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Research Paper

Enhanced phosphorus and ciprofloxacin removal in a modified BAF system by configuring Fe-C micro electrolysis: Investigation on pollutants removal and degradation mechanisms

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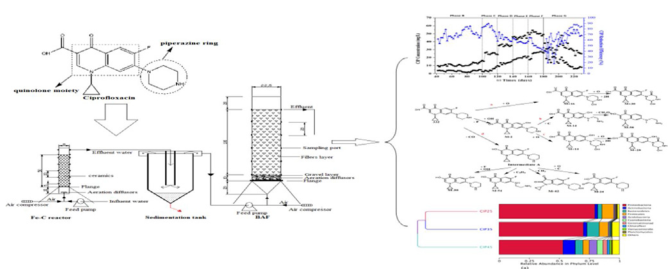
HIGHLIGHTS

- Novel sludge ceramic and SFC were separately filled into BAF and Fe-C micro electrolysis reactor.
- Configuring Fe-C micro electrolysis greatly improved the controlling of residual TP and CIP.
- Four main degradation pathways were proposed according to the LC–MS analysis.
- The richness and diversity of the microbial community increased a lot with CIP pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

A modified biological aerated filter (BAF) system configured Fe-C micro electrolysis was applied to enhance phosphorus and ciprofloxacin (CIP) removal. A novel sludge ceramic and sintering ferric-carbon ceramic (SFC) were separately packed into a lab-scale BAF and Fe-C micro electrolysis reactor. The BAF and Fe-C micro electrolysis coupled system was operated about 230 days. The enhancement of phosphorus and ciprofloxacin removals by Fe-C micro electrolysis, the degradation mechanisms of CIP and the variations of microbial population were investigated. The removal efficiencies of chemical oxygen demand (COD_{cr}), ammonia (NH_4-N), total phosphorus (TP) and CIP reached about 95%, 95%, 80% and 85% in the combined process, respectively. Configuring Fe-C micro electrolysis significantly enhanced phosphorus and CIP removal, whereas had no promotion on N removal. Four main degradation pathways were proposed according to the LC–MS analysis. More than 12 degradation products were detected through the treatment of Fe-C micro electrolysis and only 3 biodegraded products with low concentration were identified in BAF effluent. The high-throughput sequencing analysis showed that the microbial community changed a lot under CIP pressure. The relative abundance of *Sphingomonadaceae*, *Xanthomonadaceae*, *Bradyrhizobium*, *Helicobacter* and *Pseudomonas* increased with CIP influent. This study provides a promising process in CIP wastewater treatment.

1. Introduction

Fluoroquinolones is the third largest antibiotic groups accounting for 17% of global market share amounting to 7.1 billion US dollars in 2009 [1]. Ciprofloxacin (CIP), as the third generation of quinolone antibiotics, is widely used in veterinary and human

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medicine. It has received increasing attentions for its overuse and the spread of antibiotic resistance in microbial [2,3]. Only small amounts of antibiotics are removed by the traditional wastewater treatment plants due to the improper design [4,5]. To date, the treatment of CIP wastewater has been mainly focus on adsorption [6], photocatalytic degradation [7,8] and advanced oxidation processes [9,10]. But these traditional physical-chemical remediation methods commonly need high costs and are difficult to wide application. Thus, it is very necessary to explore a more effectual method. In this study, a combined system of Fe-C micro electrolysis and BAF process was applied.

Fe-C micro electrolysis has attracted great attention owing to the high efficiency, low cost and operational simplicity in refractory organic wastewater treatment. Fe^{2+} and [H] generated during the reaction have high chemical activity, which can easily break down the carbon chains of organic compounds [11], thus greatly improve the biodegradability of wastewater [12,13]. In addition, organic contaminants can also be reduced through adsorption and co-precipitation by the ferrous and ferric hydroxides that are generated from the oxidation and precipitation of Fe^{2+} [13]. However, there still existed two major problems in the Fe-C micro electrolysis system up to now. Firstly, iron and carbon powders are used directly in traditional Fe-C micro electrolysis. After a certain time, the packed scrap iron will easily harden and ditch flow, leading to frequent backwash and packing replacement. To solve the problems, iron and carbon powder are mixed in a certain proportion and burned to Fe-C ceramsite in this study. Fe-C ceramsite has larger particle size and porous inside, increasing the efficiency of micro electrolysis reaction.

Secondly, limited disposal of organic matter was observed through traditional Fe-C micro electrolysis [12,14]. Thus, biological aerated filter (BAF) is used to remove the residual organic matter existed in Fe-C micro electrolysis effluent. As a core component of the BAF system, filter media plays a key role in the immobilization of microorganisms. The novel sludge ceramics used as packing materials have been researched for several years and significant achievements have been made in our previous studies. [15,16]. Moreover, BAF mainly relies on the presence of microbes attached on medium to transform toxic substances, degrade organic pollutants and remove nutrients from urban/industrial wastewater. Previous studies mainly showed the effects of CIP at low level (ug/L) on microbial communities [17,18]. However, little information is available concerning the lone-term effects of CIP at high level (mg/L) on the microbial community during biological treatment process.

The objectives of this study were (a) to evaluate the enhancement of the modified BAF system configured Fe-C micro electrolysis in phosphorus and CIP removal; (b) to explore the degradation mechanisms of CIP in the coupled system; (c) to determine the variations of microbial community structure under increased CIP pressure.

2. Materials and methods

2.1. Materials

The ceramics for BAF were prepared by dewatered sludge and clay with the ratio of 1: (3–4), named novel sludge ceramics. Sintering ferric-carbon ceramics (SFC) used clay, iron powder and activated carbon powder as main raw material in a ratio of 8:4:1and were sintered at 600 °C. The physical properties of two novel ceramics are shown in Table 1. Ciprofloxacin (98% purity) was obtained from Sigma-Aldrich (St. Louis, MO, USA).

Table 1
Physical property of two new ceramics.

Novel sludge ceramics	Diameter	5–8 mm
	Bulk density	785.86 kg m^{-3}
	Grain density	1425.37 kg m^{-3}
	Water absorption	12.98%
	Voidage	45.61%
Fe-C ceramsite	Diameter	6–8 mm
	Bulk density	1055.74 kg m^{-3}
	Grain density	3030.87 kg m^{-3}
	Water absorption	10.96%
	Voidage	54%

2.2. System setup

A continuously running BAF connected with a Fe-C micro electrolysis reactor was applied to treat CIP wastewater in this study. The modified BAF system consisted of three main operational parts, including a Fe-C micro electrolysis reactor, an intermediate sedimentation tank and a BAF. The two lab-scale cylindrical reactors made of polymethyl methacrylate were separately filled with novel sludge ceramics and SFC. The BAF reactor had a diameter of 225 mm with an effective height of 1.5 m and the Fe-C reactor had a diameter of 80 mm with a height of 0.7 m. The working volume of three reactors was 3100, and 12 L, respectively. The schematic diagram is presented in Fig. 1.

2.3. Fe-C micro electrolysis and BAF operation

In the study, the synthetic CIP wastewater was treated by the Fe-C micro electrolysis and BAF. $C_6H_{12}O_6$, NH_4Cl and KH_2PO_4 were dosed as carbon, nitrogen and phosphorous source respectively and the C:N:P ratio was controlled at 100:5:1 for BAF. In contrast, considering the low removal efficiency of nitrogen in Fe-C micro electrolysis, the C:N:P ratio in Fe-C micro electrolysis influent was changed to 100:2.5:1. In BAF, the COD_{cr} concentration was controlled at 500 mg/L. Except nutrient substances, the CIP was added into the wastewater step by step according to the plan. For Fe-C micro electrolysis, the concentrations of COD_{cr} and CIP were respectively kept about 1000 mg/L and 50 mg/L during the whole experiment.

BAF reactor was initially inoculated with concentrated activated sludge obtained from aerobic pool of Jinan Wastewater Treatment Plant. After 2 days, synthetic wastewater was continuously fed into biofilter in an up-flow manner. The air was simultaneously injected into the reactor through an aeration diffusor (shown in Fig. 1) from the bottom and the air flow rate was controlled at 15 L/h with the air/liquid ratio (A/L) of 15:1.Other conditions of BAF were hydraulic retention time (HRT) of 12 h and total flow rate of 1 L/h. A long-time running of 230 days was conducted of the combined system. The BAF underwent several phases: (A) Startup phase with CIP below 10 mg/L for 40 d; (B) Working phase with 10 mg/L CIP for 60 d; (C) Working phase with 25 mg/L CIP for 20 d; (D) Working phase with 35 mg/L CIP for 20 d; (E) Working phase with 45 mg/L CIP for 20 d; (F) Working phase with 50 mg/L CIP for 20 d; (G) The combined phase of Fe-C micro electrolysis and BAF with 50 mg/L CIP for 50 d. The system was backwashed every 7–10 days. Three samples were taken every 2 day from the effluent tank in all operational phases.

2.4. Sample analysis

The potassium dichromate oxidation method was applied to measure the concentration of COD_{cr}. NH_4-N, total Nitrogen (TN), total Phosphorus (TP) were analyzed by colorimetric method with an ultraviolet-visible (UV–vis) spectrophotometer (UV-2450, Shimadzu) in terms of the national standard methods (State Envi-