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A novel combination of bioelectrochemical system with peroxymonosulfate oxidation for enhanced azo dye degradation and MnFe₂O₄ catalyst regeneration



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Hengduo Xu^{a, b}, Xiangchun Quan^{a, *}, Liang Chen^a

^a Key Laboratory of Water and Sediment Sciences of Ministry of Education, State Key Laboratory of Water Environment Simulation, School of Environment,

Beijing Normal University, Beijing, 100875, PR China

^b Key Laboratory of Coastal Biology and Utilization, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, Shandong, 264003, PR China

HIGHLIGHTS

- MnFe₂O₄ catalyzed PMS oxidation driven by MFCs was established.
- Complete degradation of Orange II was achieved in the MFC-MnFe₂O₄/ PMS system.
- Electricity was recovered in the MFC-MnFe₂O₄/PMS system during dye degradation.
- \equiv Mn^{2+} and \equiv Fe^{2+} was regenerated via cathode reduction of \equiv Mn^{3+} and \equiv Fe^{3+} .

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ABSTRACT

Advanced oxidation process (AOP) based on peroxymonosulfate (PMS) activation was established in microbial fuel cell (MFC) system with MnFe₂O₄ cathode (MFC-MnFe₂O₄/PMS) aimed to enhance azo dye degradation and catalyst regeneration. The effects of loading amount of MnFe₂O₄ catalyst, applied voltage, catholyte pH and PMS dosage on the degradation of Orange II were investigated. The stability of the MnFe₂O₄ cathode for successive PMS activation was also evaluated. The degradation of Orange was accelerated in the MFC-MnFe₂O₄/PMS with apparent degradation rate constant increased to 1.8 times of that in the MnFe₂O₄/PMS control. A nearly complete removal of Orange II (100 mg L⁻¹) was attained in the MFC-MnFe₂O₄/PMS under the optimum conditions of 2 mM PMS, 10 mg cm⁻² MnFe₂O₄ loading, pH 7 –8 and 480 min reaction time. MFC driven also extended the longevity of the MnFe₂O₄ catalyst for PMS activation due to the in-situ regeneration of \equiv Mn²⁺ and \equiv Fe²⁺ through accepting electrons from the cathode, and over 80% of Orange II was still removed in the 7th run. Additionally, the MFC-MnFe₂O₄/PMS system could recover electricity during Orange II degradation with a maximum power density of 206.2 ± 3.1 mW m⁻². PMS activation by MnFe₂O₄ was the primary pathway for SO²/₄ generation, and SO²/₄ based oxidation was the primary mechanism for Orange II degradation.

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* Corresponding author. E-mail address: xchquan@bnu.edu.cn (X. Quan).

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1. Introduction

Azo dyes, which are aromatic compounds with one or more -N=N- groups, are most commonly used synthetic dyes in textile industries. Most of azo dyes are resistant to microbial degradation and reported to be suspected carcinogenic and mutagenic compounds (Aguilar et al., 2017; Dai et al., 2018). Conventional biological wastewater treatment system generally cannot degrade azo dyes effectively due to their complex structure and strong toxicity (Pan et al., 2017; Zhang et al., 2015). The discharge of azo dye containing wastewater into water environment may reduce water transparency, retard light penetration for aquatic photosynthesis, and disturb ecosystem (Chen et al., 2018; Liang et al., 2018). It is therefore of great significance to find an effective approach to enhance azo dyes removal from wastewater.

Sulfate radical (SO₄) based advanced oxidation processes (AOPs), as a promising technology for organic pollutants degradation, have drawn increasing attention recently (Hou et al., 2018). Comparing to traditional hydroxyl radical (OH'), SO₄ has the advantages of high standard reduction potential (2.5-3.1 V), good selectivity and independence of pH (Qi et al., 2016). A variety of transition metal catalysts can activate peroxymonosulfate (PMS, $HSO_{\overline{5}}$) to generate $SO_{\overline{4}}$, among which mixed metal or metal oxides, such as MnFe₂O₄ has received significant interests due to its polvfunctionality, better catalytic activity, and stability (Ghanbari and Moradi, 2017; Xiao et al., 2018a). When MnFe₂O₄ is used for PMS activation, Mn^{2+} can donate electron to HSO_{5}^{-} and promote it decompose to SO₄, while the Fe³⁺ and generated Mn³⁺ need to be reduced to Mn^{2+} and Fe^{2+} to make the catalytic reaction of MnFe₂O₄ continuously. Catalysts recovery and regeneration is a bottleneck for practical application of the MnFe₂O₄ catalyst for PMS activation. Therefore, the regeneration rate of Mn^{2+} and Fe^{2+} is a key factor influencing SO₄ production and the longevity of the MnFe₂O₄ catalyst in the AOPs.

Bioelectrochemical system (BES) is novel technology for simultaneous organic pollutants degradation and electricity recovery. The electrochemically active bacteria colonized on the anodes can generate electrons through metabolizing organic compounds and deliver them to the cathodes, where some metals at high valence may be reduced after accepting electrons. For example, Fe³⁺, Cr⁶⁺, Cu^{2+} and V^{5+} could be reduced at the cathode of Microbial Fuel Cells (MFCs) (Lefebvre et al., 2012; Zhang et al., 2012; Huang et al., 2015). Depending on the redox cycles of Fe^{2+}/Fe^{3+} and H_2O_2 generation at the cathode of MFCs, Fenton based AOPs was constructed previously (Feng et al., 2010). Additionally, MFCs as an external power supply have been reported to drive PMS activation directly but with a lower efficiency comparing to metal catalysts (Yan et al., 2017). Therefore, we hypothesize here that MFCs assistance may have a positive function in promoting metal catalyst regeneration and PMS activation. Combination of MFCs with AOPs based on PMS activation has never been investigated and deserves further study.

In this research, a MFC coupled MnFe₂O₄/PMS system (named as MFC-MnFe₂O₄/PMS) was established in the cathode chamber of a MFC using a MnFe₂O₄ modified cathode with PMS containing catholyte. The degradation of azo dye Orange II and power generation capacity in the MFC-MnFe₂O₄/PMS system were investigated. The effects of loading amount of MnFe₂O₄, applied voltage, catholyte pH and PMS dosage on the degradation of Orange II were examined. The stability of the MnFe₂O₄ cathode for successive PMS activation was also evaluated, and a possible reaction mechanism for PMS activation and Orange II degradation in the system was proposed.

2. Materials and methods

2.1. Chemicals and materials

A non-wet proofed carbon cloth and carbon paper (HeSen Co. Ltd, Shanghai, China) were used as the supporting material of the anode and cathode electrodes, respectively. These carbon-based electrodes were pretreated using acetone and under high temperature prior to use. $Fe(NO_3)_3 \cdot 9H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ were purchased from Aladdin Chemical Reagent Co. (Shanghai, China). Orange II and PMS (Oxone, KHSO₅ \cdot 0.5KHSO₄ \cdot 0.5K₂SO₄, 4.7% active oxygen) were purchased from Sigma-Aldrich (purity>99%). Unless otherwise specified, all the reagents used in this study were of analytical grade.

2.2. Synthesis of MnFe₂O₄ particles

The MnFe₂O₄ particles were synthesized using a modified coprecipitation method according to the procedure previously described by Yao et al. (2014a). Briefly, 0.29 g Fe(NO₃)₃·9H₂O and $0.20 \text{ g Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 80 mL of pure water with a final molar ratio of Fe^{3+}/Mn^{2+} of 2:1, which was equal to the theoretic molar ratio of manganese and ferrite in MnFe₂O₄. The resulting mixed solution was then added by 0.64 g of NaOH and stirred for 10 min for complete dissolution. Then aqueous hydrazine solution (35 wt%) as reducing agent was added into the dispersion and stirred for another 10 min. The resulting mixture was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h in an oven. After cooling to room temperature, the precipitate of MnFe₂O₄ particles was filtered out and washed with deionized water until the pH of the suspension reached 7, and then dried at 60 °C overnight in a vacuum oven for further use.

2.3. Preparation of MnFe₂O₄ modified electrode

MnFe₂O₄ modified electrode was prepared according to the following procedure using carbon paper as the supporting material. Firstly, the synthesized MnFe₂O₄ particles was mixed with carbon black, and then added by Nafion solution (5%) to make a paste. The carbon paper was evenly spread by the mixture paste using a spray gun coupled with vacuum pump, and then dried at 25 °C overnight. The loading amount of MnFe₂O₄ particles on the electrodes varied from 2 to 20 mg cm⁻². An electrode modified with carbon black alone without MnFe₂O₄ particles was also prepared as a control. At least three repeatable samples were prepared for each type of the above electrodes and used for the following experiments.

2.4. MFC setup and operation

Dual-chamber MFCs were constructed as previously described, which had a working volume of 96 mL ($6 \text{ cm} \times 4 \text{ cm} \times 4 \text{ cm}$, length \times width \times height) for each chamber and between which separated by a proton exchange membrane (PEM) (Nafion 117, DuPont Co., USA) (Xu et al., 2018). During the start-up period, a piece of carbon cloth ($4 \times 2 \text{ cm}^2$) was used as the anode electrode, and a carbon paper ($4 \times 2 \text{ cm}^2$) with Pt (0.5 mg cm^{-2}) catalysts was used as the cathode electrode. The anodic chamber was inoculated with anaerobic sludge collected from Yanjing wastewater treatment plant (Beijing, China) to enrich electroactive bacteria. The anolyte consisted of CH₃COONa 1.64 g L⁻¹, NH₄Cl 0.31 g L⁻¹, KCl 0.13 g L⁻¹, Na₂HPO₄·12H₂O 10.32 g L⁻¹, NaH₂PO₄·2H₂O 3.32 g L⁻¹, a vitamin solution 5 mL and trace mineral solution 12.5 mL (Wu et al., 2016). The catholyte was 50 mM phosphate buffer solution (pH = 7). When the MFCs achieved stable electricity production after three-month operation, the original cathode electrode was replaced by the MnFe₂O₄ electrodes or CB control electrode, PMS at various concentrations (0.5–4 mM) was also added to the cathode chamber. In this way, a MFC-MnFe₂O₄/PMS based AOPs was established. Orange II (100 mg L⁻¹) was selected as the target azo dye and added to the cathode chamber. The anode was connected to a cathode across a 50 Ω external resistor by titanium wires. All the MFCs were operated at 30 ± 1 °C. Water samples were withdrawn from the cathode chamber at certain intervals and the remaining concentration of the azo dye was determined.

2.5. Measurements and characterization

Voltage (V) across the resistor was measured using a data acquisition system (USB8253, RBH Co., China) every 10 min. Polarization curves were measured by varying external resistances from 10000 to 100Ω . Power density and current density were normalized by the project surface area of the anode. The electrochemical catalytic properties of the MnFe₂O₄ modified electrode were investigated by scanning CV curves using a CHI660 electrochemical workstation (Chenhua, China) at a scan rate of 25 mV s⁻¹, with the MnFe₂O₄ modified electrode as the working electrode, a Pt thin film electrode as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The metal oxidation states of the MnFe₂O₄ onto the cathodes before and after application in the MFC-MnFe₂O₄/PMS system were characterized by X-ray photoelectron spectroscopy (XPS) under Cu Ka radiation (Escalab 250Xi. USA). The surface morphology of the MnFe₂O₄ was characterized by a field emission scanning electron microscopy (SEM, Hitachi S4800, Japan). An energy dispersive spectrometer (EDS, EDAX9100, USA) coupled to the SEM was used to analyze the metal elements of MnFe₂O₄. X-ray diffraction (XRD, X' Pert PRO MPD, Nederland) patterns were performed at a step of 8° min⁻¹ from 10° to 80° using a Trax theta-theta diffractometer with Cu K α radiation (40 kV and 40 mA).

The concentration of Orange II was determined using a UV–Visible spectrophotometer (DR 6000, HACH, USA) at the maximum visible absorption wavelength of 486 nm. Total organic carbon (TOC) was measured using a TOC-V analyzer (Shimadzu Co., Japan). All the above experiments were conducted in triplicates.

3. Results and discussion

3.1. Characterization of the MnFe₂O₄ modified electrode

MnFe₂O₄ modified electrodes were prepared and their surface morphology were characterized by SEM (Fig. 1 A, B). It is obvious to see that the MnFe₂O₄ particles were evenly dispersed on the surface of carbon paper electrodes. Carbon black as the support and dispersant not only prevented the MnFe₂O₄ particles from agglomeration, but also helped the catalyst particles tightly anchored to the electrode. Carbon black can also help to promote electron transfer between the MnFe₂O₄ and electrode (Higuchi et al., 2005). The EDS image (Fig. 1C) confirms the presence of the elements of Mn, Fe and O in the catalyst. The atomic ratio (%) of Fe to Mn was 1.8, which is close to the theoretical value of the designed MnFe₂O₄ (2.0) (Table S1). The XRD pattern of MnFe₂O₄ is shown in Fig. 1D. MnFe₂O₄ exhibits a typical pattern of spinel ferrite with well-defined peaks occurring at $2\theta = 18.15^{\circ}$, 30.01° , 35.06° , 43.62°, 54.18°, 56.45° and 61.86°. These peaks are indexed to (111), (220), (311), (400), (422), (511) and (440) Bragg planes of the MnFe₂O₄ cubic type (JCPDS card No. 73–1964). No other peaks are observed, implying that the synthesized MnFe₂O₄ was composed of single phase.

The electrochemical properties of the MnFe₂O₄ modified electrode were investigated through measuring CVs in a 10 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ electrolyte (Fig. 2). Both the MnFe₂O₄ modified electrode and control electrode demonstrated the property of electrocatalytic oxidation and reduction of $[Fe(CN)_6]^{4+}/[Fe(CN)_6]^{3+}$. The MnFe₂O₄ electrode showed a higher peak current density (anodic peak: 3.24 mA cm^{-2} , cathodic peak: 2.35 mA cm^{-2}) than the control electrode (anodic peak: 2.75 mA cm^{-2} , cathodic peak: 1.47 mA cm^{-2}). The electrochemical active surface area was calculated based on the Randles-Sevcik equation (detailed equation shown in Supporting Information), and the MnFe₂O₄ electrode showed a larger active surface area (195.59 cm²) than the control electrode (122.49 cm²), which is more beneficial for the occurrence of electrochemical reaction and physical adsorption (Allen and Larry, 2001). Moreover, a larger absolute area of the CV curve was found for the MnFe₂O₄ electrode comparing to the control, suggesting a relatively higher specific capacitance of the MnFe₂O₄ electrode (Peng et al., 2012). One more pair of peaks were observed for the MnFe₂O₄ modified electrode at the potential of 0.43 V and 0.76 V, which might be attributed to the redox couple of Mn^{3+} Mn²⁺

3.2. Orange II degradation in the MFC-MnFe₂O₄/PMS system

A MFC coupled MnFe₂O₄/PMS system was established through loading 10 mg cm⁻² MnFe₂O₄ to the cathode electrode and adding 2 mM PMS in the catholyte (pH = 7). For comparative purposes, a MnFe₂O₄/PMS system without MFC driven was also investigated as a control. The degradation of Orange II in the MFC-MnFe₂O₄/PMS system was evaluated (Fig. 3A) and the results were fitted to pseudo-first order kinetics according to the following equation :

$$\ln\left(\frac{C}{C_0}\right) = -k_{app}t\tag{1}$$

where *C* and *C*₀ are the real-time concentration and the initial concentration, respectively, k_{app} is the apparent rate constant, and *t* is the reaction time.

It is obvious to see that the degradation of Orange II was enhanced in the MFC-MnFe₂O₄/PMS system compared to MnFe₂O₄/ PMS alone system, with a removal percentage of $98.5 \pm 1.0\%$ and $91.2 \pm 1.2\%$ obtained within 480 min, respectively. The apparent degradation rate constant of Orange II was 0.0092 min⁻¹ in the MFC-MnFe₂O₄/PMS system, which was 1.8 times of the value (0.0051 min⁻¹) achieved in the MnFe₂O₄/PMS control system (Fig. 3B). For the MFC system with a MnFe₂O₄ cathode but no PMS in the catholyte, only 22.1 \pm 2.9% of Orange II was degraded. When the CB cathode was used as the control in the MFC system, only $15.0 \pm 3.7\%$ of Orange II was degraded no matter PMS existed or not. These results suggest that MFC loaded with the CB cathode could not activate PMS and degrade Orange II effectively under the tested conditions. Although Orange II could also be reduced at the cathode after accepting the electrons, it is not the primary way for Orange II reduction. The MnFe₂O₄ modified cathode in the MFCs played a primary role in PMS activation, which may contribute greatly to Orange II degradation in the MFC-MnFe₂O₄/PMS system.

To know the mineralization degree of Orange II, the effluent TOC was also measured during Orange II degradation, and the results were presented in Fig. S1. TOC was removed by $94.1 \pm 4.1\%$ and $81.1 \pm 7.9\%$ in the MFC-MnFe₂O₄/PMS system and MnFe₂O₄/PMS alone system, respectively, which were comparable to the degradation level of Orange II. This result indicated that most of the azo dye removed in the system was mineralized based on advanced oxidation process.



Fig. 1. SEM images (A, B) showing the surface morphology of the MnFe₂O₄ modified electrodes and their corresponding EDS (C) and XRD (D) patterns.



Fig. 2. Cyclic voltammograms for the MnFe₂O₄ electrode and the control electrode in 10 mM K₃Fe(CN)₆/K₄Fe(CN)₆ with 0.1 M KCl as the supporting electrolyte at a scanning rate of 25 mV s⁻¹ between -1 V and 1 V.

3.3. Factors influencing orange II degradation in the MFC-MnFe₂O₄/ PMS system

Effects of various factors including PMS dosage, $MnFe_2O_4$ loading amount on the electrode, catholyte medium pH, and applied voltage on the performance of the MFC-MnFe₂O₄/PMS system were further examined and the results were presented in Fig. 4. It was obvious to see that the Orange II degradation rate increased with increasing PMS dosage within the range of 0.5-4 mM (Fig. 4A), possibly because of the high SO₄ generation rate at high PMS doses. PMS dosage also determined the final

removal level of Orange II. When PMS dosage increased from 0.5 mM to 2 mM, the removal percentage of Orange II increased from $57.6 \pm 2.8\%$ to $98.5 \pm 1.0\%$, and it remained this level when the PMS dosage further increased to 4 mM possibly because of SO₄ scavenge effect at high PMS dosage (Jaafarzadeh et al., 2017; Shao et al., 2017). Similar result was also reported by Zhou et al. (2018). They found that the degradation of 2,4-dichlorophenol in FeCo₂O₄/PMS system was not strictly dependent on PMS dosage. The PMS dosage may influence degradation rate and removal level of azo dye via influencing the SO₄ generation amount and rate.

Fig. 4B showed the effect of MnFe₂O₄ loading amount on the electrode on Orange II degradation in the MFC-MnFe₂O₄/PMS system. The apparent degradation rate constant kept increasing from 0.0026 min^{-1} to 0.0092 min^{-1} when the MnFe₂O₄ loading increased from 2 to 10 mg cm^{-2} , but slightly declined to 0.0086 min^{-1} when the loading further increased to $20 mg cm^{-2}$. A removal percentage of 73.2% was obtained using the cathode of $2 \text{ mg cm}^{-2} \text{ MnFe}_2 O_4$ within 480 min, while a complete removal was achieved using the cathode of $10 \text{ mg cm}^{-2} \text{ MnFe}_2O_4$ within 240 min. The electrode with more MnFe₂O₄ catalyst may create more effective active sites for the formation of SO₄⁻ and therefore accelerated Orange II degradation. However, when the catalyst loading amount increased beyond a critical value, excessive catalyst dosage may cause ineffective PMS consumption, which may be the reason for the declined degradation rate at the high loading of 20 mg cm⁻² MnFe₂O₄ (Guan et al., 2013). Similar phenomena was reported by Xia et al. (2017), in which the amount of magnetic pyrrhotite (FeS₂) catalyst influenced SO₄⁻ generation rate in the FeS₂/PMS system, but it was not strictly proportional to the inactivation efficiency of Escherichia. Coli.

As the performance of AOPs is pH dependent mostly, the effect of catholyte pH on the degradation of Orange II in the MFC-MnFe₂O₄/PMS system was explored (Fig. 4C) (Ren et al., 2015; Zhao et al., 2017). The apparent degradation rate constant attained a



Fig. 3. Orange II degradation versus reaction time in MFC-PMS system and MFC alone, respectively, under different operation modes (A) and kinetic analysis of Orange II degradation (B). Error bars represent standard deviations from triplicate tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

maximum value of 0.0094 min^{-1} at pH = 8, while it declined to 0.0068 min^{-1} and 0.0057 min^{-1} at pH = 5 and pH = 10, respectively. The relatively low Orange II degradation rate at acidic pH was possibly because of the formation of $(Mn^{2+}(H_2O))^{2+}$ which may reduce free Mn^{2+} available on the cathode (Wang and Chu, 2011). In addition, PMS mainly exists as HSO₅⁻ at the pH of 6–8 according to the second pK_a value of PMS (second pK_a is 9.4) (Zhao et al., 2018). The stabilization effect of H⁺ on the HSO₅⁻ at acidic pH may also retard the degradation of Orange II (Rani et al., 2009). The degradation of Orange II was also inhibited slightly at pH = 10, possibly because MnFe₂O₄ is negatively charged under alkaline conditions, which was unbeneficial for the absorption of HSO₅⁻ and SO₅²⁻ (Huang et al., 2017). Therefore, the optimum pH value for Orange II degradation in the MFC-MnFe₂O₄/PMS system was 7–8.

All the above results indicated MFC driven enhanced Orange II degradation in the MnFe₂O₄/PMS system. When an external voltage was applied to the MnFe₂O₄/PMS system to improve electron transfer to the cathode, its effect on the degradation of Orange II was further investigated (Fig. 4D). Results showed that an applied voltage of 0.4 V and 0.8 V accelerated Orange II degradation with apparent rate constant increased to 0.0096 min⁻¹ and 0.0101 min⁻¹, respectively, compared to that without an applying voltage (0.0092 min⁻¹). More electrons may be delivered to the cathode electrode and used for Mn²⁺ or Fe²⁺ regeneration and PMS activation, which may be the reason for the accelerated degradation rate.

3.4. Catalyst stability after long-term application

The reusability of catalyst is a crucial factor that determines its long-term application in practice. Successive batch experiments were conducted to evaluate the catalytic stability of MnFe₂O₄ in the MFC-MnFe₂O₄/PMS system under open-circuit and close-circuit conditions (Fig. 5). Results showed that the MFC-MnFe₂O₄/PMS system maintained a good degradation towards Orange II with 98.9% removal in the 1st run and 83.9% removal in the 7th run (480 min). However, for the MnFe₂O₄/PMS control system (opening-circuit), the removal percentage of Orange II declined quickly from 92.6% in the 1st run to 49.3% in the 7th run. These data indicated that the MFC-MnFe₂O₄/PMS system not only accelerated Orange II degradation but also prolonged the longevity and reusability of MnFe₂O₄ catalyst, which may be due to the in-situ regeneration of $\equiv Mn^{2+}$ and $\equiv Fe^{2+}$ on cathode after accepting electrons from the anode of MFC. For the MnFe₂O₄/PMS control system, the MnFe₂O₄ catalyst decayed faster possibly due to the consumption of $\equiv Mn^{3+}$ and generation of SO₅ (1.1 V), which is a relatively weaker transient radical species and cannot be used for Orange II degradation (Cai et al., 2015; Li et al., 2018).

3.5. Power generation in the MFC-MnFe₂O₄/PMS system

When the MFC-MnFe₂O₄/PMS system was used for azo dye degradation, electricity could also be recovered. The power density curves and polarization curves during Orange II degradation were measured in the MFC with the MnFe₂O₄ cathode or the control CB cathode (Fig. 6). As illustrated in Fig. 6A, the MFC with the $MnFe_2O_4$ generated a maximum power cathode density of $206.2 \pm 3.1 \text{ mW m}^{-2}$ at a current density of 574.4 mA m⁻², which was 13-folds greater than that obtained with the CB control cathode $(15.5 \pm 0.4 \text{ mW m}^{-2} \text{ at a current density of } 111.2 \text{ mA m}^{-2})$. When the PMS dosage varied in the catholyte, power generation also changed, with a maximum power density of 167.1 ± 2.8 , $177.6 \pm 5.2, 206.2 \pm 3.1$ and $209.7 \pm 2.9 \text{ mW m}^{-2}$ generated in the MFC-MnFe₂O₄/PMS system at the PMS dosage of 0.5, 1, 2 and 4 mM, respectively (Fig. 6B). As the redox potential of HSO₅/SO₄ (1.82 V, vs. normal hydrogen electrode, NHE) is significantly higher than that of Mn^{3+}/Mn^{2+} (1.54 V), Fe^{3+}/Fe^{2+} (0.77 V) and O_2/H_2O (0.81 V), PMS may preferentially accept electrons (Chen et al., 2007). PMS as the dominant electron accepter in the MFC-MnFe₂O₄/PMS system determined the cathode potential and further affected the power generation (Sangeun et al., 2004). Increasing the PMS dosage in the catholyte may generate more SO₄ as electron acceptor in the MFC-MnFe₂O₄/PMS system, which may be the reason for the increased power density at a relatively high PMS dosage (2-4 mM).

3.6. Mechanism for pollutant degradation in the MFC-MnFe₂O₄/ PMS system

The XPS spectra were used to investigate the changes of chemical status of Mn and Fe on the MnFe₂O₄ cathode before and after application in the MFC-MnFe₂O₄/PMS system. Fig. S2 showed the XPS spectra of Mn 2p and Fe 2p core level regions. For the original MnFe₂O₄ samples, the peaks at the binding energy of 641.8 eV and 653.3 eV are assigned to Mn 2p_{3/2} and 2p_{1/2}, respectively, indicating that Mn element existed in the chemical state of Mn²⁺ in the MnFe₂O₄ catalyst (Fig. S2A). Meanwhile, the peak with binding energy appeared at 711.5 eV and a satellite signal at 719.3 eV were also observed, indicating the presence of Fe³⁺ in the MnFe₂O₄ catalyst (Fig. S2B) (Yao et al., 2014b). The peak areas representing Mn²⁺ and Fe³⁺ declined apparently for the used MnFe₂O₄ cathode, indicating the change of valence state of Mn²⁺ and Fe³⁺ after reaction with PMS. Similar results were also reported



Fig. 4. Effect of PMS dosage (A), MnFe₂O₄ loading amount onto the cathode (B), catholyte pH (C) and applied voltage (D) on Orange II degradation in the MFC- MnFe₂O₄/PMS system. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. The degradation of Orange II for consecutive seven batch runs in MFC-MnFe₂O₄/PMS system under close-circuit and open-circuit conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

by Ren et al. (2015). They also found that the percentage of M^{2+} (M: Co, Cu, Mn and Zn) and Fe³⁺ in the MFe₂O₄ catalyst declined to a certain degree after PMS-based oxidation reaction.

However, according to the deconvolution of Mn(2p), Mn^{2+} remained a higher fraction (72.7%) for the electrode used in the MFC assisted MnFe₂O₄/PMS system comparing to that (35.7%) in the MnFe₂O₄/PMS control (i.e. open circuit without MFC assistance). Similar results were also observed for Fe²⁺, the MnFe₂O₄ cathode used under closed-circuit conditions remained a higher fraction of Fe²⁺ (37.1%) than the one used under open-circuit conditions (17.5%). These data also suggest Mn²⁺ rather than Fe²⁺ played a primary role in PMS acitvation.

On the basis of the above results, a possible mechanism for

Orange II degradation in the MFC-MnFe₂O₄/PMS system was proposed, as shown in Fig. 7. Electroactive microbes attached on the anode of MFC may metabolize organic compounds and generate electrons and protons (Eq. (2)), and the electrons may be transferred via external circuit to the cathode. A variety of chemical or electrochemical reactions happen in the cathode chamber. PMS may be activated by \equiv Mn²⁺ and \equiv Fe²⁺ in the MnFe₂O₄ catalyst and decomposed to SO₄, along with the production of \equiv Mn³⁺ and \equiv Fe³⁺ (Eq. (3) and (4)). \equiv Mn³⁺ and \equiv Fe³⁺ can be then reduced after accepting electrons from the cathode to achieve the redox cycle (Eqs. (5) and (6)), which promote the catalytic action of the MnFe₂O₄ cathode work successively. Although it has been reported that PMS can also be activated by electrons directly and generate



Fig. 6. Power density and polarization curves of the MFCs using MnFe₂O₄ cathode and CB cathodes, respectively (A), and of the MFCs using MnFe₂O₄ cathode under different PMS dosages (B). Error bars represent standard deviations of triplicate experiments.



Fig. 7. Proposed mechanism for Orange II degradation in the MFC-MnFe₂O₄/PMS system. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

SO₄⁻ on the cathode (Eq. (7)) (Yan et al., 2017), it is not the primary mechanism for PMS activation as seen from the results presented in Fig. 3A. In addition, OH⁻ can also be generated through direct activation of PMS by electrons and the reaction of SO₄⁻ with H₂O/OH⁻ (Eqs. (8)–(10)) (Yan et al., 2017; Lin et al., 2018). The generated SO₄⁻

and OH' have strong oxidative capabilities and will react with Orange II and cause it breakdown. To discriminate the role of OH' in organic compounds transformation, we also conducted a separated experiment to quench OH' in the MFC-MnFe₂O₄/PMS system by adding tertbutyl alcohol (TAB), which can effectively scavenge OH' but had no effect on SO₄⁻ (Xie et al., 2018), and found the degradation of Orange II was inhibited slightly (Fig. S3). Therefore, we can infer that SO₄⁻ based oxidation is the primary mechanism for Orange II degradation in the MFC-MnFe₂O₄/PMS system.

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$
 (2)

$$\equiv Mn^{2+} + HSO_5^{-} \rightarrow \equiv Mn^{3+} + SO_4^{-} + OH^{-}$$
(3)

$$\equiv Fe^{2^{+}} + HSO_{5}^{-} \rightarrow \equiv Fe^{3^{+}} + SO_{4}^{\bullet-} + OH^{-}$$
(4)

$$\equiv Mn^{3+} + e^{-} \rightarrow \equiv Mn^{2+} \tag{5}$$

$$\equiv Fe^{3+} + e^{-} \rightarrow \equiv Fe^{2+} \tag{6}$$

$$HSO_5^{-+}e^{-} \rightarrow SO_4^{-+}OH^{-}$$
(7)

$$HSO_5^{-+}e^{-} \rightarrow SO_4^{-2-} + OH \bullet$$
(8)

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH \bullet + H^+$$
 (9)

$$\mathrm{SO}_4^{\bullet-} + \mathrm{OH}^- \to \mathrm{SO}_4^{2-} + \mathrm{OH} \bullet$$
 (10)

The regeneration ability of $\equiv Mn^{2+}$ and $\equiv Fe^{2+}$ greatly decides the longevity of the MnFe₂O₄ catalyst. Although $\equiv Mn^{2+}$ and $\equiv Fe^{2+}$ regeneration may be achieved through chemical reduction by HSO₅, such reaction is not always efficient because the reduction potential of HSO₅ (1.82 V) is higher than Mn³⁺/Mn²⁺ (1.54 V) and Fe³⁺/Fe²⁺ (0.77 V), which makes these reduction reactions thermodynamically unfavorable (Anipsitakis and Dionysiou, 2004; Zhang et al., 2013; Yao et al., 2014a; Xiao et al., 2018b). In this study, MFC driven as an extra electrons source promotes $\equiv Mn^{2+}$ and $\equiv Fe^{2+}$ regeneration through electrochemical reduction of $\equiv Mn^{3+}$ and $\equiv Fe^{3+}$ on the cathode, which may contribute greatly to the enhanced organic degradation rate, recyclability and longevity of the catalyst.

4. Conclusion

In this study, a novel wastewater treatment process (MFC- $MnFe_2O_4/PMS$) was developed through integrating MFC with MnFe₂O₄/PMS based AOPs technology and investigated for Orange II degradation. MFC driven enhanced Orange II degradation in the MnFe₂O₄/PMS system, with the degradation rate constant increased to 1.8 times of the control. Nearly a complete removal of Orange II (100 mg L^{-1}) was attained in the MFC-MnFe₂O₄/PMS under the optimum conditions of 2 mM PMS, 10 mg cm⁻² MnFe₂O₄ loading, pH 7-8 and 480 min reaction time. MFC driven also extended the longevity of the MnFe₂O₄ catalyst possibly due to the in-situ regeneration of $\equiv Mn^{2+}$ and $\equiv Fe^{2+}$ via accepting electrons delivered to the cathode, and over 80% of Orange II was still removed in the 7th run. Additionally, the MFC-MnFe₂O₄/PMS system could also recover electricity during Orange II degradation with a maximum power density of $206.2 \pm 3.1 \text{ mW m}^{-2}$. Advanced oxidative process based on SO4 from PMS activation by the MnFe₂O₄ catalyst was the primary mechanism for Orange II degradation in the systems. This MFC-MnFe₂O₄/PMS technology, in

nature of advanced oxidation mechanism, may also be used for the degradation of other organic compounds besides azo dyes in this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.11.077.

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