Effect of Nano-Fe$_3$O$_4$ on Bio-Electro-Fenton Microbial Fuel Cells

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Abstract. In this study, we synthesize low-cost Fe$_3$O$_4$ catalyst and spray it on carbon cloth as the cathode material while carbon cloth with low functionalization of graphene oxide (GO) as the anode material. The dairy wastewater and diesel wastewater are used as the anolyte and catholyte, respectively for microbial fuel cells (MFCs), which combine with the bio-electro-Fenton system to degrade organic wastewater. It improves the Chemical Oxygen Demand (COD) degradation efficiency of 85% of organic pollution. Moreover, the application of non-photocatalyst-Fe$_3$O$_4$ helps to improve the performance of electricity generation and achieves the goals of replacing the existing microbial fuel cells catalyst in the future.

Introduction

Microbial fuel cells (MFCs) is an electrochemical system that converts the chemical energy, which is produced by oxidizing organic matter from microorganisms into electrical energy and can be combined with Bio-Electro-Fenton System [1-3] for wastewater degradation purposes. For Fe$_3$O$_4$ synthesis process, we used chemical coprecipitation [4-7] and oil amine oleic acid [7-9] synthesis method and identify which method is smaller grain size and better for Microbial fuel cells. Mostfa et al. [10] used a phase transition method by mixing Fe$_3$O$_4$ with PES and NMP and then applied to the PES. They used Neutral Red and yeast S. cerevisiae suspension as the anolyte, phosphate buffer solution (pH 7) as the catholyte to enhance the microbial fuel cell anode power generation of efficiency.

For MFCs, the microbial oxidation of organic matter to the anode transfer rate of electrons become a main limiting factor in the performance of bio-electrochemical systems, in which the anode material and proton exchange membrane properties of the anode output current have the greatest impact [4]. Nowadays, photocatalysts are the most commonly used materials for MFCs catalysts but which needs to use a specific wavelength of the light source, This limits MFCs for the practical applications and the heat caused by the light affects the growth of microorganisms [11-13].

In this study, we optimized the process parameters, used low cost, non-photo catalyst Fe$_3$O$_4$, and spray it on the carbon cloth to improve the efficiency of MFCs power generation and degradation of organic wastewater.
Experimental Design

Reactor Construction and Operation

An acrylic dual chambered tank with dimensions of 85 mm × 70 mm × 55 mm was selected for the construction of the Bio-Electro-Fenton MFCs as shown in Figure 1. Each chamber had a total volume of 200 ml. A proton exchange membrane of Nafion-117 (80 mm × 70 mm) was used as a membrane. The carbon cloth (CC, 40 mm × 40 mm) with GO was used as the anode and Fe₃O₄ catalyst on carbon cloth as the cathode in the MFCs. The preparation method for the carbon cloth (CC) analysis shows an increased quantity of Anthraquinone [14].

![Figure 1. The experimental set-up of the proposed reactor.](image)

Anolyte and Catholyte Preparation

Kim et al.[15] proved that lactic acid wastewater can be used to sustain the production of electric energy in MFCs. They used expired dairy products as anolyte. The early stage of fermentation was used by the dairy wastewater, which was collected at Mao-Shu Jhong, No. 16 of Lane 90, Sin-Cheng Road 1, Suao Town, Ilan, Taiwan; local laboratory. Besides, the different dairy products, including yogurt, milk, and lactic acid bacteria, were mixed and cultured in an anaerobic environment for use as the electrogenic bacteria of the anode. In the chamber, the precipitation of particulates was formed, but three layers of the contents in the chamber were naturally separated when it kept stagnant for a long period. Those layers were classified as top-level supernatant (clear fluid), a mid-level interface, and a bottom-level precipitate. Prior to the study, a conductivity experiment was confirmed that the top-level supernatant in the chamber had the best conductivity with an open-circuit voltage of 0.70 V, limiting current of 0.547 mA/m², and an achievable maximum power density of 101.4 mW/m². In addition, considering the fact that viscosity would influence microbial activity and also affect power generation of MFCs [16]. Samples from the top-level supernatant were selected for further studies. In their study, artificially prepared oil wastewater was used as the catholyte by adding 1mL diesel in 1 L of water, heated with a magnetic heater, and blended with a blender for 24 hr at 50°C. Because of diesel was not water soluble, 10 g of the emulsifying agent was added to allow the dissolution of the diesel in the water.
Experimental Analysis

The electrochemical analysis was done by the workstation (Solartron (SI 1280C), Taiwan) to measure the cyclic voltammetry (CV) of the Bio-Electro-Fenton MFCs. For COD analysis, an instrument (SUNETX-V2000 photometer, Taiwan) was utilized with solutions diluted 100 X with deionized water. For material analysis instruments like X-ray diffractometer (Bruker D2 Phaser), field emission scanning electron microscope (FE-SEM) (JSM-6500F) were used.

Principles and Mechanism

Fenton’s reagent can function well under acidic conditions. During the anodic oxidation, the cathode is aerated, which increases the pH and inhibits the generation of ·OH as well as decreases the COD removal rate [17-19]. In the experiment, 10% dilute sulfuric acid is added to the cathode solution to obtain a pH value of 3.0 [3]. In the cathode reaction: 2H⁺ + 2e⁻ + O₂ → H₂O₂ (1-1) results in H₂O₂ accumulation in the cathode chamber via the two-electron reduction of dissolved O₂ in the Bio-Electro-Fenton MFCs and then FeSO₄ powder is added as a source of Fe²⁺: 2H⁺ +Fe → Fe²⁺ + H₂ (1-2); finally, the bio-electro-Fenton reaction takes place at the cathode, in which the hydroxyl radical is an important factor in the degradation of products according to the reaction: Fe²⁺ + H₂O₂ → Fe³⁺ + ·OH + OH⁻ (1-3). In conclusion, the Bio-Electro-Fenton MFCs is reported to be an effective system to treat organic wastewater as well as the bio-refractory pollutants [20].

Results and Discussion

From the XRD patterns of the Fe₃O₄, for both chemical coprecipitation (Figure 2) and oil amine oleic acid (Figure 3), the characteristic peaks of Fe₃O₄ were observed at 31.2°, 36.3°, 43.7°, 56.8°, and 63.2°, corresponding to facet indexes of (220) (311) (400) (551), and (440). The diffraction peak at a 2θ value of 36.3° was ascribed to the (311) reflection of Fe₃O₄[21]. The grain size of Fe₃O₄ is calculated by Scherrer equation, the results confirm that the grain size using oil amine oleic acid (3.58 nm) is smaller than that of using the chemical coprecipitation method (7.98 nm). As shown from the surface morphology of Fe₃O₄, the nanoparticles are agglomerated for both the chemical coprecipitation method (Figure 4) and the oil amine oleic acid method (Figure 5a and 5b). Because Fe₃O₄ is superparamagnetic [22]. As a result, the catalyst surface area is reduced by their own magnetic force, the reactivity of the catalyst and quality of the spray can also be affected, so the dispersion of the catalyst in the configuration of the liquid dispersion and the particle size is determined the quality of the elements.
Figure 2. The XRD patterns of the chemical coprecipitation method.

Figure 3. The XRD patterns of the oil amine oleic acid method.
Summary

The nano-Fe$_3$O$_4$ was synthesized by chemical coprecipitation and oil amine oleic acid methods. The Fe$_3$O$_4$ synthesized from the two methods can be successfully dispersed in the oil amine and n-hexane solvent. The grain size and PDI using the oil amine oleic acid method is 3.6 nm and 0.26, respectively while the synthesized using chemical co-precipitation can be dispersed 99.5% in ethanol but poor dispersible PDI (0.53) and large grain size about 1 µm. The Fe$_3$O$_4$ synthesized by the oil amine oleic acid method is better than chemical coprecipitation method for the microbial fuel cells.

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References


