guo et al., 2018). Moreover, O_3 could be reduced into O_2 and enhance H_2O_2 generation (Eq. (S7)) (Guo et al., 2018). Therefore, all these reactions synthetically achieve higher degradation rates of MB in the Bio-E-Peroxone system compared with ozonation or electrolysis alone.

Polarization curves and power density curves (Fig. 3c–d) showed an increased power production in the Bio-E-Peroxone system. The maximum power density in Bio-E-Peroxone system was $170 \pm 13 \text{ mW m}^{-3}$, 47% higher than that of MFC without ozone combination ($116 \pm 13 \text{ mW m}^{-3}$). Furthermore, the maximum current density in the combined system measured up to 1.48 A m^{-3} , 59% higher than that without coupling (0.93 A m^{-3}). Due to simultaneous reduction of O_2 and O_3 , and higher redox potential of mixed atmosphere, the performance of the cathode was improved (Guo et al., 2018).

In the Bio-E-Peroxone system, the bioelectricity was produced by the electroactive microorganisms on the anode using the in situ chemical energy in organics of the wastewater, and oxygen as the electron acceptor was reduced on the cathode to form H_2O_2 . H_2O_2 further reacted with ozone to form $\cdot\text{OH}$ for advanced wastewater treatment. The reactions in the cathode chamber of Bio-E-Peroxone were the same with E-Peroxone. H_2O_2 generation was a self-sustaining process driven by bioelectricity in Bio-E-Peroxone, but it required an external power supply in E-Peroxone. Bio-E-Peroxone achieved both higher power output and higher pollutant degradation rate than MFC, and also obtained higher pollutant removal performance than ozonation in this contribution.

4. Conclusions

An innovative Bio-E-Peroxone system was developed based on MFC using self-sustaining energy in the wastewater to produce electricity and H_2O_2 , coupling with O_3 to generate more oxidative $\cdot\text{OH}$. The Bio-E-Peroxone system achieved larger power output and current density than MFC. Furthermore, the Bio-E-Peroxone system attained higher removal of pollutants in comparison with ozonation and MFC in this contribution. The first-order kinetics rate constant of the Bio-E-Peroxone was 2.05 h^{-1} , 1.10 times as that of ozonation alone (1.86 h^{-1}), and 5 times as that of MFC alone (0.41 h^{-1}). The Bio-E-Peroxone system had a maximum power density of 170 mW m^{-3} , 47% higher than that in an MFC alone. These results provide a proof-of-concept for the Bio-E-Peroxone system as a new way for wastewater energy utilization and advanced treatment.

CRediT authorship contribution statement

Shuning Chen: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft. **Kajia Wei:** Methodology, Writing – review & editing. **Yujue Wang:** Writing – review & editing, Funding acquisition. **Jun Wang:** Writing – review

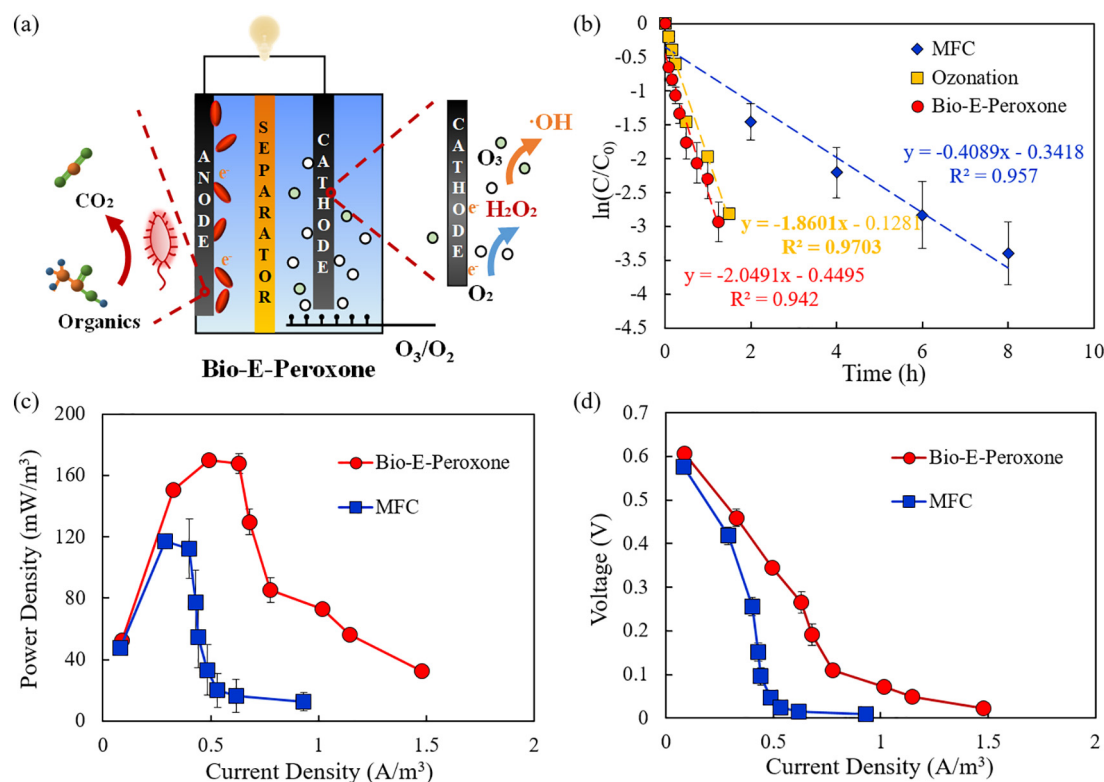


Fig. 3. (a) Schematic of Bio-E-Peroxone system; (b) First order kinetics of ozonation, MFC and Bio-E-Peroxone system; (c) Polarization curves of Bio-E-Peroxone system and MFC; (d) Current density curves of Bio-E-Peroxone system and MFC.

& editing, Funding acquisition. **Haiou Huang:** Writing – review & editing, Funding acquisition. **Xia Huang:** Writing – review & editing. **Bruce E. Logan:** Writing – review & editing. **Xiaoyuan Zhang:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.144819>.

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