Degradation of Diclofenac Sodium in Microbial fuel cells

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Abstract. Diclofenac sodium is an extensively consumed non-steroidal anti-inflammatory drug for certain non-rheumatic diseases and frequently detected at surface water. This work studied the degradation process of diclofenac sodium in an anodic chambers of microbial fuel cells. It was found that biodegradation of diclofenac sodium could be achieved in the microbial fuel cells, and the removal rate of diclofenac sodium was accelerated after bioelectrochemical activity microorganism acclimation. The highest removal rate can reach up to 30.73% after 2 weeks of operation. The results also showed that weak acid (pH=5.5) condition favour the degradation of diclofenac sodium, while low temperature condition inhibited its degradation. This work provided a new way to remove diclofenac sodium from wastewater.

1. Introduction
Owing to the wide application of non-steroidal anti-inflammatory drugs (NSAIDs), large amounts of NSAIDs were discharged to the environment. NSAIDs are the groups of emerging contaminants of extreme environmental concern [1, 2]. Diclofenac Sodium is one such synthetic NSAIDs, mostly used in medical care as an analgesic, antiarthritic and antirheumatic [3]. Global usage of diclofenac sodium exceeds 900 tons per year, and about 15% of diclofenac sodium is excreted as unchanged after human consumption [4]. Extensive usage and stable chemical structure make diclofenac sodium a recalcitrant stable environmental pollutant. Diclofenac sodium is always detected at surface water and also in drinking water, which causes a great threat to the environment and human health [5]. Removal of diclofenac sodium has always been an important aspect of research due to the increasing awareness about the environment. Bagal and Gogate [6] have reported degradation of diclofenac sodium using combined processes based on heterogeneous photocatalysis and hydrodynamic cavitation. Sutarn and Rathod [4] have assisted enzymatic degradation of diclofenac sodium using ultrasound. Recently, advanced oxidation processes used to degrade of diclofenac sodium have widely reported [7-10]. However, high operational costs and slower removal kinetics along with hazardous by-products hinder the application of these techniques. Microbial fuel cells (MFCs) provide new ways for electricity generation and pollutant degradation through metabolism of electrochemically active microorganisms [11]. Our previous study revealed that high degradation of sulfamethoxazole is achievable using MFCs [12]. In the present study, we explore the possibilities and effect factors of diclofenac sodium degraded by MFCs.

2. Methods and materials

2.1 Chemicals
Diclofenac sodium was purchased from Aladdin Industrial Corporation. Methanol and formic acid (HPLC grade) were purchased from Fisher.

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2.2 Microbial inoculum and reactor operation
Two-chamber glass MFC reactors were used in this study. The working volumes of anodic and cathodic chambers are all 100 mL. The anode and cathode are all made of graphite felt (6 cm length × 6 cm width × 1.0 cm thickness, Haoshi Carbon Fiber Co., Ltd., China) connected with titanium wire. Anodic and cathodic chambers were separated by a cation exchange membrane (10.0 cm², Zhejiang Qianqiu Group Co., Ltd., China). The Anodic chamber was inoculated with anaerobic sludge and potassium ferricyanide (50 mM, pH 7.0) as an electron acceptor filled in the cathodic chamber. The voltages of the reactors were recorded at 5 min intervals by a digital multi-meter.

2.3 Determination of diclofenac sodium
Chromatography was performed with an HPLC (LC-20A, Shimadzu, Japan) system at a flow rate of 220 μL min⁻¹ on a C18 column (4.6×250 mm, 5 μm). Methanol and 0.1% formic acid solution were used as the mobile phase.

3. Results and discussion
3.1 Reactor start up and operation
Microbes in the biofilm attached to anode play a key role in contaminants biodegradation and electricity of MFCs. Figure 1 shows one output voltage cycle of the MFCs fed with NaAc (control) and diclofenac sodium with an external resistance of 1000 Ω. As shown in Figure 1, after two months of operation, the output voltages of the reactors fed with NaAc and diclofenac sodium was in a steady state. BESs are fueled by sodium acetate and diclofenac sodium, and output voltage increases with the addition of fuel and decreases with fuel consumption. A stable output voltage of MFCs with sodium acetate as the substrate reached 0.57 V, while the diclofenac sodium fuelled MFCs platform voltage is just about 0.30 V, which may be related to the microorganisms growth in the biofilm attached to the anode which prefer to use sodium acetate as a substrate for electricity generation.

![Figure 1](image_url)

**Figure 1.** Voltage output of MFC with sodium acetate (control) and diclofenac sodium (MFC-DS) as substrate.

3.2 Standard curve drawing
Different concentrations of diclofenac sodium were determined by HPLC. Taking the peak area as the abscissa and the diclofenac sodium concentration as the ordinate to draw the standard curve (Figure 2). The relationship between diclofenac sodium concentration (C, mg/L) and peak area (x) is shown as
C = 0.00004x - 0.1396, and $R^2$ is 0.99997, indicating that the peak area has a good linear relationship with diclofenac sodium concentration.

![Figure 2. Standard curve of diclofenac sodium concentration](image)

3.3 Effect of initial concentration on diclofenac sodium degradation

The initial diclofenac sodium affects the growth of microorganisms on the surface of the anode, which in turn affects the biodegradation of diclofenac sodium by MFCs. The removal rate of diclofenac sodium at different initial concentrations is shown in Figure 3. The concentration of diclofenac sodium in anode chamber gradually decreases with the treatment time. After two weeks of treatment, the removal rates were 15.33% and 9.16% for the initial concentrations of 50 mg/L and 60 mg/L, respectively. While the removal rate was only 4.96% for initial concentrations of 70 mg/L. High concentrations of diclofenac sodium with a lower removal rate may be due to the high concentration of diclofenac sodium which inhibits the growth and metabolism of microorganisms in the anode biofilm.

![Figure 3. Effect of initial concentration on diclofenac sodium degradation.](image)

3.4 Effect of pH on diclofenac sodium degradation

pH is an important factor affecting the growth of microorganisms. To investigate the effect of pH on diclofenac sodium degradation, the pH of the anolyte in MFCs was adjusted to 5.5, 7.0 and 8.5. As shown in Figure 4, the degradation rate of acid in diclofenac sodium gradually decreased with the
increase of pH. After 14 days of treatment, in the case where the anode solution is weakly acidic (pH=5.5), the concentration of diclofenac sodium is reduced from 59.68 mg/L to 41.43 mg/L, and the removal rate is up to 30.73%; however, the removal rate is only 7.16% under neutral condition (pH=7.0), the removal rate dropped to 3.28% under weak alkaline conditions.

![Figure 4. Effect of pH on diclofenac sodium degradation](image)

3.5 **Effect of temperature on diclofenac sodium degradation**

Temperature is another important factor affecting microbial growth. We have studied the degradation efficiency of diclofenac sodium in MFCs at normal temperature (28°C) and low temperature (4°C). As shown in Figure 4, after 14 days of treatment, the concentration of diclofenac sodium is reduced from 59.98 to 54.48 mg/L at normal temperature, while there is almost no degradation of diclofenac sodium in the anode chamber when MFCs are operating at low temperatures.

![Figure 5. Effect of temperature on diclofenac sodium degradation](image)

4. **Conclusions**

This study investigated the possibility of utilizing MFCs to degrade diclofenac sodium. It was found that the ability of MFCs to degrade diclofenac sodium was accelerated in the conditions of weak acid, high initial concentration and low treatment temperature decrease removal rate of diclofenac sodium.
sodium. This study offers a feasible low cost and energy recovery choice for the elimination of diclofenac sodium in wastewater.

5. References

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