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Bio-electrochemical degradation of paracetamol in a microbial fuel cell-Fenton system

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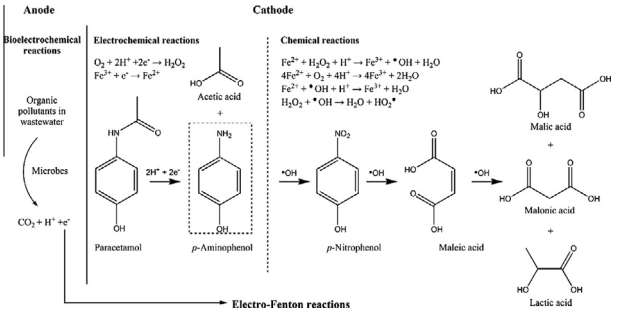
HIGHLIGHTS

- A microbial fuel cell (MFC)-Fenton system without power supply was developed.
- Paracetamol (PAM) degradation was enhanced by bio-electrons from wastewater.
- PAM mineralization could be achieved by in-situ generation of free radicals.
- Possible pathways and kinetics of PAM degradation by MFC-Fenton were proposed.
- MFC-Fenton was proved to be both energy-saving and performance-efficient.

GRAPHICAL ABSTRACT



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ABSTRACT

Paracetamol (PAM) has emerged as an important wastewater contaminant due to its wide usage. In this study, Fenton reactions were introduced to microbial fuel cells (MFCs) for bio-electrochemical degradation of PAM without external power supply. Dual-chamber MFC reactors were employed: in the anode chambers, bio-electrons were released by oxidizing biodegradable pollutants in low-strength real domestic wastewater; in the cathode chambers, the input fluxes of bio-electrons from the anode could promote the yield of free radical ·OH by facilitating the regeneration of iron source. Compared to conventional Fenton reactions in which no bio-electrons were transferred, our approach exhibited the advantage that no continuous addition of Fenton reagents was required in MFC-Fenton system. Significant changes in the UV–vis spectra of catholytes from an MFC-powered process strongly indicated that bio-electricity input played an important role in PAM degradation. The performance of electro-Fenton system was in good agreement with the bio-electricity output-capacity from MFC reactor under expected optimal conditions. At total iron concentration of 5 mg L^{-1}, initial pH value of 2.0 and external resistance of 20 Ω, the highest PAM degradation efficiency of 70% was attained within 9 h. A 25% PAM could be completely mineralized while the majority was mainly converted to intermediate metabolites of *p*-nitrophenol via *p*-aminophenol and to less hazardous dicarboxylic/carboxylic acids. These results suggested that MFC-Fenton could be applied as an energy-saving and efficient approach to PAM-containing wastewater treatment, and further to non-biocompatible pharmaceuticals degradation in aquatic environment.

1. Introduction

Pharmaceutical-contaminated wastewater is newly emerging as a public concern in recent years. Widespread survey and

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evaluation indicated that pharmaceutically active compounds are widely found in natural surface streams, groundwater, effluent from wastewater treatment plants and supplied drinking water [1–3]. Although usually low in strength (generally ng L^{-1} to μg L^{-1}), these pharmaceuticals are commonly regarded as potential hazards due to their accumulation in living tissues, which in turn will trigger chain reactions and produce unwanted biological effects on aquatic creatures and human beings [4,5]. Paracetamol (PAM), clinical trade names of acetaminophen (ACTP) or acetyl-para-aminophenol (APAP), is a common over-the-counter (OTC) analgesic and antipyretic. While generally safe for use at the recommended dose, even small overdoses may lead to fatal liver damage [6]. With its widespread application in pharmaceutical industries and daily life, PAM is becoming a key environmental research topic.

Previous studies on removal of PAM from wastewater mainly focused on advanced oxidation processes (AOPs). Hydroxyl radicals (OH) are responsible for the major ·OH-PAM reaction [7]. One commonly applied AOP method is photo-degradation catalyzed by TiO_2. Various active species besides hydroxyl radicals, including valence band holes (h^+), conductive band electrons (e^-), superoxide ions (O_2^-), hydrogen peroxide radicals (HO_2) and hydrogen peroxide (H_2O_2), can be generated to mineralize PAM when an irradiation energy is higher than the band gap energy of TiO_2 [6]. Another extensively discussed method is Fenton oxidation process where ·OH can be generated in-situ from the classical reaction between iron (II) (Fe^{2+}) and H_2O_2. Recent advances made in the improvement of conventional Fenton technology have led to various Fenton-like systems with high efficiency, such as electron-Fenton by applying external voltage, ultraviolet (UV)/photo-Fenton by exploiting light irradiation and ultrasonication (US)/sono-Fenton by introducing ultrasonication/sonolysis [8–10]. However, external energy (e.g. electricity, light and ultrasonic wave) input causes extra operating cost.

Microbial fuel cell (MFC) technology has been well developed in harvesting electric energy and powering miniature devices such as sediment-based systems and a data collector in remote ocean [11,12]. It was first introduced to Fenton reactions by Zhu and Ni [13] for simultaneous electricity generation and *p*-nitrophenol (PNP) degradation with no external power supply. Then MFC was integrated with Fenton reactions to dispose the bio-refractory and/or toxic compounds, such as various organic dyes and arsenite [14–20]. These findings shed light on the feasibility of PAM removal by MFC-based electro-Fenton without additional electricity requirements. In the past decade, the power output of MFCs has increased to as high as several watt per square meter of surface area of electrode [21], further making it practical to use MFCs as power sources for electro-Fenton systems. In an MFC, the electrochemically active microorganisms (electricigens) grown on the anode act as biological catalysts to lower the electrode overpotential effectively, promote anodic reactions and then facilitate electron transfer to the cathode on which oxidized pollutants are reduced [22]. The implementation of the separator, most commonly a membrane between the two electrodes, prevents the bio-activity of electricigens in the anode from being inhibited by the pollutants in the cathode. The performance of an MFC was affected by various factors including the degradation of substrate by electricigens grown on the anode, transfer of electron in the electrical circuit, mass transfer in bulk solution, performance of the separator, electrode and electrolyte etc. [23,24]. Among which, cathodic process, such as oxygen reduction (ORR) catalyzed by precious Pt, has the most significant roles and accounts for more than 50% of MFC's capital cost [25,26]. Therefore, there is a great demand for exploring cheaper and high-performance cathodic reactions to achieve high-efficiency degradation and removal of target species.

Electro-catalytic degradation of PAM in MFCs has rarely been studied and reported to date. Thus this project aims at exploring the feasibility of enhanced PAM degradation by an MFC-Fenton system. Some key factors influencing the PAM degradation efficiency, such as iron dosage, initial pH and external resistance, were investigated. The possible catalytic roles of iron source and bio-electrons as contributors to the bio-electrochemically reactions were discussed. To better understand the stepwise degradation of PAM, the pathway of bio-electrochemical reaction was investigated and kinetic mechanisms were proposed based on the intermediates identified.

2. Materials and methods

2.1. MFC-Fenton system configuration

A dual-chamber MFC reactor was constructed with a cathodic working volume of 216.0 mL and an anodic working volume of 108.0 mL (Fig. 1). The anode consisted of three highly porous graphite felts (6.0 cm length × 5.5 cm width × 1.0 cm thickness), which could provide sufficient surface area for the attachment and growth of electricigens. The cathode was a single graphite plate with a smaller projected surface area of 15 cm^2 and lower porosity and specific surface area as compared to the anode. Proton Exchange Membrane (PEM, 6.0 cm × 5.5 cm cross-sectional area, Nafion-117, DuPont, USA) was installed as a separator to prevent potential diffusion of dissolved oxygen (DO, aerated with gaseous oxygen from air) as well as the transfer of iron (III)/iron (II) (Fe^{3+}/Fe^{2+}) ions (sourced from $FeSO_4{\cdot}7H_2O$ added directly) from cathode to anode chamber. A data acquisition system (Adam-4017, Advantech Co., Ltd., China) was coupled to a reference electrode (Ag/AgCl, CHI 111, USA) to monitor the voltage output and anode and/or cathode potentials. The whole circuit was connected via titanium wires (>99.9%). All established MFC-Fenton systems were maintained in air-conditioned rooms controlled at 25 °C.

2.2. Start up and experiments

A successful start-up, indicated by constant and stable power output, could be accomplished by the following step-by-step operations. Firstly, the anode chamber of a dual-chamber MFC was inoculated with a selectively enriched mixed microbial culture from the effluent of a single-chamber air cathode MFC that has

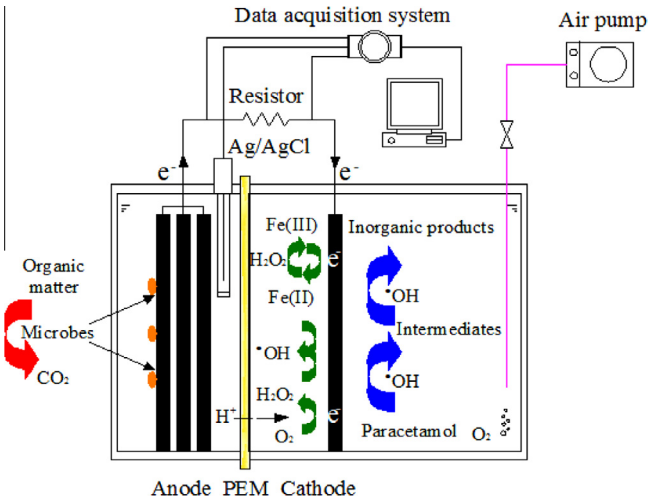

Fig. 1. Schematic diagram of the MFC-Fenton system (PEM = Proton Exchange Membrane).