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

Hengduo Xu a, b, Xiangchun Quan a, *, Liang Chen 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

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.
- ≡Mn³⁺ and ≡Fe³⁺ was regenerated via cathode reduction of ≡Mn²⁺ and ≡Fe²⁺.

**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 ≡Mn²⁺ and ≡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 SO₄²⁻ generation, and SO₄²⁻ based oxidation was the primary mechanism for Orange II degradation. MFCs driven coupled with PMS activated AOP systems provides a novel strategy for efficient and persistent azo dye degradation.

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1. Introduction

Azo dyes, which are aromatic compounds with one or more \(-\text{N}=\text{N}-\) 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 (SO\(_4^2-\)) 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\(^-\)), SO\(_4^2-\) 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\(_5^-\)) to generate SO\(_4^2-\), among which mixed metal or metal oxides, such as MnFe\(_2\)O\(_4\) has received significant interest due to its poly-functionality, better catalytic activity, and stability (Ghanbari and Moradi, 2017; Xiao et al., 2018a). When MnFe\(_2\)O\(_4\) is used for PMS activation, Mn\(^{2+}\) can donate electron to HSO\(_5^-\) and promote it to decompose to SO\(_4^2-\), while the Fe\(^{3+}\) and generated Mn\(^{3+}\) need to be reduced to Mn\(^{2+}\) and Fe\(^{2+}\) to make the catalytic reaction of MnFe\(_2\)O\(_4\) continuously. Catalysts recovery and regeneration is a bottleneck for practical application of the MnFe\(_2\)O\(_4\) catalyst for PMS activation. Therefore, the regeneration rate of Mn\(^{2+}\) and Fe\(^{2+}\) is a key factor influencing SO\(_4^2-\) production and the longevity of the MnFe\(_2\)O\(_4\) 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, Fe\(^{3+}\), Cr\(^{6+}\), 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\(^{3+}/\text{Fe}^{2+}\) and H\(_2\)O\(_2\) 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 MnFe\(_2\)O\(_4\)/PMS system (named as MFC-MnFe\(_2\)O\(_4\)/PMS) was established in the cathode chamber of a MFC using a MnFe\(_2\)O\(_4\) modified cathode with PMS containing catholyte. The degradation of azo dye Orange II and power generation capacity in the MFC-MnFe\(_2\)O\(_4\)/PMS system were investigated. The effects of loading amount of MnFe\(_2\)O\(_4\), applied voltage, catholyte pH and PMS dosage on the degradation of Orange II were examined. The stability of the MnFe\(_2\)O\(_4\) 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\(_3\))\(_3\)-3H\(_2\)O and Mn(NO\(_3\))\(_2\)-4H\(_2\)O were purchased from Aladdin Chemical Reagent Co. (Shanghai, China). Orange II and PMS (Oxone, KHSO\(_5\)), 0.5K\(_2\)SO\(_4\), 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 MnFe\(_2\)O\(_4\) particles

The MnFe\(_2\)O\(_4\) particles were synthesized using a modified co-precipitation method according to the procedure previously described by Yao et al. (2014a). Briefly, 0.29 g Fe(NO\(_3\))\(_3\)-3H\(_2\)O and 0.20 g Mn(NO\(_3\))\(_2\)-4H\(_2\)O were dissolved in 80 mL of pure water with a final molar ratio of Fe\(^{3+}/\text{Mn}^{2+}\) of 2:1, which was equal to the theoretic molar ratio of manganese and ferrite in MnFe\(_2\)O\(_4\). 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 MnFe\(_2\)O\(_4\) 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 MnFe\(_2\)O\(_4\) modified electrode

MnFe\(_2\)O\(_4\) modified electrode was prepared according to the following procedure using carbon paper as the supporting material. Firstly, the synthesized MnFe\(_2\)O\(_4\) 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 MnFe\(_2\)O\(_4\) particles on the electrodes varied from 2 to 20 mg cm\(^{-2}\). An electrode modified with carbon black alone without MnFe\(_2\)O\(_4\) 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 cm × 4 cm × 4 cm, length × width × 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 × 2 cm\(^2\)) was used as the anode electrode, and a carbon paper (4 × 2 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 CH\(_3\)COONa 1.64 g L\(^{-1}\), NH\(_4\)Cl 0.31 g L\(^{-1}\), KCl 0.13 g L\(^{-1}\), Na\(_2\)HPO\(_4\) 12H\(_2\)O 10.32 g L\(^{-1}\), NaH\(_2\)PO\(_4\) 2H\(_2\)O 3.32 g L\(^{-1}\), a vitamin solution 5 mL and trace mineral solution 12.5 mL (Wu et al.,
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 system, based on europium and other elements of Mn, Fe and O in the catalyst. The atomic ratio (%) of Fe was observed, implying that the synthesized MnFe₂O₄ was composed of MnFe₂O₄ cubic type (JCPDS card No. 73–433). The XRD pattern of MnFe₂O₄ is shown in Fig. 1D. MnFe₂O₄ exhibits a typical pattern of spinel ferrite (220), (311), (400), (422), (511) and (440) Bragg planes of the MnFe₂O₄ (2.0) (Table S1). The XRD pattern of MnFe₂O₄ is shown in Fig. 1D. MnFe₂O₄ exhibits a typical pattern of spinel ferrite (220), (311), (400), (422), (511) and (440) Bragg planes of the MnFe₂O₄ cubic type (JCPDS card No. 73–433). 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 K₂Fe(CN)₆/K₃Fe(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 active 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 Mn³⁺/Mn⁴⁺.

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:

\[
\ln \left( \frac{C}{C_0} \right) = -k_{app}t
\]

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 ± 1% and 91.2 ± 1% 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 ± 2.9% of Orange II was degraded when the CB cathode was used as the control in the MFC system, only 15.0 ± 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 ± 4.1% and 81.1 ± 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.
3.3 Factors influencing orange II degradation in the MFC-MnFe₂O₄/PMS system

Effects of various factors including PMS dosage, MnFe₂O₄ 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 SO₄²⁻ 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 ± 2.8% to 98.5 ± 1.0%, and it remained this level when the PMS dosage further increased to 4 mM possibly because of SO₄²⁻ scavenging 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 SO₄²⁻ 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 mg cm⁻² MnFe₂O₄ within 480 min, while a complete removal was achieved using the cathode of 10 mg cm⁻² MnFe₂O₄ within 240 min. The electrode with more MnFe₂O₄ catalyst may create more effective active sites for the formation of SO₄²⁻ 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 SO₄²⁻ 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
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 \((\text{Mn}^{2+}(\text{H}_2\text{O}))^{2+}\) which may reduce free Mn²⁺ available on the cathode (Wang and Chu, 2011). In addition, PMS mainly exists as \(\text{HSO}_5^-\) at the pH of 6–8 according to the second \(\text{pK}_a\) value of PMS (second \(\text{pK}_a\) is 9.4) (Zhao et al., 2018). The stabilization effect of \(\text{H}^+\) on the \(\text{HSO}_5^-\) 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 unbeneifical for the absorption of \(\text{HSO}_5^-\) and \(\text{SO}_5^{2-}\) (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 \(\text{Mn}^{2+}\) or \(\text{Fe}^{3+}\) 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 \(\equiv\text{Mn}^{2+}\) and \(\equiv\text{Fe}^{3+}\) 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 \(\equiv\text{Mn}^{2+}\) and generation of \(\text{SO}_5^{2-}\) (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., 2016).

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 MnFe₂O₄ cathode generated a maximum power density of 206.2 ± 3.1 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 ± 0.4 mW m⁻² at a current density of 111.2 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 ± 5.2, 206.2 ± 3.1 and 209.7 ± 2.9 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 \(\text{HSO}_5^-/\text{SO}_5^{2-}\) (1.82 V, vs. normal hydrogen electrode, NHE) is significantly higher than that of \(\text{Mn}^{4+}/\text{Mn}^{2+}\) (1.54 V), \(\text{Fe}^{3+}/\text{Fe}^{2+}\) (0.77 V) and \(\text{O}_2/\text{H}_2\text{O}\) (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 \(\text{SO}_5^{2-}\) 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 2p₃/₂ and 2p₃/₂, 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.
by Ren et al. (2015). They also found that the percentage of $M^{2+}$ (M: Co, Cu, Mn and Zn) and Fe$^{3+}$ in the MFe$_2$O$_4$ 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 MnFe$_2$O$_4$/PMS system comparing to that (35.7%) in the MnFe$_2$O$_4$/PMS control (i.e. open circuit without MFC assistance). Similar results were also observed for Fe$^{2+}$, the MnFe$_2$O$_4$ cathode used under closed-circuit conditions remained a higher fraction of Fe$^{2+}$ (37.1%) than the one used under open-circuit conditions (17.5%). These data also suggest Mn$^{2+}$ rather than Fe$^{2+}$ played a primary role in PMS activation.

On the basis of the above results, a possible mechanism for Orange II degradation in the MFC-MnFe$_2$O$_4$/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 $≡$Mn$^{2+}$ and $≡$Fe$^{3+}$ in the MnFe$_2$O$_4$ catalyst and decomposed to SO$_4^{2-}$/Cl$^-$, along with the production of $≡$Mn$^{3+}$ and $≡$Fe$^{3+}$ (Eq. (3) and (4)). $≡$Mn$^{3+}$ and $≡$Fe$^{3+}$ can then be reduced after accepting electrons from the cathode to achieve the redox cycle (Eqs. (5) and (6)), which promote the catalytic action of the MnFe$_2$O$_4$ cathode work successively. Although it has been reported that PMS can also be activated by electrons directly and generate...
SO$_4$$^-$/C$_{15}$ on the cathode (Eq. (7)) (Yan et al., 2017), it is not the primary mechanism for PMS activation as seen from the results presented in Fig. 3A. In addition, OH$^-$ can also be generated through direct activation of PMS by electrons and the reaction of SO$_4$$^-$/C$_{15}$ with H$_2$O/OH$^-$(Eqs. (8)–(10))(Yan et al., 2017; Lin et al., 2018). The generated SO$_4$$^-$/C$_{15}$ and OH$^-$ have strong oxidative capabilities and will react with Orange II and cause it breakdown. To discriminate the role of OH$^-$ in organic compounds transformation, we also conducted a separated experiment to quench OH$^-$ in the MFC-MnFe$_2$O$_4$/PMS system by adding tertbutyl alcohol (TAB), which can effectively scavenge OH$^-$ but had no effect on SO$_4$$^-$/C$_{15}$ (Xie et al., 2018), and found the degradation of Orange II was inhibited slightly (Fig. S3). Therefore, we can infer that SO$_4$$^-$/C$_{15}$ based oxidation is the primary mechanism for Orange II degradation in the MFC-MnFe$_2$O$_4$/PMS system.

\[
\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^-
\]

\[
\equiv \text{Mn}^{3+} + \text{HSO}_5^- \rightarrow \equiv \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{OH}^-
\]

\[
\equiv \text{Fe}^{3+} + \text{e}^- \rightarrow \equiv \text{Fe}^{2+}
\]

\[
\text{HSO}_5^- + \text{e}^- \rightarrow \text{SO}_4^{2-} + \text{OH}^-
\]

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^\bullet + \text{H}^+
\]

The regeneration ability of $\equiv \text{Mn}^{2+}$ and $\equiv \text{Fe}^{2+}$ greatly decides the longevity of the MnFe$_2$O$_4$ catalyst. Although $\equiv \text{Mn}^{3+}$ and $\equiv \text{Fe}^{3+}$ regeneration may be achieved through chemical reduction by HSO$_5^-$, such reaction is not always efficient because the reduction potential of HSO$_5^-$ (1.82 V) is higher than Mn$^{3+}$/Mn$^{2+}$ (1.54 V) and Fe$^{3+}$/Fe$^{2+}$ (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 $\equiv \text{Mn}^{2+}$ and $\equiv \text{Fe}^{2+}$ regeneration through electrochemical reduction of $\equiv \text{Mn}^{3+}$ and $\equiv \text{Fe}^{3+}$ 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$_2$O$_4$/PMS) was developed through integrating MFC with MnFe$_2$O$_4$/PMS based AOPs technology and investigated for Orange II degradation. MFC driven enhanced Orange II degradation in the MnFe$_2$O$_4$/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-MnFe$_2$O$_4$/PMS under the optimum conditions of 2 mM PMS, 10 mg cm$^{-2}$ MnFe$_2$O$_4$ loading, pH 7–8 and 480 min reaction time. MFC driven also extended the longevity of the MnFe$_2$O$_4$ catalyst possibly due to the in-situ regeneration of $\equiv \text{Mn}^{2+}$ and $\equiv \text{Fe}^{2+}$ via accepting electrons delivered to the cathode, and over 80% of Orange II was still removed in the 7th run. Additionally, the MFC-MnFe$_2$O$_4$/PMS system could also recover electricity during Orange II degradation with a maximum power density of 206.2 ± 3.1 mW m$^{-2}$. Advanced oxidative process based on SO$_4$$^-$/C$_{15}$ from PMS activation by the MnFe$_2$O$_4$ catalyst was the primary mechanism for Orange II degradation in the systems. This MFC-MnFe$_2$O$_4$/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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