Advanced oxidation of biorefractory organics in aqueous solution together with bioelectricity generation by microbial fuel cells with composite FO/GPEs

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Abstract. In this study, ferric oxide loading graphite particle electrodes (FO/GPEs) were prepared as cathode of a three-dimensional electrode MFC-Fenton system. The properties of the composite cathode were examined with higher surface area and more mesopores. FO/GPEs could work as both cathode and Fenton iron reagents, contributing to high oxidation activity and better performance of electricity generation. The application of FO/GPEs MFC-Fenton system on degrading p-nitrophenol presented high catalytic efficiency in a wide range of pH value. The removal of p-nitrophenol and TOC attained to about 85 % within 8 and 64 h at neutral pH, respectively. A neutral FO/GPEs MFC-Fenton oxidation mechanism was also proposed. Specifically, both the surface iron sites and dissolved iron ions catalyzed the decomposition of H2O2. As results, the generated hydroxyl radicals were used for p-nitrophenol degradation and the iron oxide was recycled.

1. Introduction

Concerns for environmental impact along with enhanced public awareness of effects of contamination by hazardous chemicals, has led to strict environmental controls. Technological progress and increased utilization of natural resources have resulted in larger and more diverse discharge of organics to the environment. Of these, bio-refractory organic substances are of particular concern as they resist degradation and can accumulate in the environment. Advanced oxidation process (AOP) based on Fenton’s reaction as a favorable method has been widely used for degradation of bio-refractory organic with the generation of hydroxyl radicals (•OH) from Fenton’s reagents (Fe2+ and H2O2)[1].

The electro-Fenton process is a recent development which offers many advantages over the chemical Fenton approach because of the higher efficiency of Fenton’s reagents utilization and less risk of chemical transport and storage [2]. However, it will have high power consumption leading to higher energy cost [3].

Microbial fuel cells (MFCs) are a newly developed bioelectrochemical system which generates electricity and simultaneously treats wastewater, MFCs presently enlarge the application range to be a device synthesizing H2O2 through using bio-electrons to occur two-electron oxygen reduction at carbonaceous cathode but with lower bioelectricity output [4]. Particularly, with the presence of ferrous iron, the in situ generated H2O2 by MFCs further reacts with ferrous iron to produce hydroxyl radicals, establishing a better energy-generation system with biodegradable organics elimination in anode and biorefactory organics removal in cathode. Scrap iron and natural limonite were widely used...
as the iron sources to conduct Fenton’s reaction in MFCs for organic pollutant removal in former research [3, 5]. The oxidation of pollutants is most efficient at acidic conditions in Fenton system using free iron, however, it will become weak when the pH is over 4 [6]. The formation of iron sludge attributed by pH adjustment limits the wide application and continuous addition of ferrous ion enormously increases the operation cost [2]. In this case, it is meaningful to investigate the Fenton reaction at neutral pH for a wider industry implementation. To overcome these shortages, loading iron oxides on carboneous cathode to fabricate a composite cathode has been used in MFC-Fenton system for water treatment, e.g. CNT/γ-FeOOH composite cathode [2] and Fe@Fe₂O₃/carbon felt composite cathode [1, 7].

It is noticeable that as a H₂O₂-producing device, the MFC with the three-dimensional electrode is more attractive than a two-dimensional one. It is mainly because that particle electrodes form charged microelectrodes which may increase mass transfer coefficient [8] and enhance energy production as well [4]. Graphite particle electrodes (GPEs) described in previous research [4, 9] show a high efficient cathodic catalyst for the in situ generation of H₂O₂ due to its large surface area, good conductivity and superior electrochemical activity of the two-electron oxygen reduction. Moreover, due to its excellent adsorption, GPEs can easily adsorb iron ions to fabricate a composite electrode. The ferric oxides (FO) are widely used and functioned as iron sources of the MFC-Fenton reactions [10, 11]. As for composite cathode, FO in situ generates adsorbed ferrous ion and then is dissolved to aqueous solution as Fe²⁺. A constant amount of iron ions can be self supplied by iron oxide in composite cathode and sustainably recycled after treatment.

In this study, the newly composite FO/GPEs were fabricated for the MFC-Fenton system. p-nitrophenol (PNP) was chosen as a representative of bio-refractory organic pollutant. The aim was to demonstrate the feasibility of using such a MFC-Fenton system with composite FO/GPEs as the cathode to degrade p-nitrophenol in aqueous solution under neutral condition.

2. Materials and Methods

2.1. Fabrication of composite FO/GPEs
Composite FO/GPEs in present study were prepared by loading ferric oxides onto the graphite particle electrodes. Firstly, the graphite particle electrodes were made by granulation of graphite powders and PTFE with a diameter of 2-3 mm, according to procedures described in previous studies [4, 12]. Subsequently, FeCl₃ solution (solution A; 0.1 mol·L⁻¹) and NaOH solution (solution B; 0.5 mol·L⁻¹) were prepared for loading process [13]. Solution A flew through a beaker packed with the graphite particle electrodes to preload the ferric ions. Then, solution B was used to make ferric iron precipitated onto inner surface of graphite granules. The ferric oxide loaded graphite particle electrodes was washed with deionized water and finally dried in nitrogen to fabricate ferric oxide/graphite particle electrodes (composite FO/GPEs). The quantity of Fe loading on the GPEs was measured by the weight method.

2.2. Characterization and porosity of FO/GPE composite cathode
The surface morphology of carbon powders, graphite particle electrodes and the FO/GPEs were characterized using scanning electron microscope (SEM; Nanosem 430, FEI Electron Optics Company, USA). The Fe elemental analysis of FO/GPEs was carried out by XPS (PHI1600, Physical Electronics, USA) to determine the properties of Fe element. The physical properties of carbon powders, graphite particle electrodes and composite FO/GPEs were measured using multipoint Brunauer-Emmett-Teller (BET) surface area method and Barrett-Joyner-Halenda (BJH) pore size and volume analysis through N₂ adsorption/desorption analysis on Autosorb-1 (Quantachrome Instruments, USA).

2.3. MFC configuration and experiment operation
MFC-Fenton degradation of p-nitrophenol was performed in a dual-chamber MFC with composite FO/GPEs. The anodic and cathodic compartments were separated by a cation exchange membrane (Ultrex CMI-7000, Membranes International Inc., Glen Rock, NJ, USA) into the volume of 32.0 mL and 64.0 mL, respectively. The anode was carbon felt (3.0 cm length × 3.0 cm width, Hesen, Shanghai,
China), which was soaked in acetone for 24 h to remove potential organics from surface. FO/GPEs were filled in the cathode chamber with a graphite rod (0.8 cm diameter and 6 cm length) as cathode to provide the external contact, reducing cathodic working volume of 50.0 mL. Cathode solution was 0.05 mol·L⁻¹ Na₂SO₄ (pH=7.0) fed by fresh air. The anode was set up following our previous work[4, 9]. As a comparison, three-dimensional electrode MFCs with only GPEs and 0.1 g·L⁻¹ Fe²⁺ and GPEs (Fe²⁺/GPEs) were conducted under the same conditions. In the stage of start up, an external resistor of 1000 Ω was used to connect the MFC circuit. After inoculation, MFCs were operated under open-circuit condition at least three successive batch cycles with a stable maximum voltage produced. Subsequently, all MFCs were changed the cathode solution (50 mmol·L⁻¹ Na₂SO₄ solution containing 50 mg·L⁻¹ PNP (pH=7.0)) bubbled with air before degradation experiments. The external resistor set up at 20 Ω. 0.5 mol·L⁻¹ of NaOH or H₂SO₄ were used to adjust the solution pH. The system was then stirred for 30 min to establish adsorption/desorption equilibrium between the solution and electrodes in the cathode chamber[10]. All experiments were conducted in an incubator at 30±0.5 °C.

2.4. Analytical methods
The cell voltages were monitored in one minute interval by a data acquisition system (PISO-813, ICP DAS Co., Ltd, China) and recorded by a personal computer. The polarization and power density curves used to evaluate the power performance of MFCs, which were performed by varying the external resistances over a range of 5-5000 Ω included in a resistor box during hours when stable maximum voltages produced in a steady and repeatable voltage cycle. The anode and cathode potentials were measured by saturated calomel electrodes (SCE, +0.242 V vs. SHE) for reference. The concentrations of p-nitrophenol were detected using high performance liquid chromatography (HPLC, Waters E 2695 Separation Module 2998 PDA, Waters, USA) with a C18 column (5 μm, 4.6×250 mm) and a UV detector. The mobile phase was methanol/water (60/40) and the flow rate was 1.0 mL·min⁻¹. The UV detector was set at 320 nm[14]. The dissolved iron ion concentrations were colorimetric determined using 1,10-phenanthroline at 510nm [15]. Total organic carbon (TOC) of initial and treated aqueous PNP solutions were carried out by TOC Analyzer (TOC-VC, Shimadzu Corporation, Japan) equipped with an automatic sample injector. The concentration of H₂O₂ was measured by spectrophotometry of Ti⁴⁺·H₂O₂ complex at 410nm [16].

3. Results and Discussion
3.1. Characterization of composite FO/GPEs
The morphological characterization of powders, graphite-PTFE granules (GPEs) and FO/GPEs were scanned by SEM and the results are presented in Fig. 1. Graphite powders had an obvious sheet-like morphology and random pore size distributions (Fig. 1a). The SEM images (Fig. 1b, 1c) show that more channels and pores were generated by bonding graphite powders with massive tight and brawny PTFE fibers in graphite-PTFE granules and FO/GPEs. The surface morphology of FO/GPEs, which was loaded by ferric oxides, was much rougher than graphite-PTFE granules (GPEs).

![Figure 1 SEM images of (a) graphite powders, (b) GPEs and (c) FO/GPEs at a magnification of 10 K](image-url)
The XPS analysis verified the coexistence of C, O and Fe in FO/GPE composite cathode, which demonstrated the successful preparation of the composite FO/GPEs with 9.2 % weight of ferric contents. In addition, oxygen content of FO/GPEs (14.2 %) was higher than that of GPEs (7.3 %), which indicated that the ferric element was loaded on composite cathode mainly in the form of ferric oxides. The further analysis of Fe 2p spectra was carried out to determine the properties of Fe element on FO/GPEs. The results demonstrated the existence of FeO (709.3 eV)[16] and α-Fe$_2$O$_3$ (711.4 eV) [17] on composite electrode.

3.2. Porosity of composite FO/GPEs
The porous properties and the structure on pore size distribution were measured by BET and BJH technology. N$_2$ adsorption/desorption isotherms of graphite powders, GPEs and FO/GPEs all belonged to type IV with a pronounced hysteresis at higher P/P$_0$[18]. The type H4 hysteresis loops in isotherms indicated the existence of slit-like mesopores [19] in three samples, corresponding to the morphology shown in the SEM images. Detailed information regarding porous properties is summarized in Table 1. As expected, the absorption volume of GPEs and FO/GPEs were relatively high when compared to that of graphite powders due to the larger surface area of GPEs and FO/GPEs than graphite powders. More channels and pores were generated by plenty of binder fibers in graphite-PTFE granules, which led to the larger surface area and more mesopores of GPEs (46.9 m$^2$.g$^{-1}$ and 28.2 m$^2$.g$^{-1}$) than graphite powders(38.7m$^2$.g$^{-1}$ and 21.3 m$^2$.g$^{-1}$). Simultaneously, graphite-PTFE granules loaded with ferric oxides (FO/GPEs) had higher surface area (68.6 m$^2$.g$^{-1}$) and larger pore volume (0.049 m$^3$.g$^{-1}$) than unloaded graphite-PTFE granules (GPEs, 46.9 m$^2$.g$^{-1}$ and 0.043 m$^3$.g$^{-1}$) due to the ferric oxides dispersed on the inner and external of graphite-PTFE granules. More micropores and mesopores were also formed by loading iron oxides on GPEs, corresponding to the rougher surface of FO/GPEs in SEM images. The results of XPS clearly demonstrate that the higher percentage of mesoposity was presented in FO/GPEs over GPEs, which would strongly increase the metal leaching and further enhance the catalytic performance [20].

Table 1. Porous structural characteristics of GPEs and FO/GPEs

| Sample                  | graphite powders | GPEs   | FO/GPEs |
|-------------------------|------------------|--------|---------|
| $S_{BET}$ (m$^2$.g$^{-1}$) | 38.7             | 46.9   | 68.6    |
| Micropore area (m$^2$.g$^{-1}$) | 17.4             | 18.7   | 21.7    |
| Mesopore area (m$^2$.g$^{-1}$) | 21.3             | 28.2   | 46.9    |
| Total pore volume(cm$^3$.g$^{-1}$) | 0.041           | 0.043  | 0.049   |
| Micropore volume (cm$^3$.g$^{-1}$) | 0.024           | 0.020  | 0.021   |
| Mesopore volume (cm$^3$.g$^{-1}$) | 0.017           | 0.023  | 0.027   |
| Average pore diameter (nm) | 4.936           | 5.233  | 7.301   |

* Specific surface area

3.3. Simultaneous electricity generation in MFC using composite FO/GPEs as cathode
The power density and polarization curves of MFCs using GPEs, Fe$^{2+}$/GPEs and FO/GPEs as cathode were tested by varying external resistance from 5 Ω to 5000 Ω and compared in Fig. 2. MFC-FO/GPEs produced the highest open circuit voltages (OCV) of 0.555 V, followed by the MFC-Fe$^{2+}$/GPEs of 0.527 V and then the MFC-GPEs of 0.477 V (Fig. 2A). No obvious activation polarization loss was displayed in MFCs. The maximum power density of MFC-FO/GPEs (5.11 W.m$^{-3}$) and MFC-Fe$^{2+}$/GPEs (4.66 W.m$^{-3}$) were 28.0 % and 40.4 % higher than that of MFC-GPEs (3.64 W.m$^{-3}$) (Fig. 2A). The external resistance of all MFCs was 200 Ω. According to the polarization curves (Fig. 2B), the differences of electricity outputs were contributed by the differences in cathode potentials since the anode potentials of all MFCs were similar. An excellent power output was produced by MFC using FO/GPEs which had a higher specific surface. Additional ORR sites were provided by more micropores and mesopores in FO/GPEs, contributing to a better performance than GPEs. Meanwhile, the existence of Fenton iron reagent improved the MFC performance mainly due to the high redox
potential of •OH from Fenton’s reaction [21]. The increasing electricity generation of MFC-FO/GPEs over MFC-Fe²⁺/GPEs was caused by the more kinetic favorability of leached Fe²⁺ from FO/GPEs than Fe²⁺ in the bulk solution in MFC-Fenton system [7].

![Graph](image)

**Figure. 2** (a) Power density (normalized to the cathode effective) and Cell Voltages as a function of the current density in MFCs using GPEs, Fe²⁺/GPEs and FO/GPEs; (b) Electrode potentials for the MFCs using GPEs, Fe²⁺/GPEs and FO/GPEs.

### 3.4. The degradation of p-nitrophenol in FO/GPEs MFC-Fenton system

The degradation of PNP during 8 h in MFC-GPEs process, Fe²⁺/GPEs MFC-Fenton system and FO/GPEs MFC-Fenton system at pH 3 and pH 7 was displayed in Fig. 3. Without any Fenton iron reagents in MFC, the electrochemical degradation of PNP on GPEs were merely 17.6 % (pH=3) and 14.4 % (pH=7) in 8 hours. The low degradation efficiencies might be attributed to cathode reduction on GPEs and relative weaker oxidation of H₂O₂ [5]. Simultaneously, the FO/GPEs MFC-Fenton system achieved better performance of PNP over Fe²⁺/GPEs MFC-Fenton system, which indicated that leached Fe²⁺ from FO/GPEs were more favor to involve in Fenton reaction than free Fe²⁺ in solution. The experimental data from Fig. 3 was replotted using a logarithmic linear scale (Fig. 4), kinetic constants and coefficients (R²) of which were summarized in Table 2. The PNP decomposition followed the pseudo-first-order kinetic reaction. The kinetic constant of FO/GPEs MFC-Fenton system at pH 7 was 0.267 h⁻¹, close to those at acid condition (0.296 h⁻¹), which confirmed the feasibility of FO/GPE MFC-Fenton system at neutral pH. Fig. 5 shows the removal of PNP and TOC in Fe²⁺/GPEs MFC-Fenton system and FO/GPEs MFC-Fenton system at different pH values. The removal of PNP and TOC quickly declined after 8h and 64 h in Fe²⁺/GPEs MFC-Fenton system from pH 3 to 7, since the acidity is the optimal reaction condition for hydroxyl radical generation by ferrous iron catalyzing hydrogen peroxide. While both a slight decrease of 2.6 % and 5.1 % in PNP degradation and TOC removal were observed from an acidic FO/GPEs MFC-Fenton system to a neutral process. This is possibly due to the coexistence of the mineral surface-catalyzed heterogeneous reactions on composite electrode to generate oxidants. The removal of PNP and TOC at pH 7 reached 87.9 % in 8 h and 82.1 % in 64 h, respectively, which were even larger than those using Fe²⁺/GPEs at pH 3, revealing the high activity of FO/GPEs MFC-Fenton system for PNP removal in a wide pH range.

**Table 2** Pseudo-first-order kinetic constants and the corresponding coefficients of PNP degradation

| pH | Reactor     | Kinetic constant(h⁻¹) | Coefficient(R²) |
|----|-------------|-----------------------|-----------------|
| 3  | MFC-GPEs    | 0.020                 | 0.981           |
| 3  | MFC-Fe²⁺/GPEs | 0.201                | 0.996           |
| 3  | MFC-FO/GPE  | 0.267                 | 0.995           |
| 7  | MFC-GPEs    | 0.025                 | 0.975           |
| 7  | MFC-Fe²⁺/GPEs | 0.121                | 0.984           |
| 7  | MFC-FO/GPE  | 0.296                 | 0.993           |
To understand the high degradation efficiency of this MFC-Fenton process at neutral pH, the concentrations of hydrogen peroxide and iron ions produced during PNP degradation at pH 3 and pH 7 were measured and the results are displayed in Fig. 5. The H$_2$O$_2$ concentration started to increase with the reaction time and then stabilized after approximately 32 hours due to the accumulation. The decomposition and generation processes of hydrogen peroxide reached a balance in the cathode chamber during the last half period. The production of H$_2$O$_2$ at acidic condition was much less than that at neutral pH for the reason that the optimum pH value for the electrochemical generation of hydrogen peroxide was around 10[22]. Moreover, the concentration of iron ions after 64 h in the FO/GPEs MFC-Fenton process at pH 7 (12.5 mg·L$^{-1}$) was 74.7 % lower than that at pH 3 (about 49.5 mg·L$^{-1}$). This is mostly because that the leaching process of iron ion from FO/GPEs to solution prefers to occur under acidic condition (Eq. (1)). The concentration of iron ions in FO/GPEs MFC-Fenton system under neutral condition only increased quickly at the beginning but did not rise any more after 24 h, demonstrating that H$_2$O$_2$ decomposition at higher pH trended to a surface-catalyzed process. This result suggested that the composite FO/GPEs could be reused.

3.5. The proposed mechanism of FO/GPEs MFC-Fenton system

On the basis of the results above, a possible mechanism for the PNP degradation in the FO/GPEs MFC-Fenton system was proposed. Specifically, acetate was oxidized by electricigens in anode chamber to release electrons and protons. After that, the electrons collected in the anode were conducted through the external resistor to the cathode and the cation migrated through the proton exchange membrane into the cathode chamber. In cathode chamber, the dissolved oxygen was firstly adsorbed on the surface of FO/GPEs and immediately electrochemically reduced to produce H$_2$O$_2$. At the same time, $\equiv$Fe(II) and $\equiv$Fe(III) species were corroded from FO/GPEs, which could be depicted...
by the reaction where \( \equiv \text{Fe(II)} \) and \( \equiv \text{Fe(III)} \) species stands for Fe(II) and Fe(III) sites on the catalyst FO surface. The initially generated \( \equiv \text{Fe(II)} \) further reacted with \( \text{H}_2\text{O}_2 \) to generate surface-bound \( \cdot \text{OH}_{\text{ads}} \) on FO/GPEs [23]. Simultaneously, the formed \( \equiv \text{Fe(II)} \) and \( \equiv \text{Fe(III)} \) on FO/GPEs was leached into the cathodic solution, but the porous structure in FO/GPEs might absorb partial \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) to prevent the complete leaching [2, 7]. The absorbed iron \( (\text{Fe}^{2+}_{\text{ads}}) \) could catalyze the decomposition of \( \text{H}_2\text{O}_2 \) both on FO/GPEs and in bulk solution to generate \( \cdot \text{OH}_{\text{ads}} \) and \( \cdot \text{OH}_{\text{aq}} \), respectively. Also, the dissolved iron \( (\text{Fe}^{3+}_{\text{aq}}) \) was dispersed into bulk solution to initiate the decomposition of \( \text{H}_2\text{O}_2 \) to \( \cdot \text{OH}_{\text{aq}} \). The \( \cdot \text{OH}_{\text{ads}} \) from the surface of FO/GPEs might be minimally diffused into the bulk. Finally, PNP was degraded mainly by hydroxyl radicals including \( \cdot \text{OH} \) on the surface of FO/GPEs and in bulk solution[3, 14]. The main recycle of \( \equiv \text{Fe(II)} \) from \( \equiv \text{Fe(III)} \) was a direct cathode reaction [11].

Therefore, a reasonable oxidation mechanism of this novel FO/GPEs MFC-Fenton system combined a typical Haber–Weiss mechanism and heterogeneous surface-catalyze reactions was proposed, contributing to the good performance on PNP degradation in this system at neutral pH.

4. Conclusions
A three-dimensional electrode MFC-Fenton system based on the novel composite FO/GPEs as cathode for PNP degradation was investigated in this paper. The prepared FO/GPEs in this study showed multiplicated porosities including micropores and mesopores. The hematite and magnetite were dispersed on the surface of composite FO/GPEs electrode, as indicated by XPS. Higher surface area and more mesoporosity in FO/GPEs increased the efficiency of in-situ electro-generation of \( \text{H}_2\text{O}_2 \) and improved Fenton catalytic performance as well. When at the optimum pH 3, FO/GPEs MFC-Fenton system presented higher PNP degradation efficiency compared to the system with \( \text{Fe}^{2+} \) as the iron reagents. As pH increased to neutral, this system kept in good performance without sacrificing efficiency. The removal of PNP and TOC reached respectively around 85 % within 8 h and 64 h, respectively. Finally, the oxidation mechanism of MFC-Fenton system with novel FO/GPEs combined a typical Haber–Weiss mechanism and heterogeneous surface-catalyze reactions was proposed and showed good performance on the PNP degradation in this system at neutral pH.

5. References
[1] Zhuang L, Zhou S, Yuan Y, et al. (2010) A novel bioelectro-Fenton system for coupling anodic COD removal with cathodic dye degradation Chemical Engineering Journal, 163, pp.160-163.
[2] Feng C-H, Li F-B, Mai H-J, et al. (2010) Bio-Electro-Fenton Process Driven by Microbial Fuel Cell for Wastewater Treatment. Environmental science & technology, 2010, 44, pp.1875-1880.
[3] Tao H-C, Wei X-Y, Zhang L-J, et al. (2013) Degradation of p-nitrophenol in a BES-Fenton system based on limonite. Journal of hazardous materials, 254-255, pp.236-241.
[4] Chen J-y, Li N, Zhao L. (2014) Three-dimensional electrode microbial fuel cell for hydrogen peroxide synthesis coupled to wastewater treatment. Journal of Power Sources, 254, pp.316-322.
[5] Zhu X, Ni J. (2009) Simultaneous processes of electricity generation and p-nitrophenol degradation in a microbial fuel cell. Electrochemistry Communications, 11, pp.274-277.
[6] Smith B A, Teel A L, Watts R J. (2004) Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. Environmental science & technology, 38, pp.5465-5469.
[7] Zhuang L, Zhou S, Li Y, et al. (2010) In situ Fenton-enhanced cathodic reaction for sustainable increased electricity generation in microbial fuel cells. Journal of Power Sources, 195, pp.1379-1382.
[8] Wei L, Guo S, Yan G, et al. (2010) Electrochemical pretreatment of heavy oil refinery wastewater using a three-dimensional electrode reactor. Electrochimica Acta, 55, pp.8615-8620.
[9] Chen J-y, Zhao L, Li N, et al. (2015) A microbial fuel cell with the three-dimensional electrode applied an external voltage for synthesis of hydrogen peroxide from organic matter. Journal of Power Sources, 287, 291-296.
[10] Li J, Ai Z, Zhang L. (2009) Design of a neutral electro-Fenton system with \( \text{Fe}@(\text{Fe}_2\text{O}_3)/\text{ACF} \) composite cathode for wastewater treatment. Journal of hazardous materials, 164, pp.18-25.
[11] Zhao H, Wang Y, Wang Y, et al. (2012) Electro-Fenton oxidation of pesticides with a novel Fe₃O₄@Fe₂O₃/activated carbon aerogel cathode: High activity, wide pH range and catalytic mechanism. *Applied Catalysis B: Environmental*, 125, 120-127.

[12] Dong H, Yu H, Wang X. (2012) Catalysis kinetics and porous analysis of rolling activated carbon-PTFE air-cathode in microbial fuel cells. *Environmental science & technology*, 46, pp.13009-15.

[13] Ren J, Li N, Li L, et al. (2015) Granulation and ferric oxides loading enable biochar derived from cotton stalk to remove phosphate from water. *Bioresource technology*, 178, pp.119-25.

[14] Sun S-P, Lemley A T. (2011) p-Nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-magnetite: Process optimization, kinetics, and degradation pathways. *Journal of Molecular Catalysis A: Chemical*, 349, pp. 71-79.

[15] Federation W E, Association A P H. (2005) Standard methods for the examination of water and wastewater. *American Public Health Association (APHA): Washington, DC, USA*, 2005.

[16] Lovley D R, Phillips E J. (1988) Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Applied and environmental microbiology*, 54, pp.1472-80.

[17] Grosvenor A P, Kobe B A, Biesinger M C, et al. (2004) Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds. *Surface and Interface Analysis*, 36, pp. 564-1574.

[18] Pierotti R, Rouquerol J. (1985) Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl Chem*, 57, pp.603-619.

[19] Kumagai S, Ishizawa H, Aoki Y, et al. (2010) Molded micro- and mesoporous carbon/silica composite from rice husk and beet sugar. *Chemical Engineering Journal*, 56, pp.270-277.

[20] Duarte F, Maldonado-Hódar F, Pérez-Cadenas A, et al. (2009) Fenton-like degradation of azo-dye Orange II catalyzed by transition metals on carbon aerogels. *Applied Catalysis B: Environmental*, 85, pp.139-147.

[21] Wood P M. The potential diagram for oxygen at pH 7 (1988). *Biochemical Journal*, 253, pp. 287-289.

[22] Hanaoka K, Sun D, Lawrence R, et al. (2004) The mechanism of the enhanced antioxidant effects against superoxide anion radicals of reduced water produced by electrolysis. *Biophysical Chemistry*, 107, pp.71-82.

[23] Xu L, Wang J. (2012) Magnetic nanoscaled Fe₃O₄/CeO₂ composite as an efficient Fenton-like heterogeneous catalyst for degradation of 4-chlorophenol. *Environmental science & technology*, 46, pp.10145-53.